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## Hydrolytic Depolymerization of Lignin for the Preparation of Polyols and Rigid Polyurethane Foams

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A thesis submitted in partial fulfillment of the requirements for the Doctor of Philosophy degree in Chemical and Biochemical Engineering

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**HYDROLYTIC DEPOLYMERIZATION OF LIGNIN FOR THE PREPARATION OF  
POLYOLS AND RIGID POLYURETHANE FOAMS**  
(Thesis format: Integrated Article)

by

Nubla Mahmood

Graduate Program in Chemical and Biochemical Engineering

A thesis submitted in partial fulfillment  
of the requirements for the degree of  
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The School of Graduate and Postdoctoral Studies  
The University of Western Ontario  
London, Ontario, Canada

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## Abstract

This doctoral study was aimed to produce bio-polyols from Kraft lignin (KL) and hydrolysis lignin (HL) via depolymerization and utilize the lignin-derived bio-polyols in the preparation of bio-based rigid polyurethane (BRPU) foams at high percentage of bio-contents (50-70 wt.%). This study demonstrated that depolymerization is a practical and effective approach to unleash the potential of utilization of lignin, of complex structures and low reactivity/functionality, for bioproducts and biomaterials.

Depolymerization of KL was realized in alkaline medium using water alone as a solvent or employing water-ethylene glycol (EG) mixture via a low pressure (<150 psig) proprietary process, both effective for producing low molecular weight depolymerized KL (DKL). The KL depolymerization process conditions were optimized. BRPU foams were prepared by incorporating DKL via two routes: (1) direct utilization of DKL by replacing 50 wt.% of sucrose polyol and PPG400 and, (2) oxypropylation of DKL to make a single polyol feedstock for the foam preparation.

Similarly, HL was effectively depolymerized employing water alone or water-ethanol (50:50, v/v) mixture with or without catalysts, or employing EG as a solvent under acidic conditions via a low pressure (<150 psig) process. The obtained depolymerized HL (DHL) products were also used as bio-polyols for the preparation of BRPU foams via two routes: direct replacement or oxypropylation.

The main academic contribution of this work is that this study has led to the development of a novel/proprietary process for efficient and cost effective depolymerization of KL and HL under low pressure (<150 psig), viable approaches to prepare BRPU foams containing 50-70 wt.% of bio-contents. All BRPU foams exhibit good physical, mechanical and thermal properties for their potential application as an insulation material. The major industrial significance of this project is that it helps transform the largely available KL and HL resources into value-added bioproducts i.e., bio-polyols and BRPU foams. As a result, it will help reduce the dependency of RPU foams production on petroleum derived polyols, generate additional revenue streams to the associated industries (particularly, pulp/paper mills and cellulosic ethanol plants), and also improve their sustainability.

## Keywords

Kraft lignin, hydrolysis lignin, depolymerization, hydrolysis, depolymerized Kraft lignin, depolymerized hydrolysis lignin, ethylene glycol, polyols, oxypropylation, rigid polyurethane foam.

## Co-Authorship Statement

### **Chapter 2: Depolymerization of lignins and their applications for the preparation of polyols and rigid polyurethane foams (Literature review)**

*Authors: Nubla Mahmood, Zhongshun Yuan, John Schmidt, Chunbao (Charles) Xu*

*Status: To be submitted to Renewable and Sustainable Energy Reviews*

Experimental work and data analysis were performed by Nubla Mahmood. Chunbao (Charles) Xu and Zhongshun Yuan provided consultation regarding experimental work and interpretation of results. The manuscript was written and revised by Nubla Mahmood, and reviewed by Zhongshun Yuan, Chunbao (Charles) Xu and John Schmidt.

### **Chapter 3: Production of polyols via direct hydrolysis of Kraft lignin: Effects of process parameters**

*Authors: Nubla Mahmood, Zhongshun Yuan, John Schmidt, Chunbao (Charles) Xu*

*Status: Published in Bioresource Technology*

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### **Chapter 4: Production of polyols via direct hydrolysis of Kraft lignin: Optimization of process parameters**

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### **Chapter 5: Preparation of bio-based rigid polyurethane foam using hydrolytically depolymerized Kraft lignin via direct replacement or oxypropylation**

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### **Chapter 6: Hydrolytic depolymerization of hydrolysis lignin: Effects of catalysts and solvents**

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### **Chapter 7: Valorization of hydrolysis lignin for polyols and its direct incorporation in rigid polyurethane foams**

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**Chapter 8: Hydrolytic depolymerization of hydrolysis lignin for the preparation of bio-based rigid polyurethane foam: Effects of process parameters**

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**Chapter 10: Low pressure hydrolytic depolymerization of Kraft lignin for the preparation of bio-based rigid polyurethane foam**

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## List of Abbreviations and Symbols

ANOVA- Analysis of Variance

Aq- Aqueous

ASTM- American Society for Testing and Materials

ATR- Attenuated Total Reflectance

BRPUF- Bio-based Rigid Polyurethane Foam

C- Carbon

CCD- Central Composite Design

CH<sub>2</sub>Br<sub>2</sub>- Dibromomethane

d.a.f. - Dry Ash Free

d.b. - Dry Basis

DBTDL- Dibutyltin Dilaurate

DHL- Depolymerized Hydrolysis Lignin

DKL- Depolymerized Kraft Lignin

DL- Depolymerized Lignin

DMSO-*d*<sub>6</sub> – Dimethyl Sulfoxide-*d*<sub>6</sub>

DSC- Differential Scanning Calorimetry

DTG- Derivative Thermogravimetric Analysis

EG- Ethylene Glycol

EtOH- Ethanol

F- Functionality

FC- Fixed Carbon

FTIR- Fourier Transform Infrared Spectroscopy

GC/MS- Gas Chromatography/Mass Spectrometry

GC-TCD- Gas Chromatography/Thermal Conductivity Detector

GPC- Gel Permeation Chromatography

GPC/HPLC- Gel Permeation Chromatography/High Performance Liquid Chromatography

H- Hydrogen

$^1\text{H}$  NMR spectra- Proton Nuclear Magnetic Resonance Spectrometry

$\text{H}_2\text{O}$ - Water

$\text{H}_2\text{SO}_4$ - Sulfuric Acid

HL- Hydrolysis Lignin

IR- Infrared

$I_{\text{TAC}}$ - Integration of Protons of Total Acetate Groups

KL- Kraft lignin

KOH- Potassium Hydroxide

MC- Moisture Content

$M_{\text{DBM}}$ - Moles of Dibromomethane

MDI- 4, 4'-diphenylmethane diisocyanate

$M_n$ - Number Average Molecular Weight

MS- Mean Square

$M_{\text{TOH}}$ - Moles of Total –OH

$M_w$ - Weight Average Molecular Weight

N- Nitrogen

NaOH- Sodium Hydroxide

O- Oxygen

OH number- Hydroxyl Number

$\text{OH}_{\text{Aliphatic}}$ - Aliphatic –OH

$\text{OH}_{\text{Phenolic}}$ - Phenolic –OH

$\text{OH}_{\text{Total}}$ - Aliphatic –OH

PDI- Polydispersity Index

PG- Propylene Glycol

PO- Propylene Oxide

PPG- Poly(Propylene Glycol)

PUF- Polyurethane Foam

RPUF- Rigid Polyurethane Foam

RSM- Response Surface Methodology

SEM- Scanning Electronic Microscope

SR- Solid Residues

SS- Sum of Squares

S-Sulfur

TEA- Triethanol Amine

TEDA- Triethylene Diamine

Temp- Temperature

T<sub>g</sub>- Glass Transition Temperature

TGA- Thermogravimetric Analysis

THF- Tetrahydrofuran

UV- Ultraviolet

VM- Volatile Matter

W<sub>AC</sub>- Weight of Acetylated Sample

W<sub>DBM</sub>- Amount of Dibromomethane

α- Level of Significance

λ- Thermal Conductivity

# Dedication

*To the most important people in my life:*

*my husband Mahmood*

*my daughter Eshal*

*my parents and parent's in-laws*

## Chapter 1

### 1 Introduction

#### 1.1 Background and motivation

Bio-based fuels, chemicals and materials are gaining increasing attention due to the worldwide increased concerns over declining non-renewable fossil resources, climate changes, energy security and sustainability of economy (McGowan, 1991; Hall et al., 1992). Agricultural and forestry residues, wastes and byproducts are of top most interest because of their low cost and abundant availability (Sricharoenchaikul, 2009). As the demand continues to grow, new and better methods must be developed to utilize bioresources for fuels, chemicals and materials.

Lignocellulosic biomass represents a renewable and low-cost alternative source for the production of low sulfur/nitrogen containing fuels and chemicals (Connor & Piskorz, 1994). Lignocellulosic biomass is composed of hemicellulose, cellulose, and lignin. Depending on the biomass species, lignin comprises around 15-30% of lignocellulosic biomass dry weight and has higher energy content of 9000-11000 Btu/lb compared to that of cellulose, which is estimated to be around 7300-7500 Btu/lb (Nimani, 2011; Effendi et al., 2008). Overcoming the recalcitrance of lignocellulosic biomass is a key step in the production of fuels and chemicals (Brodeur et al., 2011). Although much of the public attention has been paid towards the production of industrial bioproducts (bio-fuels, bio-based chemicals and biomaterials) derived from biomass, still it has to go a long way to achieve economically viable production of these industrial bioproducts. The following criteria: availability, economics, public acceptability, environmental emissions, national security, technology and versatility, must be addressed in developing innovative technologies to replace petroleum-derived products with bioproducts.

Lignin molecule is composed of 3D phenyl propanol units (monomers) (Tejado et al., 2007), namely guaiacyl alcohol (G), syringyl alcohol (S), p-coumaryl alcohol (H) and is the most abundant and natural source of phenolic compounds (Amen-Chen et al., 2001). Kraft lignin (KL) is mainly generated as a byproduct of chemical pulping process in pulp



and paper industry at an estimated annual production rate of 50Mt (Lora & Glasser, 2002). Being a by-product stream of Kraft pulping process, black liquor contains typically 30-34% of lignin on dry solid weight basis (Araújo, 2008). Currently majority of the lignin produced in pulp/paper mills is combusted for heat/power generation in recovery boilers. The large amount of lignin produced in the pulping process is problematic as almost 60-70% of North America's pulp/papers mills have a bottleneck in their recovery boilers capacity, which limits their productivities. Thus a significant proportion of lignin can be removed to debottleneck the recovery boilers without effecting heat production of a mill (Pandey and Kim, 2008). Today, roughly only 1-2% of KL is isolated for other value-added applications such as for chemicals (Lora & Glasser, 2002). Thus, there is a remarkable opportunity in isolating KL from black liquor specifically for the production of various value-added bio-chemicals and biomaterials. Hydrolysis lignin (HL) is another type of lignin left as a residue or by-product from enzymatic hydrolysis of lignocellulosic biomass in cellulosic ethanol plants after separating carbohydrates (cellulose and hemicelluloses) from the whole biomass (Yuan et al., 2012). In fact, these days the following have becoming the driving forces for the utilization of lignin for chemicals and materials: (1) ease of availability of lignin, a special case exists in 60-70% of North American Kraft mills which have an operation bottleneck in recovery boilers, (2) availability of sulfur free lignins (HL or organosolv lignin, OL), (3) the steadily increasing market demand for natural and sustainable products, and (4) the development of biorefinery technologies, etc.

In the recent years, there is an intensive research carried out to seek for technical routes to valorization of KL for various high value bio-chemicals, biofuels and biomaterials (Cheng, 2011). Meanwhile, extensive research was also undertaken in the former Soviet Union to explore applications of HL for biomaterials, which was not very successful and majority of HL was still disposed because the required modifications were too expensive or materials synthesized from HL did not function well. A common challenge for utilization KL and HL for chemicals and materials is related to lignin's lower reactivity and high steric hindrance effects, caused by its branched molecular structure. Such challenge limits direct use of lignin for the replacement of petroleum-based components

in materials, especially for HL lignin with more complex structure where lignin and cellulose are crosslinked with each other.

## 1.2 Depolymerization of lignin

Although with much lower reactivity, even crude lignin can be directly used for the synthesis of biomaterials such as bio-based phenol formaldehyde (PF) resins and bio-based polyurethane (PU) foam as insulation materials, due to the presence of phenolic and hydroxyl groups (aliphatic and aromatic) in its structure as the reactive sites (Cheng, 2011; Cateto et al., 2008). However, the percentage replacement for petroleum phenols or polyols by crude lignin is not normally more than 30 wt.% for the synthesis of bio-based PF or PU foam. Further increasing the replacement ratio, would lead to markedly deteriorated properties of the products. On the other hand in HL, lignin and cellulose are cross-linked and is unable to dissolve in any solvent therefore, it cannot be directly incorporated in the PF or PU foam's structure. Because of lignin's special phenyl propanol structure linked by the aryl-alkyl ether linkage, depolymerization of KL or HL into oligomers and aromatic chemicals would be a viable route for increasing their percentage replacement for petroleum-based feedstock in the preparation of bio-based PF adhesives, PU foams and other biomaterials such as bio-epoxy resins, etc. without sacrificing properties of the prepared biomaterials in comparison with the petroleum-based products (Khitrin et al., 2012; Cheng, 2011).

Various lignin depolymerization routes have been reported in literature, mainly classified into two major categories: biochemical processes and thermo-chemical processes. Biochemical processes are very slow and complex, requiring enzymes to breakdown lignocellulosic materials normally with an aim of producing ethanol and other chemicals via hydrolyzing cellulose into glucose (Pandey and Kim, 2011). Thermo-chemical processes for lignin depolymerization, mainly for the production of liquid bio-fuels, include direct liquefaction technologies such as pyrolysis and high pressure liquefaction processes as well as hydrolytic and oxidative/reductive de-polymerization of lignin (Pandey and Kim, 2011). The most important parameters for thermochemical processes are reaction temperature, pressure, time, type and composition of feedstock, and catalysts (Küçük and Demirbas, 1997). Pyrolysis of lignin usually operates at high temperatures

(400-800 °C), thus with high energy consumption but the oil yields from lignin are commonly only 20-40 wt.% (Pandey and Kim, 2011).

The bio-oils/bio-crudes resulting from pyrolysis/high pressure liquefaction of lignocellulosic biomass are complex mixtures of oxygen containing compounds in the form of phenols and benzene derivatives, aliphatic and aromatic alcohols, esters and carboxylic acids and hydroxyketones, all contributing to high oxygen contents of oils (Appell et al., 1970; Minowa et al., 1998; Qu et al., 2003). These oxygenated hydrocarbons contain also an appreciable proportion of water both from the original moisture and as a reaction product (Bridgwater, 2003; Czernik and Bridgwater, 2004). Depending on the biomass origin and process conditions (temperature, residence time, heating rate and catalyst used) total contents of oxygen varies in bio-oils, like 35-50 wt.% for pyrolysis oil and 20-30 wt.% for bio-crudes from high pressure liquefaction process (Bridgwater, 1994; Furimsky, 2000; Xu and Etcheverry, 2008). There are some limitations associated with pyrolysis oils due to high oxygen content which results in high viscosity, low heating value, thermal and chemical instability, and corrosivity (due to the presence of organic acids), etc. (Bridgwater, 1996; Yaman, 2004).

Depolymerization of lignin/lignocellulosic biomasses can produce multitude of products depending on the processing methods and conditions. It can be carried out via employing various solvents such as water, alcohols (Xu and Etcheverry, 2008), ethylene glycol (Miller et al., 1999) etc., catalysts (alkalis such as NaOH, KOH, K<sub>2</sub>CO<sub>3</sub> etc.; acids like HCl, H<sub>2</sub>SO<sub>4</sub>, H<sub>3</sub>PO<sub>4</sub> etc.; metals and non-metals, etc.), temperatures, pressures etc. From an economic perspective, use of lignin as a source of biophenols/polyols in chemicals market is promising. The de-polymerized lignin products are darker in color (almost black) and scarcely retain the molecular characteristics of native lignin, because of the structural modifications like condensation, dehydration, rearrangement and intra & intermolecular hydrogen bonding during the depolymerization process (Lundquist, 1976). Most of the depolymerization methods reported in literature are either high pressure or high temperatures, thus cost intensive.

### 1.3 Lignin derived polyols and polyurethane foams

Polyol, a polyhydroxy compound, is an important building block of polyurethanes (PUs). PU is a polymeric material containing a huge amount of urethane group, which results from the addition polymerization reaction between -NCO group from polyisocyanate, and hydroxyl groups from polyols (i.e., polyether and polyesters). PU's are versatile engineering materials which find a wide range of applications because their properties can be readily tailored by the type and composition of their components (Hakim et al., 2011). PUs has found a wide range of applications such as insulation, construction, coatings agents, adhesives, sealants, elastomers, and resins, etc. Polyols are traditionally produced from petroleum where, polyether and polyester are two major types of polyols consumed in the global polyols market. In 1994, nearly 90% of 1.8 million metric tons of polyurethanes consumed in the United States were based on polyethers, 9% on polyesters and 1% on other specialty polyols (Tu, 2008). However, the production of polyols from petrochemicals is not only costly but has adverse effects on the environment. Research in recent years has focused on alternative, non-petroleum based polyols that are less costly, renewable and eco-friendly.

Rigid polyurethane (RPU) foams have the lowest thermal conductivity among all foamed polymers used commercially (Kacperski and Spychaj, 1999). They have been widely utilized in the appliance and construction industry because of their excellent and unique combination of thermal insulation and mechanical properties. RPU foams constitute more than 50% of total polyurethane foam consumption in China and Mexico, which are important manufacturing sites for refrigerators and freezer. RPU foams are conventionally made with petroleum-based polyols. However, with the dwindling non-renewable petroleum resources, extensive research has been concentrating on developing bio-based polyols (biopolyols) and PU products from renewable sources (Hu et al., 2012).

In this work, KL (isolated from black liquor) and HL (residue from enzymatic hydrolysis of wood) were employed for the preparation of bio-polyols after their de-polymerization and the lignin-derived bio-polyols were utilized for the preparation of bio-based rigid PU (BRPU) foams with acceptable physical, mechanical and thermal characteristics. Effects

of various operation parameters on hydrolytic de-polymerization of KL and their optimization were comprehensively studied. The depolymerized KL (DKL) obtained at optimized reaction conditions was employed as a bio-polyol for the preparation of BRPU foam replacing 50 wt.% of petroleum-based polyol and sucrose polyol. Hydrolytic de-polymerization is a high pressure process therefore; a new low-pressure lignin de-polymerization process was developed in this research for the depolymerization of KL employing a polyalcohol-water mixture (under low pressure  $\leq 150$  psig) under alkaline medium. The new low-pressure lignin de-polymerization process resulted in DKL products of a high yield and low molecular weight. The obtained DKL, although in solid form, can be transferred into liquid polyols via oxypropylation in a unique medium that consists of a mixture of glycerol, acetone and KOH. Using DKL as bio-polyols BRPU foams were realized up to 70 wt.% bio-contents. On the other hand, HL was also depolymerized/liquefied employing hot-compressed water-ethanol mixture as a solvent (a high-pressure process) in acidic and alkaline media. Similarly, low-pressure depolymerization of HL lignin was also performed in water-ethylene glycol (EG) under low pressure ( $<150$  psig). The resulting depolymerized HL products (DHLs) were also incorporated in the preparation of BRPU foams by direct replacement for polypropylene glycol (PPG400) or sucrose polyols, or using oxypropylated DHL, first transferred to liquid polyols before being used, for the preparation of BRPU foams. Replacing petroleum-based polyols with bio-polyols derived from renewable resources would have a deep impact on the polyurethane industry.

## 1.4 Research objectives

Kraft lignin (KL) and hydrolysis lignin (HL) are the abundantly available residual streams from pulp and paper industry and cellulosic ethanol industry, respectively. The overall objective of this work is to depolymerize KL and HL into DKL and DHL products of a lower  $M_w$  and appropriate hydroxyl number, and utilize DKL or DHL as bio-polyols to substitute for up to 50-70 wt.% of petroleum-based polyols or sucrose polyols for the preparation of bio-based rigid PU (BRPU) foams, without compromising the foams properties (density, compression modulus, compression strengths, thermal conductivity).

Specific research objectives of this PhD project are to,

(1) Depolymerize KL and HL for the production of depolymerized KL (DKL) and depolymerized HL (DHL) with the following characteristics:

- i. High yield ( $\geq 70$  wt.%),
- ii. Low molecular weight ( $M_w \approx 1000-2000$  g/mole),
- iii. Moderately high hydroxyl number.

(2) Oxypropylation of the obtained DKL and DHL, in solid form, using propylene oxide (PO) to produce liquid bio-polyols.

(3) Prepare BRPU foams utilizing DKL or DHL as bio-polyols either via their direct incorporation to substitute for up to 50 wt.% of petroleum-based polyols or sucrose polyols or using their oxypropylated samples up to 70 wt.% bio-contents.

Figure 1-1 and Figure 1-2 shows the proposed approaches in this thesis project for producing bio-polyols for BRPU foams from KL and HL, respectively.

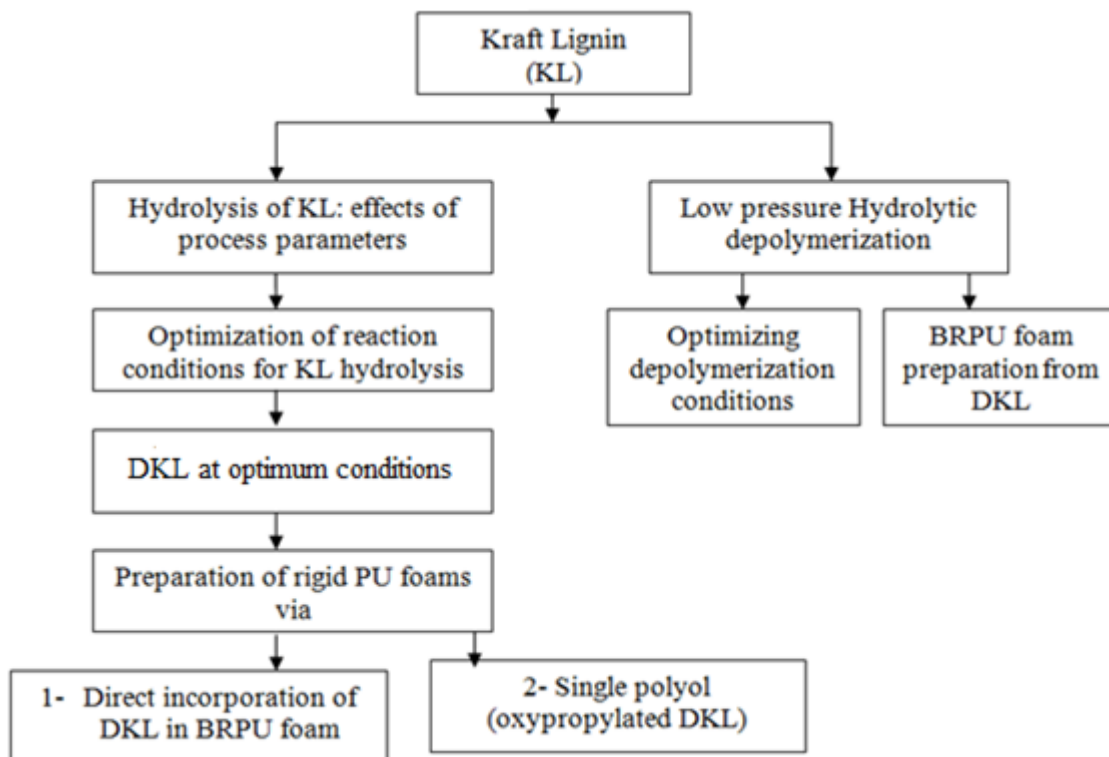


Figure 1-1 Proposed approaches for producing bio-polyols from KL for BRPU foams

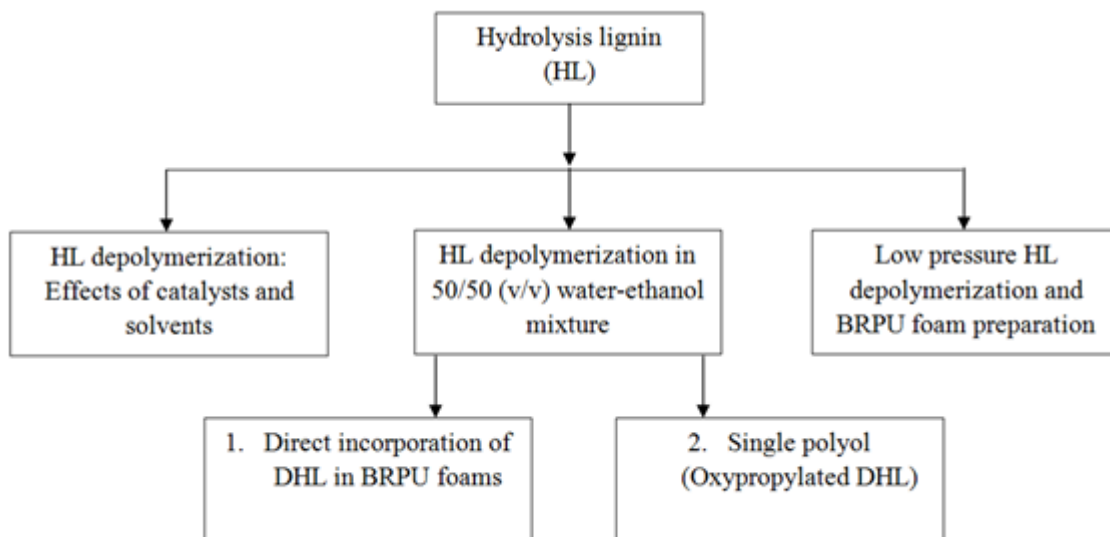


Figure 1-2 Proposed approaches for producing bio-polyols from HL for BRPU foams

## 1.5 Thesis organization

This PhD thesis is organized to consist of 12 chapters. Chapter 1 is a general introduction on the background, motivations and objectives. Chapter 2 is a comprehensive literature review on the state-of-the-art of the lignin depolymerization and preparation of polyols/polyurethane foams.

Chapter 3-4 are two manuscripts based on the hydrolysis of Kraft lignin (KL) employing water alone as a solvent under alkaline conditions. In Chapter 3, the effects of process parameters were studied, while the process optimization was studied in Chapter 4.

Chapter 5 is a comparative study for the preparation of bio-based rigid polyurethane (BRPU) foams employing depolymerized KL (DKL) obtained from Kraft lignin (KL) depolymerization at the optimized reaction conditions. Three BRPU foam preparation routes were investigated and compared, i.e., (1) directly replacing PPG400 polyols, (2) directly replacing sucrose polyols and, (3) producing a single polyol feedstock by oxypropylation of DKL. In comparison with reference RPU foams from pure PPG400 or sucrose polyol, the prepared BRPU foams were investigated for their physical, mechanical and thermal properties.

Chapter 6 is a comparative study on HL depolymerization employing water and water-ethanol mixture under catalytic (acidic and basic) and non-catalytic conditions.

Chapter 7 explains the preparation of BRPU foams from the DHL prepared via HL depolymerization in water-ethanol mixture at the best operating conditions. The foams were prepared by directly replacing 50 wt.% of PPG400 or sucrose polyols, and the foams were characterized for various properties. Chapter 8 deals with the transformation of solid DHL to liquid polyols for BRPU foam preparation via oxypropylation using PO in a unique medium consists of acetone, glycerol and KOH. Chapter 9 describes a comprehensive study on low-pressure depolymerization of HL employing EG as a solvent to obtain the best operating conditions for HL depolymerization. The DHL obtained at the best operating conditions was oxypropylated and employed as single polyol feedstock for the preparation of BRPU foams with 50-70 wt.% bio-contents. The



prepared BRPU foams were analyzed in terms of their physical, mechanical and thermal properties and compared with reference foam.

Chapter 10 presents a comprehensive study on low-pressure hydrolytic depolymerization of KL to obtain the best operating conditions, and utilizing the oxypropylated DKL to employ as a single polyol feedstock for the preparation of BRPU foams with 50-70 wt.% bio-contents. The prepared BRPU foams were analyzed in terms of their physical, mechanical and thermal properties and compared with reference foam.

Chapter 11 summarizes the main conclusions, contributions and novelties for the entire research work. Chapter 12 proposes some future work for the commercialization of bio-based rigid polyurethane foams.

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## Chapter 2

### 2 Literature Review

#### 2.1 Lignin as a potential source of chemicals and materials

Approximately 92% of organic chemical products are currently produced from fossil fuels (mainly petroleum oil and natural gas) (Bennett, 2012). For a hundred years or more, oil and natural gas have supplied fuel and other raw chemicals to support economic growth. The ever-increasing rates of petroleum usage and the consequent depletion of its reserves as well as the increased environmental concerns over the use of fossil fuels have intensified the needs for seeking alternative and sustainable resources for energy and chemicals production. In the last two decades, attention has focused towards creating biofuels (such as cellulosic ethanol – a second generation biofuels) from lignocellulosic residues. However more attention shall be placed on producing new value-added biochemicals and biomaterials through “biorefinery” approaches using non-food bioresources such as forestry/agricultural processing wastes such as sawdust, bark, forestry harvesting residues, byproducts (lignin) from pulp/paper mills and various crop residues (Deutschmann and Dekker, 2012; Sricharoenchaikul, 2009).

In nature, lignin is the second most abundant natural polymers after cellulose. Agricultural residues are typically comprised of 10-20 wt.% lignin, 40 wt.% cellulose and rest being the hemicelluloses, while forestry biomass contains almost 20-35 wt.% lignin, 30-40 wt.% cellulose and 20-30 wt.% hemicelluloses (S'anchez, 2009). Lignin presents a complex three dimensional structure that includes a variety of functional groups, namely hydroxyl, methoxyl, carbonyl and carboxyl moieties (Fang et al., 2008). Hydroxyl groups and the aromatic/phenolic rings are the most characteristic functions in the lignin, which determine its reactivity and constitute the reactive sites to be exploited in macromolecular chemistry (Cateto et al., 2009).

Native lignin is a high molecular weight biopolymer composed of phenyl propanol units (Tejado et al., 2007), heterogeneous in nature and mainly composed of two types of

linkages: condensed linkages (e.g., 5-5 and  $\beta$ -1 linkages) and ether linkages (e.g.,  $\alpha$ -O-4 and  $\beta$ -O-4) (Chakar and Ragauskas, 2004). The percentage of ether linkages in soft- and hardwood lignin are 56% and 72%, respectively (Pu et al., 2008). Aryl ether linkages can be more easily cleaved by lignin depolymerization/liquefaction processes, producing depolymerized lignin or phenolic bio-crude oils (Yuan et al., 2010) that are potential sources for the production of bio-fuels, bio-chemicals and biomaterials.

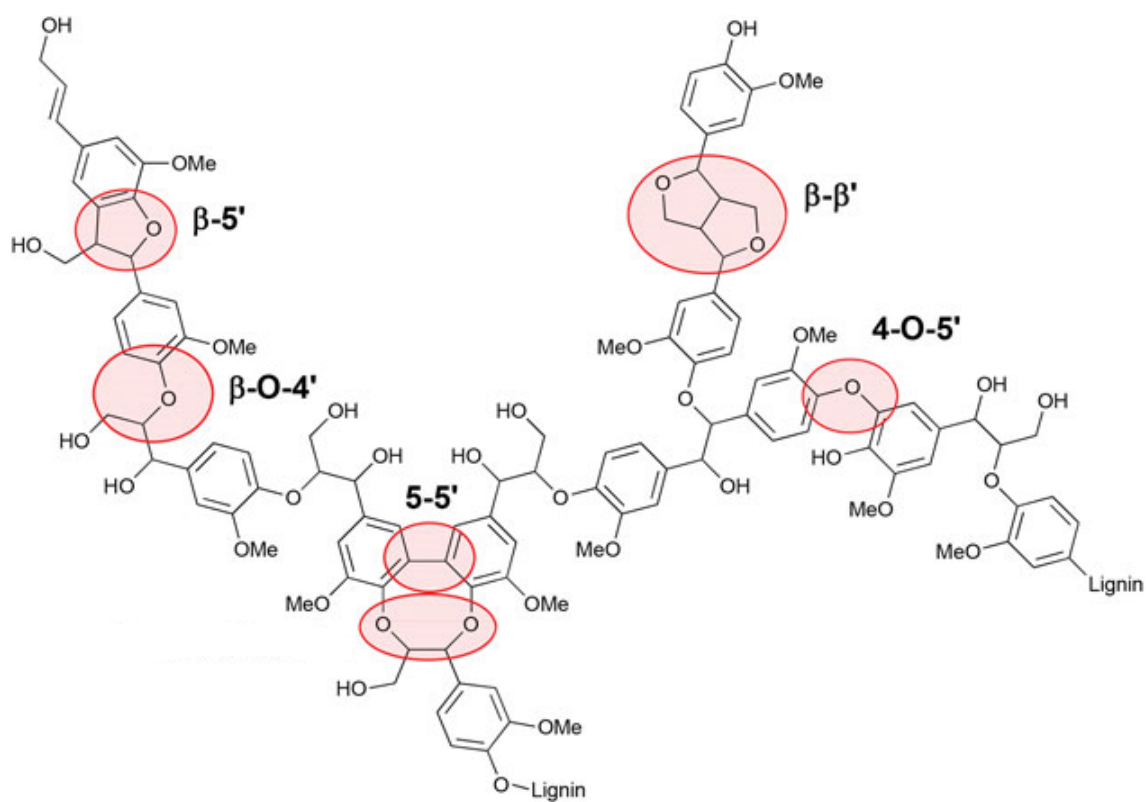


Figure 2-1 Representative substructure of lignin, reprinted (adapted) with permission from (Forsythe et al., 2013). Copyright © (2013) Royal Society of Chemistry.

## 2.2 Lignin sources, types and extraction methods

### 2.2.1 Sources of lignin

The major industrial source of lignin (Kraft lignin and lignosulfonates) is the pulp and paper industry, and annually, more than 50 million metric tons of lignin is produced by this industry. However, utilization of lignin as a fuel is not economically rational due to its relatively low heating value, and the money equivalent of using lignin as a fuel is only 0.18 US\$/kg (Vishtal and Kraslawski, 2011; Lebo et al., 2001). Thus, lignin has traditionally been viewed as a waste material or used predominantly as a solid fuel for heat generation in the recovery boilers in pulp/paper mills (Stewart, 2008). In North America, Lignotech produces about 120,000 tonnes/yr of lignosulfonate by purchasing sulfite liquors from nearby mills. Worldwide, about 1.06 million tonnes of lignosulfonates are produced annually, again primarily from sulfite black liquor and are used as dispersants for dyes, pesticides, cement, asphalt and a variety of other applications (Bozell et al., 2007). Crude lignin is also generated as a waste stream in the organosolv delignification process and the steam explosion process for cellulosic ethanol production.

However, nowadays sulfate or Kraft pulping accounts for 80% of the world's chemical pulp production and 50-55 million metric tons of lignin are produced annually in the form of black liquor; the liquid phase remaining after alkaline pulping has dissolved lignin (Borges da Silva, 2009). Black liquor is conventionally burned in recovery boilers to regenerate pulping chemicals and produce steam and electricity for mill operations. While most KL is thus not available for isolation, a special case exists in the 60-70% of North American Kraft mills that have production bottlenecks due to the thermal capacity of their recovery boilers. An interesting solution to this problem is to extract some of the lignin in black liquor by precipitation. In North America alone, the potential of precipitated lignin was estimated at 1.5 Mt/year (Schmidt and Laberge, 2008) and nearly 1 million tons per year worldwide (Lora and Glasser, 2002). The removed lignin can be further utilized as a raw material for value-added bio-products which would diversify the mill's economic base.



Because of lignin's special phenyl propanol structure and aryl-alkyl ether bonding, lignin from Kraft pulping mills can be a good source of polyols. Polyols are the polymers have multiple hydroxyl groups in their structure and are one of the essential raw materials for polyurethane (PU) production (Demharter, 1998). Although due to much lower reactivity, even crude lignin can be directly incorporated into PU formulations due to the presence of aliphatic and aromatic hydroxyl groups in its structure as the reactive sites, replacing <30 wt.% of petroleum-based polyols (Cateto et al., 2008) or into phenol-formaldehyde (PF) resins/adhesives at a phenol replacement ratio of <30-50 wt.% (Cheng et al., 2012). Polyols can be polyether or polyester polyols (Tu, 2008), with the most critical properties being equivalent weight and hydroxyl number/functionality. Petroleum derived polyols are typically used, but the rising petroleum prices and sustainability concerns have shifted attention towards bio-based polyols such as sucrose polyol and lignin-derived bio-polyols (Bueno-Ferrer et al., 2012; Borges da Silva et al., 2009).

## 2.2.2 Types of lignin and their extraction methods

Lignin from trees, plants, and agricultural crops with different chemical composition and properties can be obtained by using several extraction methods. Two types of lignin have been produced from lignocellulosic materials, sulfur-containing lignin and sulfur-free lignin, via commercial chemical pulping processes and cellulosic ethanol production processes. Commercial chemical pulping processes mainly produce sulfur-containing lignin such as liginosulfonates (LS) and Kraft lignin (KL). The sulfur-free lignin, including soda, organosolv, and steam-explosion, oxygen delignification and hydrolysis lignin are mainly from either the pulping processes or cellulosic ethanol plants.

### 2.2.2.1 Kraft lignin

Almost 80% of chemical pulping lignin comes from the widely used Kraft process (El Mansouri and Salvadó, 2006). Lignin can be extracted from the black liquor through acid precipitation approaches using  $H_2SO_4$ ,  $CO_2$  or by some electrochemical methods. For example, the following experimental procedure for lignin extraction from black liquor was proposed by Olivares et al. (1988). The black liquor normally with  $pH > 13$  was first acidified using  $H_2SO_4$  to  $pH$  8-9.5 at temperature 75-85 °C and filtered while hot. The

filtrate was further acidified to pH~ 2.0, followed by final filtration, washing and drying to get highly pure lignin. This procedure is advantageous since it allows recycling of a solution rich in  $\text{Na}^+$  and  $\text{SO}_4^{2-}$  to the Kraft process. KL contains a small number of aliphatic thiol groups that give the isolated product a characteristic odor (Lora and Glasser, 2002). Ideally, an effective pretreatment method should have following characteristics: low energy demand, low operational/capital cost, high removal of hemicellulose and lignin, easy operation, producing no or very limited amounts of sugar and lignin degradation products, etc. (Galbe and Zacchi, 2007). The researchers at FPInnovations developed a proprietary process, *LignoForce System*<sup>TM</sup>, aiming to address the problem related with lignin poor filterability reported by many researchers previously due to a high filtration resistance (Kouisni et al., 2012). In the LignoForce process, the black liquor (BL) is oxidized under controlled conditions before the acidification step of conventional lignin recovery processes. Based on the results reported, BL oxidation improves the filterability of the acid-precipitated lignin by providing suitable conditions with respect to pH (leads to a lower pH) and temperature (leads to a higher temperature) for lignin colloid agglomeration, leading to the formation of particles of a size and size distribution that are easy to filter and wash. Based on the results obtained in laboratory studies, a lignin demonstration plant was designed and built by FPInnovations at the Resolute – Thunder Bay mill for the production of 12.5 kg/h of high-quality lignin.

The KL can also be sulphonated to introduce  $-\text{SO}_3\text{H}$  group on the lignin unit, and in fact currently commercial KL is mainly sold in the sulphonated form or as lignin amines (Borges da Silva et al., 2009). Figure 2-2 illustrates the structural characteristic of Kraft pine lignin (Fig. 2-2a) and liginosulfonate lignin (Zakzeski et al., 2010) (Fig. 2-2b).

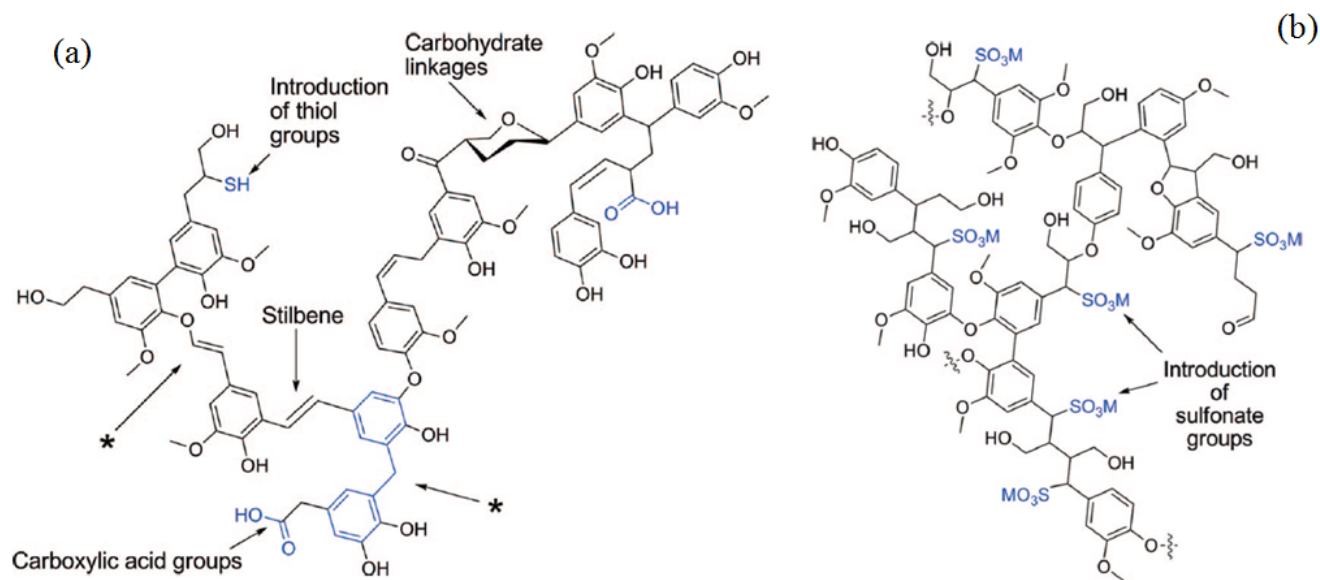


Figure 2-2 Structural characteristic of Kraft pine lignin (a) and liginosulfonate lignin (b), reprinted (adapted) with permission from (Zakzeski et al., 2010). Copyright © (2010) American Chemical Society.

### 2.2.2.2 Hydrolysis lignin

Hydrolysis lignin (HL) – a byproduct from pretreatment processes in cellulosic ethanol plants, is expected to produce in a large quantity if the many proposed projects for cellulosic sugar-based chemicals or ethanol are realized. FPIinnovations researchers (Yuan et al., 2012) patented a biomass fractionation process for producing value-added products from a lignocellulosic biomass, such as wood-derived sugar and hydrolysis lignin. Lignocellulosic biomass from any type of plant biomass that is composed of cellulose, hemicellulose and lignin, typically in amounts of 30-55 wt.%, cellulose; 15-35 wt.%, hemicellulose; and 5-31 wt.%, lignin, was used. The novel bio-conversion process used comprises of low- pressure mechanical refining to disintegrate biomass feedstock, hemicellulose extraction, enzymatic hydrolysis, sugar/lignin separation, and fermentation. After hemicellulose extraction and a subsequent hydrolysis, the remaining substrate (solid) residue contains a high percentage of lignin which was being recovered and further purified to produce high-quality lignin products. Compared to traditional Kraft lignin and steam-explosion lignin, the high-quality sulfur free lignin produced from

this invention has little degradation, resembles the native lignin. The obtained lignin was named as hydrolysis lignin (HL), composed mainly of lignin (56-57 wt.%), unreacted cellulose and mono & oligosaccharides. The chemical composition (d.a.f) of HL is given in Table 2-1. Compared to the traditional industrial lignins, HL is not extensively studied (Liittä et al., 2014). The presence of high contents of residual carbohydrates cause problems in HL applications. A lot of chemical modifications of hydrolysis lignin have been attempted to improve HL's reactivity and properties. These include amination, alkylation, carboxylation, halogenation, nitration, oxyalkylation, sulfonation, sulfomethylation, silylation, phosphorylation, polycomplexes, and metal complexing, etc. (Monica, 2005; Vishtal and Kraslawski, 2011; Rabinovich, 2010). Possible uses of HL after extensive modifications could range from soil additives to dispersants for environment protection, soil quality improvement, crop farming, live stock farming, leather processing, or recycling of valuable chemicals by waste water treatment, etc. Unfortunately, a majority of the hydrolysis lignin was simply disposed without use as either the required modifications were too expensive or the material did not function well enough, which are the same problems that today's researchers are facing while looking for valorization of hydrolysis lignin (Monica, 2005).

The Department of Energy, under the National Biomass Initiative, has funded research into processes for efficient production of sugars from biomass. Although there is not much on utilization of the hydrolysis lignin, NREL is working with collaborators trying to convert this lignin to gasoline additives through thermal treatments (Monica, 2005). The USDA also funds biorefinery research, but hydrolysis lignin is not in their current publications. Most published articles by far are from either former members of the Soviet Union or from Japan. The proposed uses for this material after chemical modifications typically involve agricultural products (Monica, 2005), sorbents (Keane and Ghoshal, 2001), resins (Matsushita and Yasuda, 2003; Yasuda and Asano, 2000), and some limited dispersing applications (Monica, 2005). These factors, jointly with lack of efficient utilization of HL, give a strong need of further research in cost-effective valorization of HL, such as depolymerization of HL and utilization of depolymerized lignin products for the production of valuable biomaterials like bio-based PU foams.

Lignin can also be prepared from organosolv pretreatment following organic-solvent based procedures. The effects of pretreatment on lignocellulosic materials are shown in Figure 2-3 (Mosier et al., 2005).

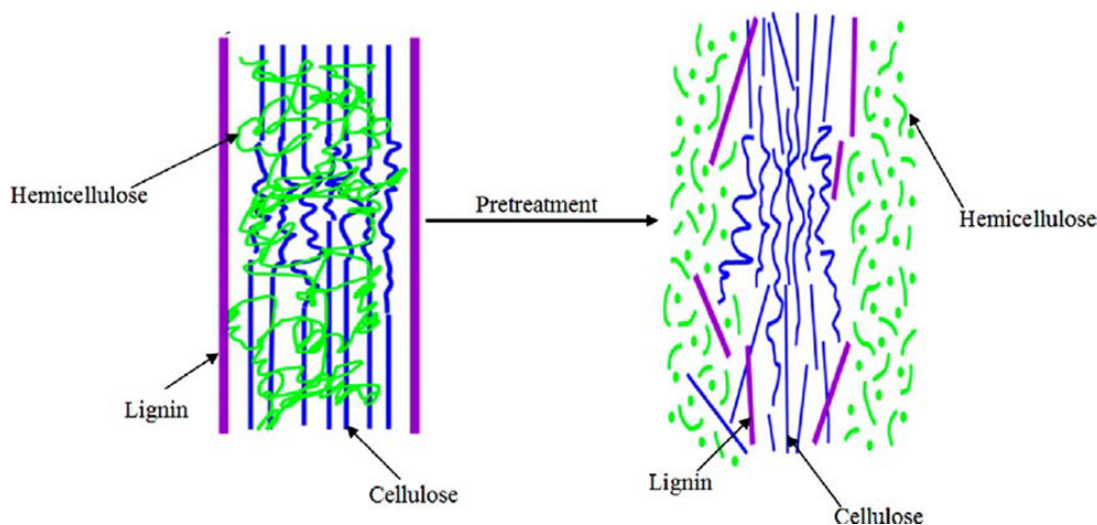


Figure 2-3 The effect of pretreatment on lignocellulosic materials, reprinted (adapted) with permission from (Mosier et al., 2005). Copyright © (2005) Elsevier.

Table 2-1 Chemical composition of the hydrolysis lignin (HL) used (Yuan et al., 2012)

Lignin <sup>a</sup> wt.%	56.7
Carbohydrates <sup>a</sup> wt.%	29.8
Ash <sup>a</sup> wt.%	1.2
Others, wt.%	12.3
Carbon <sup>b</sup> , wt.%	62.8
Hydrogen <sup>b</sup> , wt.%	6.1
Nitrogen <sup>b</sup> , wt.%	4.0
Others <sup>b</sup> , wt.%	28.3

<sup>a</sup> On dry basis

<sup>b</sup> On dry and ash free basis

### 2.2.3 Lignin applications in polymer and materials industries

Kraft lignin (KL) comprises almost the whole market of commercially available lignin. Beside the traditional use as energy source and in leather tanning, lignin is now used for food stabilization (Boeriu et al., 2004), due to its antioxidant and antifungal, anti-carcinogenic properties (Lu et al., 1998). Lignin was also employed for the production various other products (Gosselink et al., 2004), however, they were still expensive. Lignin itself is by-product from pulping or cellulosic ethanol processes therefore; it must be used in a way that can enhance the profits of these processes, and it is more promising for the applications where the brown/dark coloration it imparts does not affect the applications. The promoting factor for utilizing lignin as a raw material for polymeric synthesis can be summarized as follows (Cui et al., 2008): lignin is a (1) renewable and abundant raw material that constitutes about 15-30% of the wood and 12-20% of other annual plants; (2) material with intrinsic biodegradability which is expected to be transmitted to polymers where lignin is incorporated; (3) material with various reactive points that can be used in a wide range of chemical reactions; (4) byproduct of the pulp industry available in a large quantity. HL has only been utilized as a sorbent, resin and dispersant applications. The utilization of HL as polyols for the preparation of foams has not been reported in the literature. For applications of HL, it is also necessary to depolymerize HL cost effectively and efficiently to enhance lignin reactivity.

## 2.3 Polyurethane (PU) and rigid PU foams

Since the invention of polyurethanes by Professor Otto Bayer in 1937, the utilization of polyurethanes is ubiquitous. These polymers have found applications in a wide range of products, from thermal insulation to medical implants (Chian and Gan, 1998). Polyurethanes are block copolymers containing blocks of low molecular weight polyesters or polyethers covalently bonded by a urethane group (-NHCO-O-). PUs are synthesized by reacting three components comprised of polyisocyanate; polyhydroxyl containing polymer (i.e., polyester or polyether polyols); and a chain extender, which is usually a low molecular weight diols (e.g., 1, 4-butanediol) or diamines (e.g. 1,4-

dibutylamine). Currently, there is a very wide range of polyisocyanates, polyols, and chain extenders commercially available and this has led to almost unlimited formulation possibilities for polyurethane materials. Because of the inherent versatility in polyurethane syntheses, the properties of this class of polymers can be easily engineered to suit various applications (Xu et al., 2014). PU has rapidly grown to be one of the most diverse and widely used plastics with a continuously increasing global market. Polyurethane has its own unique merits, such as low density, low thermal conductivity and moisture permeability, a high strength to weight ratio, and high dimensional stability (Lim et al., 2008). Foams represent one of the most important commercial products of PU. The PU foams are commonly classified as flexible, semi-rigid, or rigid foams, depending on their mechanical performances and core densities (Cinelli et al., 2013).

### 2.3.1 Global market and typical properties of rigid PU foams

Polyurethane rigid foams are widely used as insulation and structural materials for insulation, construction, transportation, and decoration etc. Those foams accounts for almost one-third of the polyurethane market. Out of annual 2.8 billion lbs of North American polyol market, approximately 1.3 billion lbs of polyols are used for the manufacturing of polyurethane rigid foams (Luo et al., 2000). Rigid PU foam is a highly cross-linked polymer with an essentially close cell structure and low thermal conductivity which have made rigid PU foam a dominant material on a global basis (Banik and Sain, 2008). Recently, it has been reported that Polyurethanes (PU) markets in North America are projected to grow steadily through to the end of 2014 and into 2015. According to ICIS, in particular, rigid PU foam consumption is expected to increase in auto applications and construction. Table 2-2 summarizes some typical properties of commercial rigid PU foams (BASF, 2010; ENERLAB, 2012; INSTA-PANELS, 2012; BING, 2006).

Table 2-2 Typical properties of commercial rigid PU foams (BASF, 2010; ENERLAB, 2012; INSTA-PANELS, 2012; BING, 2006)

Property (unit)	Measured value
Density (core) (kg/m <sup>3</sup> )	42.0

Density (apparent overall) (kg/m <sup>3</sup> )	40.0
Young's modulus (kPa)	124-152
Compression strength @ 10% deformation (kPa)	200
Thermal conductivity (W/mK)	0.0233
Closed cell contents (%)	>90
Water absorption (% by volume)	0.20
Dimensional stability at -20 °C (%)	<1.0
Dimensional stability at +70 °C (%)	<2.0

### 2.3.2 Preparation of rigid PU foams and its essential raw materials

A typical rigid PU foam formulation includes an isocyanate, a polyol, a co-crosslinking agent, physical and/or chemical blowing agents, catalysts, and a surfactant, with each one having a specific role in the chemical reactions involved in the formation of rigid PU foam. The reactions involved in this process include urethane formation, crosslinking reactions, and foaming reactions if chemical blowing agent is used. The heat of reaction for PU formation is ~100-110 kJ/mole of urethane. The hydrogen next to nitrogen atom in the urethane group is capable of reacting with additional isocyanates to form an allophanate group as shown in Figure 2-4 (Tu, 2008). Further reactions of amine with additional isocyanate will generate distributed urea (Figure 2-4) and the approximate total heat released per mole of water is 196 kJ. The distributed urea can further react with additional isocyanate to form Biuret linkage as shown in Figure 2-4.



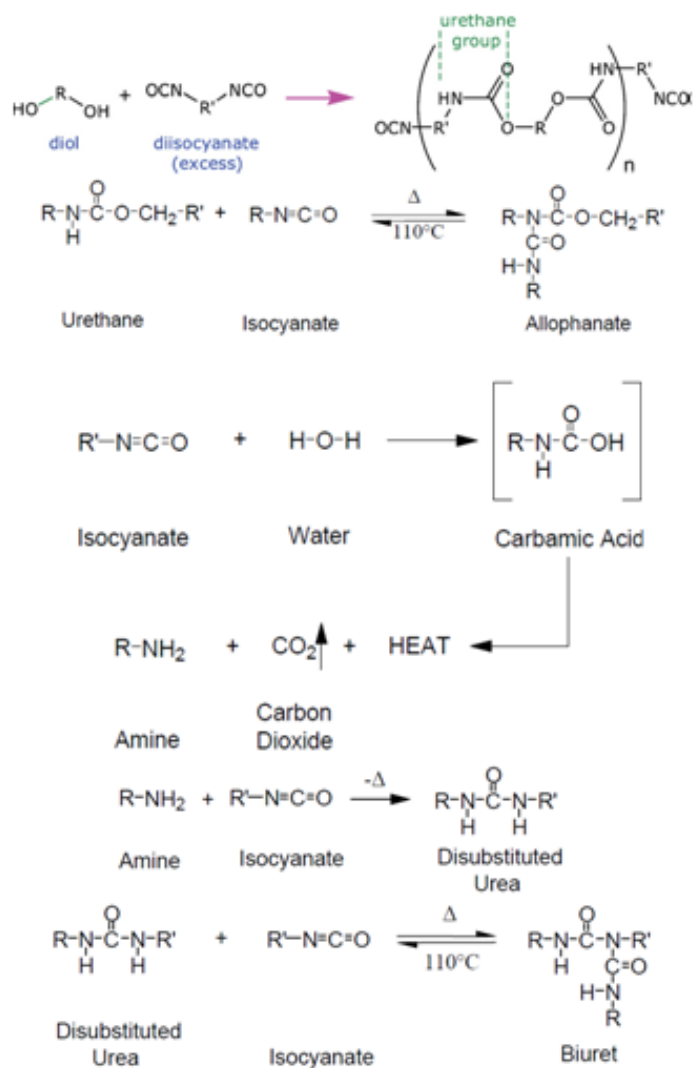


Figure 2-2 Main and side reactions in polyurethane production (Tu, 2008)

The foaming can be done by one shot or two shot methods. In one shot method, all materials loaded into a mixing container and mixed homogeneously before they are poured into a mold. In the two shot method, in the first stage all other ingredients (polyols, blowing agents, catalysts etc.) were premixed and then isocyanate is added to the mixture at the second stage. The foaming can be carried out with a physical blowing agent, chemical blowing agent, or with a mixture of the two (Mondal and Khakhar, 2004). In physical blowing, reactions between isocyanate and polyol produce polyurethane linkages with the emission of heat of reaction. Then, the blowing agent vaporizes and the gas trapped in the closed cells of the foam (Lim et al., 2008). Typically,

thermal conductivity of the blown gas is very low. This, with small closed cell structure gives extremely low thermal conductivity of the rigid PU foams. In chemical blowing, water (most widely used blowing agent) reacts with isocyanate to form unstable carbamic acid which immediately decomposes into an amine and CO<sub>2</sub> (Kwon et al., 2007). The amount of water needed during the reaction should be accurately estimated otherwise, the use of excessive water can cause a negative pressure gradient due to the rapid diffusion of CO<sub>2</sub> through the cell wall causing cell deformation (Kim et al., 2008).

### 2.3.2.1 Isocyanate

The most commonly used aromatic isocyanates in rigid PU foam formulations are TDI (toluene diisocyanate) and polymeric MDI (diphenylmethane diisocyanate), although later have gained increasing popularity in recent years. The average functionality of MDI is 2.7 (NCO contents ~31.2 %).

### 2.3.2.2 Polyol

The most important polyols used in rigid PU foam formulations are primary and secondary hydroxyl terminated polyether polyols followed by polyester polyols, normally of aromatic nature. This tendency results from the enormous variety of molecular structures regarding hydroxyl functionality and molecular weight of polyether polyols. More, recently, some aromatic polyester polyols have gained an increased attention from rigid PU foam producers, partly motivated by its low cost and also due to its aromatic nature which ensures more internal cohesion of materials (Li, 2012). The polyols used in rigid PU foam preparation have normally a high total hydroxyl number (amount of KOH in mg consumed for the neutralization of acid from 1 g of polyol) between 200-800 mgKOH/g. Until now petroleum polyols have been employed for foams preparation however, due to high prices of petroleum products coupled with their depletion in resources there are more interests for the preparation of polyols from renewable and low cost materials (Mahmood et al., 2013).

### 2.3.2.3 Catalyst, blowing agent, surfactant and crosslinking agent

PU polymerization reaction is catalyzed by tertiary amines, such as dimethylcyclohexylamine, and organometallic compounds, such as dibutyltin dilaurate or bismuth octanoate. Furthermore, specific catalysts can be chosen based on whether they favor urethane (gelation) reaction, such as 1,4-diazabicyclo[2.2.2]octane (also called DABCO or TEDA), or the urea (blowing) reaction, such as bis-(2-dimethylaminoethyl)ether, or specifically drive the isocyanate trimerization reaction such as potassium octoate (Twitchett, 1965; Duggal et al., 2013).

One of the most desirable attributes of PU is its ability to be turned into foams. Blowing agents such as water (chemical blowing agent) or n-pentane (physical blowing agent) can be formulated into the poly side or added as an auxiliary stream (Fleurent and Thijs, 1995). In the preparation of PU foams blowing agents can be used alone or in combination depending on the final density of the foam desired. Since the polymerization reaction is exothermic, these blowing agents vaporize to a gas during the reaction process, and thus they fill and expand the cellular polymer matrix, creating foam structure.

Surfactants are used to modify the characteristics of the polymer matrix during the foaming process. They are used to emulsify the liquid components, regulate cell size, and stabilize the cell structure to prevent collapse and surface defects. Rigid foam surfactants are designed to produce very fine cells and very high closed cell contents. The most commonly used surfactants are silicon surfactants. Crosslinking agents are employed to enhance the crosslinking of the polymer for better dimensional stability for the foams.

## 2.4 Lignin depolymerization via multiple routes

Owing to lignin's special phenyl propanol structure and aryl-alkyl ether bonding, lignin can be a good source of polyols for PU production (Demharter, 1998). Crude lignin can be directly incorporated into PU formulations due to the presence of aliphatic and aromatic hydroxyl groups in its structure as the reactive sites, replacing <30 wt.% of petroleum-based polyols (Cateto et al., 2008). However, crude lignin has a much lower reactivity not only because it has less reactive sites, but also because the reactive

positions of the macromolecules of lignin or its fragments have lesser accessibility due to the steric hindrance (Cheng et al., 2012). It is thus an effective way to improve lignin's reactivity through depolymerization of lignin into oligomeric products of reduced molecular weights with higher functionality (Alma et al., 2001; Lee et al., 2000). Despite the anticipated improvements in engineered lignin structures and tailored pretreatment chemistries, some lignin fractions from biorefinery are not expected to be suitable for material applications but can still be valuable for conversion into fuels and chemicals. Lignin depolymerization is challenging given the broad distribution of bond strengths in the various C-O and C-C linkages in lignin and the tendency for low molecular weight intermediates to undergo recondensation/repolymerization, often to more recalcitrant species (Ragauskas et al., 2014). To date, multiple strategies have emerged for lignin depolymerization including thermochemical treatments, homogeneous and heterogeneous catalysis and biological depolymerization.

Crude lignin is heterogeneous in nature and mainly composed of two types of linkages: condensed linkages (e.g., 5-5 and  $\beta$ -1 linkages) and ether linkages (e.g.,  $\alpha$ -O-4 and  $\beta$ -O-4) (Chakar and Ragauskas, 2004). The percentage of ether linkages in soft- and hardwood lignin are 56% and 72%, respectively (Pu et al., 2008). Aryl ether linkages can be more easily cleaved by lignin depolymerization/liquefaction processes (Yuan et al., 2010). The major objective of all the depolymerization strategies is to cleave the ether linkages in lignin structure (Zakzeski et al., 2010; Boerjan et al., 2003). To achieve this target chemically, various types of solvents, alone or in combination of co-solvents mixture, and catalysts have already been investigated. Chemical depolymerization of lignin can be divided into five categories by Wang et al. (2013) according to the different chemicals applied in the depolymerization process: (1) acid-catalyzed, (2) metallic catalyzed, (3) ionic liquids-assisted, and (4) sub- or supercritical fluids-assisted lignin depolymerization, (5) base-catalyzed lignin depolymerization.

#### 2.4.1 Lignin depolymerization with acid catalysis

Lignin hydrolytic depolymerization under acidic conditions was carried out on hydrolysis lignin using 0.2 M hydrogen chloride (HCl) in dioxane-water (9:1), resulting in the formation of low molecular weight compounds (Lundquist, 1976; Matsushita and

Yasuda, 2005). Later degradation of Kraft lignin, dissolved in 50% (v/v) dioxane-water, by using hemin and hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) was investigated to produce phenolic compounds as a substitute for leather tanning (Suparno et al., 2005). Depolymerization of Indulin Kraft lignin was carried out using silica-alumina (Si/Al: 2) catalyst in water and 1-butanol solution, which led to a yield of liquid products at 85-88 mol-C % (Yoshikawa et al., 2013). Matsushita and Yasuda (2005) carried out hydrolytic depolymerization of lignin using sulfuric acid (72%) at 60-80 °C for producing lignin sulfonate or sulfuric lignin, which can be further utilized for the synthesis of ion exchange resins.

Although, lignin can be depolymerized to some extent via depolymerization in acidic media; its major drawback is the unavoidable repolymerization/condensation of intermediate products formed during the reaction (Yuan et al., 2010), proceeding mainly between phenol reactive sites and  $\alpha$ -position of phenol propanol. This results in the increased molecular weight of the end products. Other problems encountered in hydrolytic depolymerization with  $\text{H}_2\text{SO}_4$  catalyst are related to the difficulty in treating the waste sulfuric acid from the acid catalyzed reactions. As such, lignin depolymerization with metallic catalysts, alkaline catalysts, ionic liquids and organic solvents has gained more attentions, as described in details below.

#### 2.4.2 Lignin depolymerization with metallic catalysis

Disruption of the complicated lignin polymer into smaller oligomers is an important step for lignin valorization for chemicals. Catalysts, in many cases, are required to assist selective bond cleavage, leading to high selectivity for a particular compound in the product stream. Various catalysts have been tested for different processes and substrates including both model compounds and lignin extracts. Zakzeski et al. (2010) and Pandey & Kim (2011) have published comprehensive literature reviews in this regard (Zakzeski et al., 2010; Pandey and Kim, 2011). Catalytic reductive depolymerization of lignin typically requires high pressure of hydrogen or a reducing agent such as formic acid. Metallic catalysts demonstrated effective to improve the selectivity towards the desired product. However, the major issue of using metallic catalysts was their fast deactivation which made their use expensive (Ye et al., 2012).

### 2.4.3 Ionic liquid assisted lignin depolymerization

Ionic liquids are salts with melting points below an arbitrary set point of 373 K. They often have tunable physical properties based on the choice of cation and anion pairs, negligible vapor pressure, and good thermal stability (Zakzeski et al., 2010). Ionic liquids have proved to be appropriate solvents for the dissolution of biomass (Zakzeski et al., 2010) and lignin (Kilpeläinen et al., 2007). However, the high cost of ionic liquids (Zhu, 2008) and the difficulty in separation of them from depolymerized products made their use in lignin depolymerization very limited and less practical (Zakzeski et al., 2010).

### 2.4.4 Sub- or supercritical fluid assisted lignin depolymerization

Solvents in supercritical conditions behave differently from those in subcritical and ambient conditions and have many interesting properties. Various researchers have studied the conversion of biomass, lignin and lignin model compounds in supercritical water ( $T_c = 374.15$  °C and  $P_c = 22.1$  MPa) (Pandey and Kim, 2011). These studies have shown that hydrolysis in supercritical water is a probable pathway in lignin depolymerization. However, the yields of monomeric phenols were reported to be lower than expected, probably due to repolymerization of intermediates or monomers forming heavy products or char. It has been suggested by some researchers that the addition of phenol can prevent char formation, but phenol, primarily produced from petroleum derived benzene through the cumene process, is very costly (Xu et al., 2011), making the overall process very expensive. Sub- and supercritical organic solvents/fluids alone or in combinations with alkaline catalysts have been reported very efficient in the depolymerization of lignin (Yuan et al., 2010; Cheng et al., 2012). Similar to ionic liquids, sub- and supercritical organic solvents/fluids have been employed as they showed good solubility for lignin. However, these processes normally operate at high temperatures and pressures, so the overall cost of the depolymerization process is still high.

### 2.4.5 Lignin depolymerization with base catalysis

Catalysts used in lignin depolymerization should promote high conversion and suppress char formation and condensation, while keeping the reaction severity under a permissible

limit. Alkaline catalysts could reduce the formation of char/coke in lignin depolymerization (Nenkova et al., 2011). The depolymerization of Kraft and organosolv lignin using KOH in supercritical methanol/ethanol was studied in a rapidly heated batch microreactor, where a high lignin conversion was achieved with only 7% ether insoluble materials (char) remaining after treating organosolv lignin in KOH/ethanol at 290°C (Miller et al., 1999). Further studies with NaOH, CsOH, LiOH, Ca(OH)<sub>2</sub> and Na<sub>2</sub>CO<sub>3</sub> indicated that strong bases gave superior conversion, and an excess base relative to lignin monomer was required for maximum conversion. Recently, Yuan et al. (2010) produced oligomers/polyols ( $M_w \approx 1000$  g/mol and  $M_n \approx 450$  g/mol) through hydrolytic degradation of Kraft lignin ( $M_w \approx 60,000$  g/mol and  $M_n \approx 10,000$  g/mol) using NaOH in a water-ethanol mixture and phenol as a capping agent (lignin to phenol ratio = 1:1 (w/w)). Under optimal conditions (260 °C and 1 hr), char and gas production was negligible. Further studies by Yoshikawa et al. (2012) indicated that strong bases like KOH or NaOH resulted in superior conversion and effective reduction in char formation. Recently, Beauchet et al. (2012) carried out base-catalyzed de-polymerization of KL (10 wt.% concentration) in a continuous flow reactor over 270-315 °C and 130 bar for the production of a monomers-rich fraction, small organic compounds and oligomers.

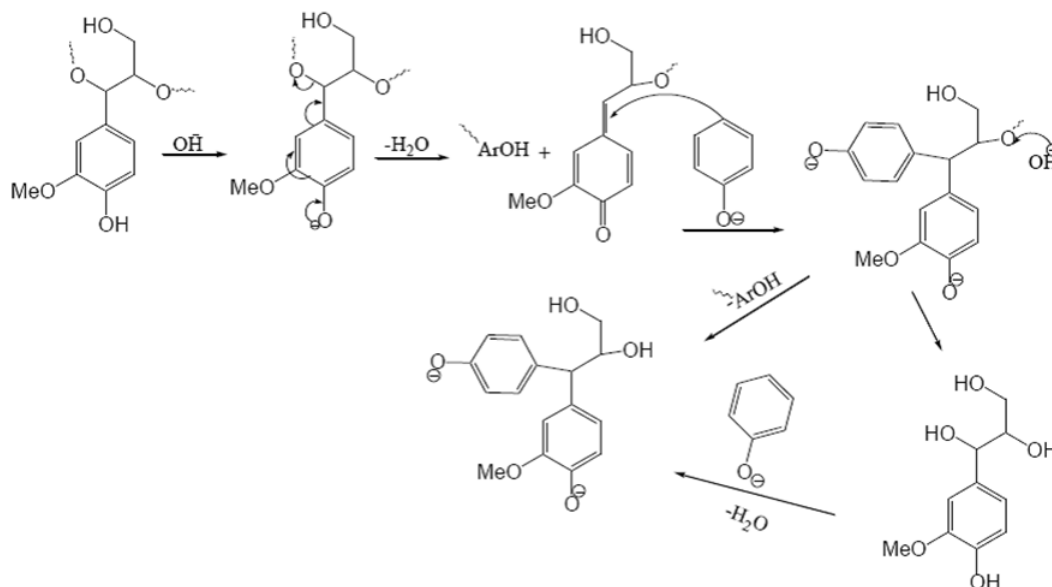


Figure 2-3 Hydrolytic depolymerization mechanism of alkaline lignin catalyzed by NaOH in water-ethanol medium with phenol capping agent, reprinted (adapted) with permission from (Yuan et al., 2010). Copyright © (2010) Elsevier.

Hydrolytic depolymerization has gained much attention recently for the depolymerization of KL into low molecular weight products employing water alone as a solvent. [Mahmood et al. \(2013\)](#) successfully depolymerized KL (DKL) hydrolytically using water alone as a solvent under alkaline medium without employing any organic solvent/capping agent. The obtained depolymerized KL (DKL) (yield ~ 90%) was in solid or powdered form soluble in organic solvents and the DKLs have acceptable characteristics as bio-polyols for PU synthesis. Although there were no waste streams were generated during this depolymerization process, this process may be challenging for industrial applications due to the severity of the reaction conditions (250-300°C and 5-10 MPa pressures) and the required post-treatment steps. Therefore, further research is needed to explore cost effective process with lower operating temperature and pressure for lignin depolymerization.



#### 2.4.6 Lignin depolymerization via oxidative route

Oxidative processes for lignin depolymerization can be realized by catalytic side-chain oxidation and fragmentation reactions. Typically the targeted products from lignin oxidation, wherein the aromatic character is preserved, include aromatic acids and aldehydes with smaller market volumes (Ragauskas et al., 2014). However, oxidation can enable production of ring-opened organic acids that can be effectively separated for highly valuable products. Oxidative depolymerization of lignin usually employed noble metal as an appropriate catalyst and H<sub>2</sub>O<sub>2</sub> as an environment friendly and low cost oxygen atom donor (Crestini et al., 2006), and after oxidation treatment of spruce lignin more soluble lignin fragments with a high degree of depolymerization were produced, indicated by lower contents of aliphatic and condensed -OH groups, and higher amounts of carboxylic acid moieties in the de-polymerized lignin products. Manganese peroxidase (MnP) is also a common catalyst for lignin oxidative depolymerization (Hofrichter, 2002). According to Thring et al. (2000), solvolysis lignin could be converted to liquid products mainly consisting of aromatic hydrocarbons (mostly benzene, toluene and xylene with toluene dominating) over HZSM-5 catalyst under atmospheric pressure and 500-650°C temperature (conditions similar to pyrolysis). Lately, some research interest was focused on selective lignin polymer oxidative depolymerization to obtain poly-functional monomeric compounds (Crestini et al., 2006).

#### 2.4.7 Lignin depolymerization under low pressure

Due to the complex methods, intense reaction conditions and high costs associated with the existing methods for the hydrolytic or reductive depolymerization of lignin as described previously, it is of great interest and significance to explore alternative routes with lower operating pressure and temperature.

Cinelli et al. (2013) liquefied Indulin AT lignin in polyols (glycerol and PEG 400) in a glass flask under microwave treatment in oven at 180 °C for 3 min, to prepare feedstock for preparation of flexible PUs. However, the resulting sample was of very high viscosity and needs the addition of another solvent before further application. Hu et al. (2012) liquefied soybean straw (loading from 10%-25%) under atmospheric pressure employing

crude glycerol and concentrated sulfuric acid (0-5%) at 120-240 °C over 45-360 min, aiming to produce bio-polyols for polyurethane foams too. [Hassan and Shukry \(2008\)](#) conducted the liquefaction of bagasse and cotton stalks by using polyhydric alcohols (PEG400 and glycerine) in the presence of sulfuric acid as a catalyst and found that PEG400 alone was not suitable due to the large formation of solid residues, while replacing 10% PEG400 with glycerine helped to reduce yield of solid residue by 50%. [Zheng et al. \(2011\)](#) compared the conventional bath heating with microwave heating on the degree of wood liquefaction in polyhydric alcohols for polyols and PU foams preparation, and found that microwave heating was more advantageous in terms of product yields. Interestingly, [Jasiukaityte-Grojzdek et al. \(2012\)](#) used milled-wood lignin as a model substrate for lignin liquefaction using either p-toluene sulfonic acid monohydrate or sulfuric acid as the catalysts and studied the structural changes that lignin undergoes during the treatment by  $^1\text{H}$  NMR, FTIR, SEC and HPLC.

Most of the depolymerization approaches under low pressure are using polyhydric alcohols for producing polyols for the preparation of PUs, where the polyhydric alcohols used were not recyclable. Recently, in the author's group depolymerization of lignin (KL and HL) was successfully carried at low pressure ( $\leq 150$  psig) with a high yield of ~90% and low molecular weight ~1000 g/mole, where the solvent used was recyclable. The obtained depolymerized lignin (DKL & DHL), although in solid form, has a suitable hydroxyl number, and can be used as polyols for preparation of rigid PU foams.

#### 2.4.8 The global trend of lignin application in PUs

The interest for developing lignin-based bioproducts, including lignin-based polymers and materials, has been intensified in the past few years, owing to several major reasons, namely (1) the greater demand of green chemicals and products, (2) the availability of new lignin sources such as sulfur-free lignin such as hydrolysis lignin (HL), and (3) the growing interest in lignin valorization for pulp/paper mills which have a capacity bottleneck in recovery boilers ([Borges da Silva et al., 2009](#)). In this regard, exploring lignin as a raw material for polyurethane synthesis has received the most intensive and extensive interest for lignin valorization for some reasons, i.e., (1) the random non-crystalline network structure of lignin contributes to better mechanical properties and

thermal stability for the lignin-based PU foams (Thring et al., 1997), (2) the natural properties of lignin contribute to an improvement of the moisture and flame resistance of PU foams (Glasser et al., 1991), and (3) its aliphatic and phenolic hydroxyl functionalities provide good reacting sites towards isocyanates (Thring et al., 1997). Various types of lignin-based polyurethane materials including elastomers and foams have been produced (Borges da Silva et al., 2009). The exhibited properties were comparable or in some cases even superior to those of the conventional polyurethanes (Li, 2012).

#### 2.4.9 Lignin application in the preparation of PUs

Preparation of polyurethanes from lignin is not an easy task because of the complex structure of lignin. The utilization of lignin in polyurethane synthesis follows two global approaches (Borges da Silva et al., 2009): (1) direct utilization of lignin without any preliminary chemical modification, alone or in combination with other polyols, and (2) utilization after chemical modification, such as esterification and etherification reactions to make hydroxyl functions more readily available. Recently, Mahmood et al. (2013) demonstrated that hydrolytic depolymerization of Kraft lignin (KL) and hydrolysis lignin (HL) could be a viable route for the preparation of depolymerized products (DKL & DHL) with low molecular weights and acceptably high hydroxyl numbers, and these depolymerized products can be incorporated in the preparation of rigid PU foams at higher replacement ratios ( $\geq 50\%$ ) without much compromising the properties of the final foams.

##### 2.4.9.1 Direct incorporation of lignin in PU foam without modification

Several works have been reported aiming to incorporate lignin directly in PU formulations, taking advantage of both aliphatic and aromatic –OH functionalities within lignin structure (Demharter, 1998). Among the selected studies it is worth mention the review of Belgacem and Gandini (2008) which highlights the work performed by several research groups on the utilization of non-modified lignin in PU formulations. Hatakeyama and Hatakeyama (2010) also reported the use of non-modified lignin in

combination with oligoether diols as the polyol component in PU foam formulations. [Pan and Saddler \(2013\)](#) replaced petroleum-based polyol (Voranol 270) with hardwood ethanol organosolv lignin (HEL) or hardwood Kraft lignin (HKL) from 25% to 70% (molar percentage) in preparing rigid polyurethane foam. The foams produced contained 12-36% (w/w) HEL or 9-28% (w/w) HKL. They reported that the lignin was chemically crosslinked and the lignin-containing foams had comparable structure and strength up to 25-30% (w/w) HEL or 19-23% (w/w) HKL addition. However, the densities of lignin-based PU foams were normally higher than the commercial foams. However, with the increasing ratio of HKL in PU foam from 9% (w/w) to 19% (w/w) respectively, the density of pure polyurethane foam reduced from 116 kg/m<sup>3</sup> for PU foam derived from pure Voranol 270 to 100 kg/m<sup>3</sup> and 70 kg/m<sup>3</sup> when increasing ratio of HKL in PU foams from 9%(w/w) to 19% (w/w), respectively. With further increasing the ratio of HKL in PU foam from 19% (w/w), to 28% (w/w), the foam density increased from 70 to 85 kg/m<sup>3</sup> perhaps due to the non-uniform dispersion of HKL and granule formation in the foaming process ([Pan and Saddler, 2013](#)). There is a limitation regarding the percentage replacement of petroleum polyols by employing crude lignin. The major issue for incorporating crude lignin into the PU formulation is related to the low solubility of the lignin in polyol system for PU foams. Thus, direct replacement of petroleum-based polyols with crude lignin generally achieved PU foams at lower bio-replacement ratios.

#### 2.4.9.2 Modified lignin via oxypropylation and its incorporation in PU foam

Incorporation of crude lignin in a powder form directly into PU foam to replace petroleum-based polyols limits the percentage replacement due to the high molecular weight, lower solubility in polyols and lower aliphatic hydroxyl numbers of the lignin. Compared with incorporation of lignin into PU materials directly to replace petroleum-based polyols, utilization of lignin after chemical modification (esterification and etherification reactions) appeared to be more advantageous for a higher replacement ratio ([Cateto et al., 2011](#)). Among the various synthetic routes for the production of rigid polyurethane foams (RPU), oxypropylated lignin seems to be the most feasible one. Through oxypropylation, the aromatic hydroxyl groups, that is not very reactive towards

isocyanates as they are entrapped inside the molecule and difficult to access, are converted to aliphatic hydroxyl group and liberated from the steric and/or electronic constraints (Cateto et al., 2009). Meanwhile, the solid lignin becomes a liquid polyol, as a result of the introduction of multiple ether moieties. Nadji et al. (2005) carried out the oxypropylation of Kraft lignin (KL) and the resulting polyols were employed for the preparation of rigid PU foams. Although the KL/PO ratio was low varying from 10/90 to 20/80, Cateto et al. (2009) synthesized polyether polyols, using four technical lignins (Alcell, Indulin AT, Curan 27-11P, and Sarkanda) via oxypropylation. Cateto et al. (2011) monitored the formation of lignin based polyurethanes, prepared from lignin derived polyether polyols via oxypropylation, by FTIR-ATR and the kinetics was analyzed according to a global second order model. Solid Kraft pine lignin could also be converted to a liquid polyol through oxypropylation, and the resulting polyol was characterized and a series of lignin-based PU was synthesized by replacing varying weight percentages of the amount of sucrose polyol and glycerol polyol (Li and Ragauskas, 2012). All foams had a low density of  $\sim 30 \text{ kg/m}^3$ . Interestingly, the optimal compressive property of rigid PU foams was obtained using lignin polyol without the addition of any other commercial polyols primarily attributed to the rigidity of lignin aromatic structure and the high functionality of lignin hydroxyl groups.

## 2.4.10 Depolymerized lignin application for PU foam preparation

### 2.4.10.1 Direct incorporation of depolymerized lignin in PU foams

Extensive efforts have been made to explore high value applications of lignin, in particular in polymeric materials, in particular PU (Pan and Saddler, 2013). Preparation of low-cost polyols from abundant and renewable resources has long been an important subject in the PU industry. PU has rapidly grown to be one of the most widely used synthetic polymers with a continuously increasing global market. Rigid PU foam is a highly cross-linked polymer with closed-cell structure. KL was first incorporated into a polyether triol, forming a cross-linked network of PU (Yoshida et al., 1990). Hatakeyama et al. (2004) prepared rigid PU foam from Kraft lignin together with diethylene glycol (DEG), triethylene glycol (TEG) and polyethylene glycol (PEG) with molecular mass of 200 (PEG200). Sulfur-free lignin from straw steam explosion was also investigated for

polyurethane preparation (Bonini et al., 2005). Cinelli et al. (2013) liquefied Indulin AT lignin with polyols (glycerol and PEG 400) in a glass flask under microwave treatment in oven at 180 °C for 3 min, and utilized the liquid product with in the preparation of flexible PUs. However, the liquid products obtained from liquefaction could not be used for the production of flexible PUs due to excessive viscosity and very high OH values. Therefore PPG and castor oil was further added to reduce viscosity and glass transition temperature of the final materials while increasing the flexibility. Thus, the lignin contents in the final PU foam product were very low. Hu et al. (2012) studied the feasibility of using crude glycerol to liquefy soybean straw for the production of biopolyols ad polyurethane foams. Biopolyols produced showed a hydroxyl number of 440-540 mgKOH/g and the foams produced showed densities of 33-37 kg/m<sup>3</sup> and compressive strength from 148-227 kPa.

However, in spite of a lot of efforts for the incorporation of even depolymerized lignin with or without modification, the lignin contents are limited. Most of the research work presented in literature shows that the wt.% replacement of petroleum-based polyols with crude lignin in PU foams structure is not more than 30 wt.%. At the same time the molecular weight of lignin/depolymerized lignin is also an important factor responsible for deteriorated properties for the lignin-based PU foams. With the increase of replacement ratio glassy materials foam materials were resulted. To address this problem, the most viable route would be depolymerization of lignin prior to its application in the synthesis of PU foam. Depolymerization of lignin results in de-polymerized lignin (DL) products with lower molecular weights suitably high aliphatic and total hydroxy numbers, making them suitable for the preparation of PU foams at higher replacement ratios.

The author's group successfully depolymerized KL into low molecular weight products via direct hydrolysis using NaOH as a catalyst, without any organic solvent/capping agent (Mahmood et al., 2013). At the best operating conditions (250 °C, 1 h, and NaOH/KL ratio  $\approx$ 0.28 (w/w) with 20 wt.% substrate concentration) yield of depolymerized KL (DKL) was  $\sim$ 92 wt.% with solid residues  $<$ 0.5 wt.% ( $M_w \approx$ 3310 g/mole & aliphatic hydroxyl number  $\approx$ 352 mgKOH/g). The molecular weight of DKL was slightly higher than the desirable molecular weight of polyols for the preparation of

rigid PU foams (Li and Ragauskas, 2012). Therefore, the author's group carried out an optimization study subjected to several constraints: (1) yield of DKL  $\geq 75$  wt.%; (2) moderately high aliphatic-hydroxyl number ( $\geq 300$  mgKOH/g) and; (3) lowest possible  $M_w$ . The optimized reaction conditions determined for the hydrolytic depolymerization are: 250 °C, 2 h, and NaOH/KL ratio  $\approx 0.28$  (w/w) with 10 wt.% substrate concentration, under which the KL depolymerization produced DKL at a yield of  $\sim 77$  wt.%, with  $M_w \approx 1700$  g/mole and aliphatic-hydroxyl number  $\sim 365$  mgKOH/g. The produced DKL was successfully utilized as bio-polyols replacing 50 wt.% of PPG400 and sucrose polyols for the preparation of rigid polyurethane foams. The bio-based foams prepared with DKL and sucrose polyols showed superior compression modulus (5152.0 kPa) and thermal conductivity (0.032 W/mK) than those with DKL and PPG400. Mahmood et al. (2013) also successfully depolymerized hydrolysis lignin (HL) in 50/50 (v/v) water-ethanol mixture under  $N_2$  atmosphere at 250 °C for 1 h, and the depolymerized HL (DHL) was also utilized as bio-polyols for the preparation of bio-based rigid PU (BRPU) foams, replacing at 30 wt.% and 50 wt.% of PPG400 and sucrose polyols. Again, BRPU prepared with DHL and sucrose polyols showed superior compression strengths at 10% ( $216 \pm 31$  kPa) and lower thermal conductivities ( $0.036 \pm 0.001$  W/mK) than those with DHL and PPG400.

#### 2.4.10.2 Modified depolymerized lignin via oxypropylation and its incorporation in PU foams

Depolymerized lignins after removing solvents are still in powder form and there exist less accessible hydroxyl groups in the molecular structure. Thus, chemical modification such as oxypropylation with alkylene oxide was found to be beneficial as it could improve the accessibility of the hydroxyl groups and convert lignin from solid form into a liquid polyol with extended chain and exposed hydroxyl groups (Pan and Saddler, 2013). To the best of the author's knowledge, no study has been reported on the utilization of depolymerized KL and HL for the preparation of BRPU foams with satisfactory physical, mechanical and thermal characteristics, replacing 50 wt.% or more petroleum-based polyol and sucrose polyol. In the author's group, DKL obtained from the hydrolytic depolymerization of KL was used for the preparation of polyols via oxypropylation in a

unique medium consisting of propylene oxide (PO), glycerol+KOH (11 wt.% KOH) and acetone. The prepared polyols were employed as a single polyol in the preparation of BRPU with high bio-contents up to 70 wt.%. Similarly, oxypropylated DHL was also successfully incorporated in the BRPU foams at high percentage of bio-contents.

## 2.5 Concluding Remarks

Lignin, nature's dominant aromatic polymer, is found in most terrestrial plants in the approximate range of 15-40 % dry weight and provides structural integrity. Kraft lignin (KL), sulfur containing lignin, is a major by-product of the pulp & paper industry, and hydrolysis lignin (HL), sulfur free lignin, is the solid residue left from the enzymatic hydrolysis of wood after the pretreatment processes in cellulosic ethanol plants. Currently, most of the lignin in pulp/paper mills is burned in recovery boilers to generate heat and electricity. Only 1% of the annually produced lignin is being commercialized mainly for lignin sulfonate. Although with much lower reactivity, crude lignin can be directly incorporated into PU formulations as a natural polyol to replace petroleum polyols due to the presence of aliphatic and aromatic hydroxyl groups in its structure. However, with crude lignin the replacement ratios are usually low in the range of ~20-30 wt.%. Further increasing replacement ratios would result in fragile and low strength PU foams. Lignin depolymerization with selective bond cleavage is a promising approach for converting it into value-added precursors especially for its utilization in the preparation of rigid polyurethane (PU) foams. Depolymerization of these macromolecules can result in valuable products with improved functionality and reduced molecular weights, which in turn will increase the percentage replacement of bio-based polyols in the foam formulations. Depolymerization is realized by hydrolysis/reduction/oxidation employing solvents, catalysts, appropriate atmosphere (inert, reductive or oxidative) at elevated temperature and pressure.

Over the past few decades, much research has been conducted to investigate the production of value added bioproducts from KL. Recently, HL also comes to the front due to its sulfur free nature and its abundant availability from cellulosic ethanol plants. Value-added utilization of lignin is critical for the accelerated development and deployment of the bio-refinery. The direct incorporation of KL in PU foams improves the



mechanical characteristics of rigid PU foams however; with increasing the percentage bio-replacement in the foam to above 30% would negatively affect the foam rigidity. Therefore, to improve the percentage of bio-replacement in PU foams depolymerization of lignin to produce de-polymerized lignin as bio-polyols with a lower  $M_w$  and better reactivity is a feasible way. Depolymerization of lignin not only reduces the molecular weights of the resulting products but also improves their functionalities, facilitating their utilization in PU foam preparation. Depolymerized products (DKL and DHL) were effectively utilized for the preparation of rigid bio-based PU foams without any modification achieving 50 wt.% replacements of PPG400 and sucrose polyols. The resulting foams showed good mechanical and thermal characteristics with improved physical and thermal stability compared with commercial RPU foams. Oxypropylation of depolymerized products could transfer solid DHL and DKL into liquid polyols via chain extension reactions, for their utilization as bio-polyols for the preparation of BRPU foams at high percentage of bio-contents i.e., up to 70 wt.%. The resulting foams showed high dimensional stability, good mechanical strengths and low density and thermal conductivities which makes them a suitable candidate as an insulation material. However, further research is needed to improve morphological characteristics of foams with increased bio-replacements and to scale up the processes for industrial production of lignin-derived polyols and rigid PU foams.

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## Chapter 3

### 3 Production of polyols via direct hydrolysis of Kraft lignin: Effects of process parameters

#### Abstract

Kraft lignin (KL) was successfully depolymerized into polyols of moderately high hydroxyl number and yield with moderately low weight-average molecular weight ( $M_w$ ) via direct hydrolysis using NaOH as a catalyst, without any organic solvent/capping agent. The effects of process parameters including reaction temperature, reaction time, NaOH/lignin ratio (w/w) and substrate concentration were investigated and the polyols/depolymerized lignins (DLs) obtained were characterized with GPC-UV, FTIR-ATR,  $^1\text{H-NMR}$ , Elemental & TOC analyzer. The best operating conditions appeared to be at 250 °C, 1 h, and NaOH/lignin ratio  $\approx 0.28$  with 20 wt.% substrate concentration, leading to <0.5% solid residues and  $\sim 92\%$  yield of DL (aliphatic-hydroxyl number  $\approx 352$  mgKOH/mg and  $M_w \approx 3310$  g/mole), suitable for replacement of polyols in polyurethane foam synthesis. The overall % carbon recovery under the above best conditions was  $\sim 90\%$ . A higher temperature favored reduced  $M_w$  of the polyols while a longer reaction time promoted dehydration/condensation reactions.

**Keywords:** Kraft lignin, hydrolysis, depolymerization, polyols, catalyst.

### 3.1 Introduction

Due to increased concerns worldwide of declining low-cost petroleum reserves, energy security, climate change and sustainability, more attention has been focused towards the exploration of renewable resources such as agricultural and industrial wastes/by-products for fuels and chemicals (Sricharoenchaikul, 2009). Lignin (20-30 wt.% in wood) (Fang et al., 2008), a natural, aromatic three dimensional high molecular weight biopolymer composed of phenyl propanol units (Tejado et al., 2007), is a potential candidate for the production of fuels, chemicals and bio-based materials. All native lignins are heterogeneous in nature and mainly composed of two types of linkages: condensed linkages (e.g., 5-5 and  $\beta$ -1 linkages) and ether linkages (e.g.,  $\alpha$ -O-4 and  $\beta$ -O-4) (Chakar and Ragauskas, 2004). The percentage of ether linkages in soft- and hardwood lignins are 56% and 72%, respectively (Pu, 2008). Aryl ether linkages can be more easily cleaved than the stable C-C linkages since the latter are stable and resistant to chemical depolymerization.

The major source of lignin (Kraft lignin and lignosulfonates) is the pulp and paper industry. About one million tons/year of lignosulfonates, derived from sulfite pulping liquors, are used as dispersants for dyes, pesticides, cement, asphalt and a variety of other applications (Holladay et al., 2007). Nowadays Kraft pulping accounts for 80% of the world's chemical pulp production and 50-55 million metric tons of lignin are produced annually in the form of black liquor; the liquid phase remaining after alkaline pulping has liberated the cellulose fibers (Borges da Silva et al., 2009). Black liquor is conventionally burned in recovery boilers to regenerate pulping chemicals and to produce steam and electricity for mill operations. While most Kraft lignin is thus not available for isolation, a special case exists in the 60-70% of North American Kraft mills that have production bottlenecks due to the thermal capacity of their recovery boilers. An interesting solution to this problem is to extract some of the lignin in black liquor by precipitation. In North America alone, the potential of precipitated lignin was estimated at 1.5 Mt/year. The removed lignin can be further utilized as a raw material for value-added bio-products which would diversify the mill's economic base.

Because of lignin's special phenyl propanol structure and aryl-alkyl ether bonding, lignin from Kraft pulping mills can be a good source of polyols. These polymers have multiple hydroxyl groups in their structure and are one of the essential raw materials for polyurethane (PU) production (Demharter, 1998). Although with much lower reactivity (Cheng et al., 2012), even crude lignin can be directly incorporated into PU formulations due to the presence of aliphatic and aromatic hydroxyl groups in its structure as the reactive sites (Cateto et al., 2008). Polyols can be polyether or polyester polyols (Tu, 2008), with the most critical properties being equivalent weight and hydroxyl number/functionality. Petroleum derived polyols are typically used, but rising petroleum prices and sustainability concerns have focused attention towards bio-based polyols (Bueno-Ferrer et al., 2012) or ligno-polyols (Borges da Silva et al., 2009).

Hydrolysis of lignin can produce a multitude of high value products via acid- or base-catalyzed cleavage of ether bonds (Fang et al., 2008). Hydrolysis is a milder process than pyrolysis, but wide structural heterogeneity of the products remains a great challenge (Roberts et al., 2011; Xu et al., 2008). Lignin hydrolysis under acidic conditions has been extensively studied (Lundquist, 1976; Matsushita and Yasuda, 2005); its major drawback is the unavoidable repolymerization/condensation of intermediate products formed during the reaction (Yuan et al., 2010). Alkaline catalysis or organic solvents are preferable in this regard; however, organic solvents have the disadvantage of increased costs and process complexity arising from the need to recover spent solvent. Depolymerization of lignin in alkali also occurs through the rupture of ether bonds (Nenkova et al., 2011); however, the alkaline catalyst not only hinders coke/char formation but also increases the yield of depolymerized products. Miller et al., (1999) observed high conversions during Kraft lignin depolymerization using KOH in supercritical methanol or ethanol at 290 °C. Later, Yuan et al. (2010) produced oligomers/polyols ( $M_w \approx 1000$  g/mol and  $M_n \approx 450$  g/mol) through hydrolytic degradation of alkaline lignin ( $M_w \approx 60,000$  g/mol and  $M_n \approx 10,000$  g/mol) using NaOH in a water-ethanol mixture and phenol as a capping agent (lignin to phenol ratio = 1:1 (w/w)). Under optimal conditions (260 °C and 1 hr), char and gas production was negligible. Further studies by Yoshikawa et al. (2012) indicated that strong bases like KOH or NaOH gave superior conversion and were effective in reducing

char formation. Recently, [Beauchet et al. \(2012\)](#) carried out base-catalyzed depolymerization of KL (10 wt.% concentration) in a continuous flow reactor over 270-315 °C and 130 bar for the production of a monomers-rich fraction as well as fractions of gas, small organic compounds and oligomers. Monomers can be suitable precursors for the production of L-Chemicals, and oligomers for L-fuels.

Nowadays, Kraft lignin has gained more attention as a potential non-food, biopolyols ([Cateto et al., 2008](#)). Proposed reactions include oxypropylation ([Li and Ragauskas, 2012](#)), oxidation followed by membrane/ultra-filtration ([Borges da Silva et al., 2009](#)) and hydrolytic degradation using organic solvents and a petroleum derived capping agent (phenol) ([Yuan et al., 2010](#)). These approaches may be insufficiently “green” or economic due to the use of large amount of petroleum-derived products (phenols, polypropylene glycol, polyethylene glycol etc) or costly separation techniques.

The major objective of this work is thus to produce polyols via direct hydrolysis of Kraft lignin (KL) of  $M_w \approx 10,000$  g/mol, in water. This process is expected to produce renewable polyols from Kraft lignin (or simply black liquor) with desirable characteristics for rigid polyurethane foam synthesis like low  $M_w$ , moderately high aliphatic hydroxyl number/functionality, and high yields. This work presents the preliminary results from a parametric study to determine the key process factors, while detailed process optimization will be reported in our future work.

## 3.2 Materials and Methods

### 3.2.1 Materials

Kraft lignin (KL) used in this study was provided by FPIInnovations, produced using the proprietary LignoForce process ([Kouisni, 2012](#)) in its pilot plant in Thunder Bay, Ontario and was completely soluble in aqueous alkali (pH >10). It is a yellow-brown powder with weak odor and specific gravity of 0.80. The relative weight-average molecular weight ( $M_w$ ) of KL is  $\approx 10,000$  g/mol (PDI  $\approx 2.0$ ) based on GPC-UV analysis. The proximate and ultimate analysis of KL is given in Table 3-1. The dried sample contained 0.57 wt.% ash

and 5.2 wt.% sulfur (on dry ash free basis). The ash content of lignin was determined gravimetrically in a muffle furnace at 700 °C for 4 hours. The ultimate analysis was done on a CHNSO Elemental Analyzer and reported on a dry and ash free basis. Other chemicals used include NaOH (96%), sulfuric acid (99%), acetone (99.5%), *d*<sub>6</sub>-DMSO and *d*-chloroform, tetrahydrofuran (THF, HPLC grade), pyridine, acetic anhydride and dibromomethane, all CAS reagent grade, purchased from Sigma-Aldrich and used without further purification.

Table 3-1 Proximate & ultimate analysis of original Kraft lignin (KL)

Proximate analysis, wt.% (d.b) <sup>a</sup>				Ultimate analysis, wt.% (d.a.f.) <sup>f</sup>				
VM <sup>b</sup>	FC <sup>c</sup>	Ash <sup>d</sup>	TS/MC <sup>e</sup>	C	H	N	S	O <sup>g</sup>
56.3	43.1	0.57	98.5/1.5	63.8	5.4	0.02	5.2	25.6

<sup>a</sup> On dry basis; <sup>b</sup> VM: volatile matter; <sup>c</sup> FC: Fixed carbon (VM and FC was determined by thermogravimetric analysis (TGA) in N<sub>2</sub> at 10 °C/min to 900 °C); <sup>d</sup> Ash content determined gravimetrically in a muffle furnace at 700 °C for 4 hours; <sup>e</sup> TS/MC: Total solids /moisture contents in the sample was determined by placing 1-2 g of sample in an oven at 105 °C for 24 hours; <sup>f</sup> On dry and ash free basis; <sup>g</sup> By difference.

### 3.2.2 Kraft lignin hydrolysis experiments

The hydrolysis experiments were carried out in a 100 mL Parr Model 4848 reactor, equipped with a pressure gauge, thermocouple, stirrer, gas line and sampling line. In a typical run, 12 g KL, 33 g NaOH (10 wt.% solution in distilled water) and 15 g of distilled water were loaded into the reactor. The reactor was sealed, evacuated and purged thrice with N<sub>2</sub> to ensure complete removal of residual air. The reactor was then finally pressurized with N<sub>2</sub> to a cold pressure of 2 MPa and tested for leaks. The reactor was heated under a fixed stirring rate (390 rpm) and allowed to run over a pre-specified length of reaction time after reaching the required temperature. During the reaction the pressure of the reactor system will increase depending on the temperature mainly due to the water vapor pressure (e.g., 5 MPa at 250 °C, 8 MPa at 300 °C up to 16 MPa at 350 °C). After the pre-set reaction time elapsed, the reactor was immediately quenched with water to stop further reaction. After the system reached a low temperature (near room



temperature), the gas was collected in a gas cylinder of known volume (2800 mL) and the pressure of the gas cylinder was adjusted to 1.0 atm (abs.) using high purity nitrogen as a makeup gas. The gaseous products were analyzed using a Micro-GC-TCD analyzer and the overall gas yield was determined. The gaseous products are mainly composed of H<sub>2</sub>, CO, CH<sub>4</sub> and C<sub>2</sub>-C<sub>3</sub>. Each experiment was conducted 2-3 times to ensure that the relative experimental errors in DL yield be within  $\pm 10\%$ .

The reactor contents were then completely rinsed into a beaker using distilled water. The pH value of the washed reactor contents (varying from 11.0 to 9.5 depending on the reaction conditions) was adjusted to approximately 2.0 using 1.0 M H<sub>2</sub>SO<sub>4</sub> solution to precipitate the DKL products. The acidified reaction mixture was then filtered through a Buchner funnel. The aqueous (Aq) phase was analyzed by TOC-analyzer. As the gas yield was found to be very low ( $\leq 1$  wt %) in all tests, a lumped yield of (Gas+Aq) phase was reported in this study for simplicity. The solid cake containing depolymerized KL was dissolved in acetone (20-25 mL) under sonication and then filtered under vacuum with Buchner funnel to get acetone soluble depolymerized lignin (DKL) or polyols and solid residues (SR). The SRs were dried at 105 °C for 24 h in an oven and weighed to obtain SR yield as wt.% of the original KL on a dry basis. The acetone soluble filtrate was transferred to a pre-weighed Erlenmeyer flask to remove acetone with rotary evaporator at 60 °C followed by 24 hr drying in a vacuum oven to obtain the DL products. The yield of DKL was calculated based on the mass of original KL on dry basis. As mentioned previously, the data presented in this work are the average of triplicate runs.

### 3.2.3 Product characterization

The DKL were analyzed by Nicolet 6700 Fourier Transform Infrared Spectroscopy (FT-IR) with smart itr/ATR accessory to verify the presence of hydroxyl groups in the polyols structure and other functional groups present in them the range of 500-4000 cm<sup>-1</sup> with attenuated total reflectance (ATR). Proton nuclear magnetic resonance (<sup>1</sup>H-NMR) spectra for DLs were acquired at 25 °C using a Varian Inova 600 NMR spectrometer equipped with a Varian 5mm triple-resonance indirect-detection H<sub>2</sub>CX probe. A total of 16-32 scans

were accumulated using a 2s recycle delay, 3.6s acquisition time, a 45-degree tip angle (pw =4.8 us), and a spectral width from -2 ppm to 14 ppm (sw =9000.9 Hz).  $d_6$ -DMSO and  $d$ -chloroform were used as the  $^1\text{H}$ -NMR solvents for qualitative study. Quantitative  $^1\text{H}$ -NMR analysis was realized using acetylated samples of the KL and DLs. Briefly, 1 g of dried KL or DKL was dissolved in a 1:1 (v/v) mixture of pyridine (5 mL) and acetic anhydride (5 mL) in a vial followed by stirring for 24 to 48 hr. The well-stirred mixture was then transferred into a beaker containing 100 mL of ice-cooled 1 wt.% HCl solution. The resulting precipitates of acetylated samples were washed with distilled water to pH  $\approx 7$ . The samples were then dried at 105 °C for 24 hr to remove residual water before further utilization. Dibromomethane ( $\text{CH}_2\text{Br}_2$ ) was selected as an internal standard as its characteristic peak at 4.9 ppm does not overlap with any other peaks in the KL/DKLs. Also the solvent selected for the quantitative analysis was  $d$ -chloroform instead of  $d_6$ -DMSO as peak of the latter overlaps with that of aliphatic acetate. For determining hydroxyl number through  $^1\text{H}$ -NMR, the samples were prepared by first weighing 15 mg of the acetylated KL or DKL and 10 mg of internal standard in a vial and then the sample was transferred into a 5 mm NMR tube via a transfer pipette using  $d$ -chloroform ( $\approx 1000$ -1500 mg) for the subsequent NMR analysis.

The relative molecular weight distributions ( $M_w$  and  $M_n$ ) of DKLs were measured with a Waters Breeze GPC-HPLC instrument (1525 binary pump, UV detector set at 270 nm, Waters Styragel HR1 column at 40 °C) using THF as the eluent at a flow rate of 1 ml/min with linear polystyrene standards for the molecular weight calibration curve). The range of linear polystyrene standard was 100 to 1 million and the reported molecular weights are based on polystyrene equivalent weight. Although there is a limitation on utilization of linear polystyrene standard for KL or DKL because of KL/DKL multi-branched structure however, relative molecular weights can provide useful information for their further utilization. Elemental analysis of the DKLs was obtained using a CHNS-O Flash Elemental Analyzer 1112 series (Thermo) for determining the contents of CHNS (carbon, hydrogen, nitrogen and sulfur) in the samples. The ash contents of KL and DKLs were obtained by combustion of 1-2 g of the pre-dried sample of KL or DKLs in a crucible in a

muffle furnace at 700 °C for 4 hours. The total organic carbon contents in the aqueous phase were obtained with a TOC-analyzer.

### 3.3 Results and Discussions

The hydrolytic depolymerization products were soluble in water, but after acidification and subsequent filtration the DKL products were soluble in organic solvent like acetone. Thus, we were able to determine their molecular weight distributions and ( $M_w$ ,  $M_n$  and PDI) by gel permeation chromatography and UV detection (GPC-UV) using THF as the eluent.

#### 3.3.1 Effects of reaction temperature

Temperature is the critical parameter for lignin hydrolysis in water (Xu et al., 2008). Figure 3-1 shows the effects of reaction temperature on the yields of DL, SR, (Gas+Aq) phase and  $M_w$  of the DKL from the tests carried out at a temperature ranging from 200 to 350 °C for 45 min. At 200 °C there was a relatively lower degree of KL depolymerization: a DKL yield of ~ 67 wt.% with 9 wt.% SR yield. The remaining mass (~24 wt.%) could be attributed to water and aqueous products (monomers, aldehydes, alcohols, etc.), understanding that the yield of gases, usually formed due to the cleavage of the aliphatic propane chain and removal of ring substituents (Gosselink et al., 2012) was relatively low in this work ( $\leq 1$  wt %). The other possible reason of low yield at 200 °C may be the presence of  $-\text{SO}_3\text{H}$  group on lignin unit which shows lesser solubility in acetone. From a practical point of view, an overall process can generate minimal waste as the aqueous byproduct stream can be either further utilized by supercritical water gasification (SCWG) or sent back to the recovery system, if the hydrolysis is integrated into pulp mill operations.

At 250 °C, the DKL yield increased to 92 wt.%, which may occur because lignin depolymerization is endothermic and hence thermodynamically favorable at a higher temperature (Cheng et al., 2012). Increasing lignin solubility at temperature  $>200$  °C also helps to improve the yield of DKL by further instigating the lignin hydrolysis reaction (Mok and Antal, 1992). Another possible reason of the increased yield of DKL at higher temperatures like 250 °C may be related to the special properties of water at elevated

pressure (hot-compressed water, or sub-/supercritical water) which greatly increases the value of the ion product ( $K_w = [H^+][OH^-]$ ), e.g., at 400 °C and 50 MPa, the value  $K_w$  is more than 100 times that at ambient conditions (Marshall et al., 1981), which may efficiently catalyze lignin hydrolysis by  $[H^+]$  and  $[OH^-]$  ions. The solid residues yield at 250 °C was as low as 1-1.4 wt.%. The results (Figure 3-1) clearly indicate that the yield of DKL is greatly reduced from ~85 wt.% to 27-28 wt.% as temperature further increases from 300 °C to 350 °C, accompanied by a marked increase of SR yield from nearly 1.4-1.5 wt.% (at 300 °C) to ~38 wt.% (at 350 °C). At 350 °C these results may be explained by the presence of prominent dehydration and crosslinking reactions (Knežević, 2009). The high yield of SR or char may be attributed to the presence of crosslinking reactions between carbon-carbon double bonds (C=C) which lead to the formation of a highly crosslinked structure resulting in the formation of char which was insoluble in water/acetone. Some researchers consider these char/solid residues as low value soil amendment materials (Lehmann and Joseph, 2009).

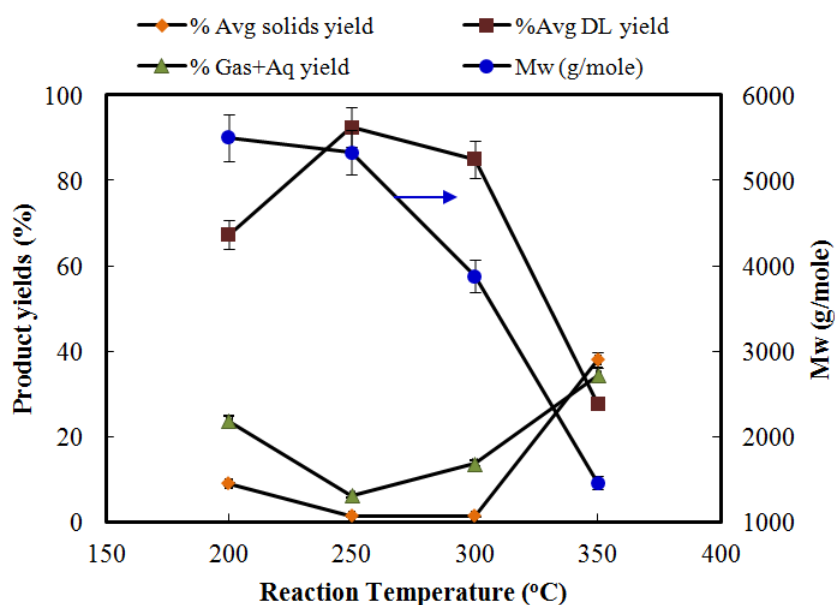


Figure 3-1 Product yields and  $M_w$  of DKLs at various reaction temperatures (°C)  
 (Reaction time: 45 min; 20 wt.% substrate concentration; NaOH/lignin mass ratio  $\approx$ 0.27-0.28)

We observed an inverse relationship between temperature and  $M_w$  of the DKLs, consistent with earlier work (Yuan et al., 2010) and suggesting that temperature has a drastic effect on the cleavage of alkyl-aryl ether linkages in lignin. Although, at higher temperatures like 350 °C the yield of polyols was lesser than at lower temperatures however, the  $M_w$  of the polyols reduced significantly at higher temperatures due to the sufficient energy available to break the ether linkages. Considering both yield and  $M_w$  of the DKL, 250-300 °C appears to be the best temperature range for direct hydrolysis of KL. However,  $M_w$  at 250 °C was considerably high (~5330 g/mole) which makes the DKL product unsuitable as a polyol replacement for PU production. Molecular weight distribution can be a useful indicator for process optimization, and the  $M_w$  can be further reduced by optimizing the reaction conditions (e.g., reaction time, pH and substrate concentrations).

### 3.3.2 Effects of reaction time

The hydrolysis experiments were conducted at 250 °C and 300 °C for reaction times ranging from 30-240 min and 45-120 min, respectively. The product yields and their respective  $M_w$  are shown in Figures 3-2 and 3-3. As shown in Figure 3-2, at 250 °C an increase in reaction time from 30 min to 60 min increased the yield of DKL from 74.6 wt.% to 92.5 wt.% which could be due to the presence of  $-SO_3H$  group on lignin unit. At lower reaction times it showed non-polar behavior in acetone however, with the increasing reaction time  $-SO_3H$  group could be replaced by  $-OH$  group resulting in enhanced solubility in acetone. Further increasing the reaction time to 90 min and 240 min decreased the yield of DKLs to 85.9 wt.% and 76.6 wt.%, respectively, with correspondingly increased SR yield. The increased yield of SRs could be due to the cross-linking reactions which were prominent at longer reaction times. Where, the increasing reaction time from 30 min to 120 min decreased the DKL  $M_w$ s from ~5330 g/mole to 2670 g/mole, suggesting that the hydrolytic depolymerization reaction proceeded to a greater extent at this longer reaction time. The increase in  $M_w$  to 4200 g/mole caused by further increasing the reaction time to 240 min up was likely caused by repolymerization/condensation reactions, as discussed previously in Figure 3-1.

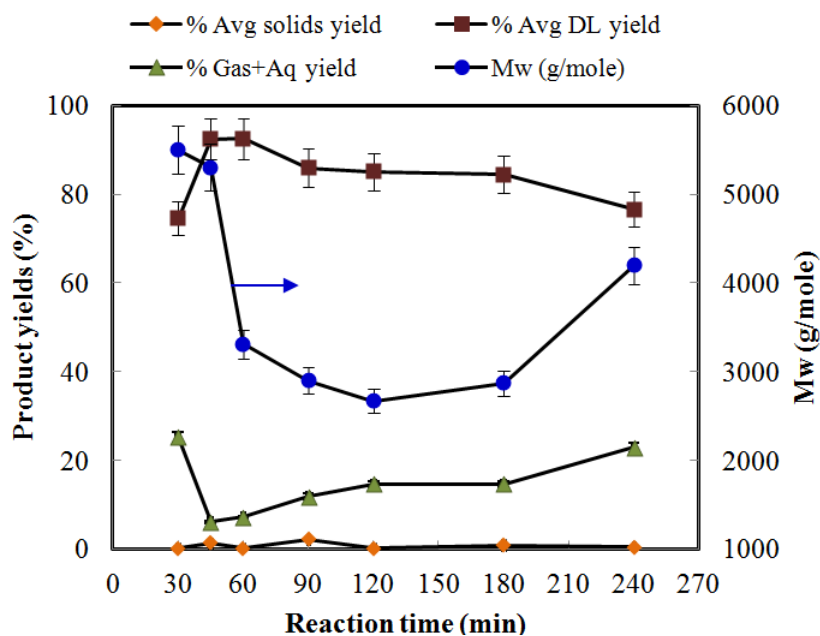


Figure 3-2 Product yields and  $M_w$  of DKLs vs. reaction time at 250 °C (other reaction conditions: 20 wt.% substrate conc.; NaOH/lignin mass ratios  $\approx 0.27-0.28$ )

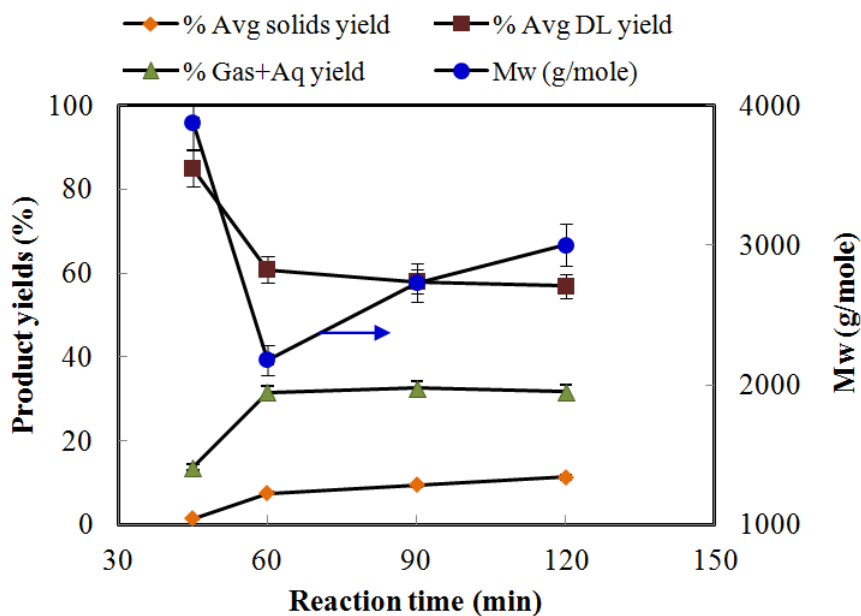


Figure 3-3 Product yields and  $M_w$  of DKLs vs. reaction time at 300 °C (other reaction conditions: 20 wt.% substrate conc.; NaOH/lignin mass ratios  $\approx 0.27-0.28$ )

Figure 3-3 shows the product yield and  $M_w$  of DKLs vs. reaction time at 300 °C. The yield of DKL decreased from ~85 wt.% to ~61 wt.% when the reaction time increased from 45 min to 60 min; further increases in reaction time had a minimal effect on the DKL yield. It appears that the system might have already reached an equilibrium state.

The  $M_w$  of DKLs decreased from ~3900 g/mole to ~2200 g/mole when the reaction time was increased from 45 min to 60 min at 300 °C. After 60 min, the  $M_w$  increased with further increases in reaction time up to 120 min. This is again attributed to repolymerization/condensation reactions between lignin-derived intermediate products which become main reaction at longer reaction times and depolymerization of ether bond as secondary reaction. Comparing Figures 3-2 and 3-3 indicates that the  $M_w$  values were almost identical at 120 min reaction time at 250 °C or 300 °C, but the DKL yields at 250 °C were significantly higher than those at 300 °C. Hence, with respect to both yield and  $M_w$  of the DKL products, the best reaction conditions appear to be 120 min at 250 °C.

### 3.3.3 Effects of NaOH to lignin mass ratio (pH effect)

The effect of NaOH concentration on lignin hydrolysis was determined by varying NaOH to lignin mass ratios from 0.23 to 0.33, while keeping all other variables or process parameters constant. Note that the NaOH/lignin  $\approx 0.23$  (w/w) corresponds to a 1:1 molecular ratio of NaOH/lignin, assuming the average molecular weight of each lignin monomer to be 180 g/mole.

The product yields and  $M_w$ s of DKL from the experiments at 250 °C, 120 min and 20 wt.% substrate concentrations at various NaOH/lignin mass ratios are shown in Figure 3-4. The yield of DKL was the highest (~91%) at NaOH/lignin  $\approx 0.23$  (w/w), the corresponding  $M_w$  for the DKL product was very high (~5800 g/mol), likely due to the repolymerization of intermediate products at low pH corresponding to this mass ratio. The DKL yield dropped to approximately 81% when the NaOH/lignin ratio was increased from 0.23 to 0.25 and subsequently remained almost constant with further increases in NaOH/lignin from to 0.27 and 0.33. Similarly, the  $M_w$  of the DKLs decreased from 5800 g/mole at NaOH/lignin ratio  $\approx 0.23$  to 2700 g/mole at NaOH/lignin ratio  $\approx 0.25$

and remained constant with further increases in NaOH/lignin ratio. These results suggest that the effect of NaOH is minimal after the NaOH/lignin mass ratio is above 0.25-0.27. Here the reported NaOH/lignin ratio is on weight basis (w/w) which for unit moles basis is much higher than 1.0. At such high molar ratio already all the phenols were transferred to their sodium phenolate form and dissolved in the water solvent. The hydrolysis of KL was mainly due to the breakage of ether linkages attacked by water or hydroxyl ions, resulting in lowering the  $M_w$  of the products. Hence, a further increase in NaOH/lignin ratio could not further decrease the  $M_w$  of DKLs. Therefore, in the further experimentation, NaOH/lignin mass ratio was fixed at around 0.27-0.28.

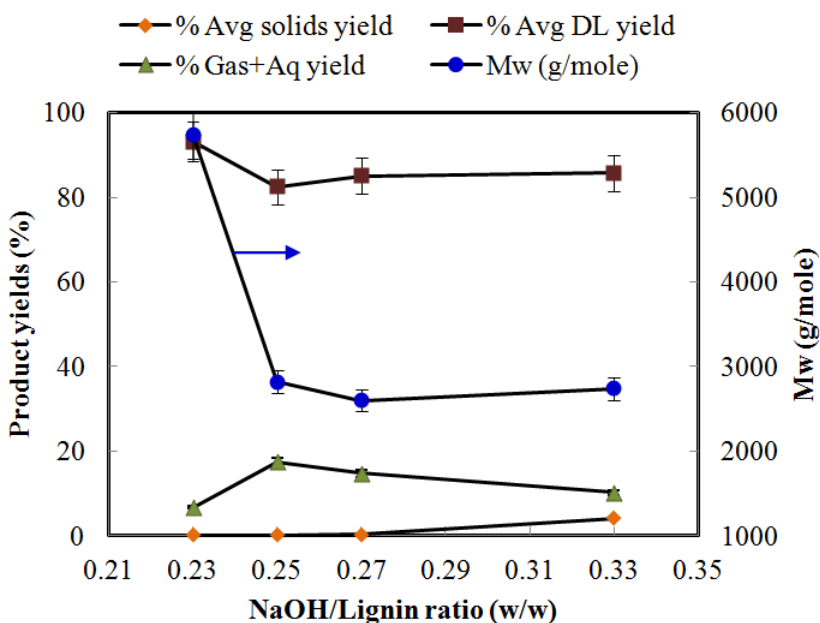


Figure 3-4 Products yields and  $M_w$  of DKLs at various NaOH/lignin mass ratios (Reaction temperature: 250 °C; Reaction time: 120 min; 20 wt.% substrate concentration)

### 3.3.4 Effects of substrate (KL) concentration

Figure 3-5 displays the product yields and  $M_w$  of DLs from experiments at 250 °C for 120 min with a NaOH/lignin ratio of  $\approx 0.27$ -0.28 (w/w) at various substrate concentrations. Figure 3.4 indicates that the yield of DKL almost remained constant (81 wt.% vs. 80 wt.%) when the substrate concentration was increased from 15 wt.% to 30 wt.%, while



$M_w$  and SR yield both increased significantly. The reason could be that, at higher substrate concentration the amount of the solvent was insufficiently to obtain a homogeneous solution/suspension of lignin, and water as the reactant for hydrolysis was less available for the lignin hydrolysis reactions (ether bond cleavage). As a result, higher substrate concentration would lead to a lower extent of the de-polymerization reactions, hence increasing the  $M_w$  of the DKLs. Therefore, for the production of bio-based polyols of a lower  $M_w$  via direct hydrolysis of Kraft lignin, it is recommended that the substrate concentration be less than 20 wt.%.

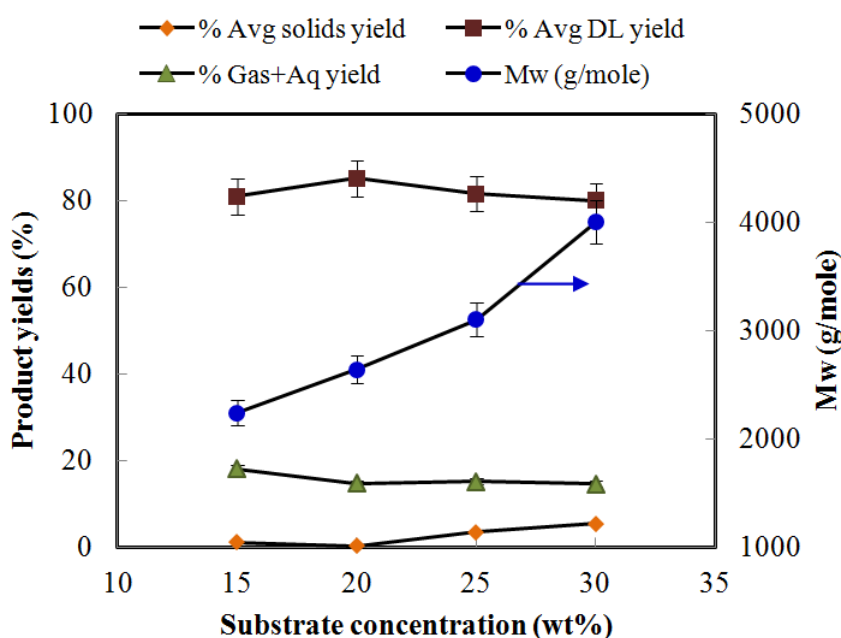


Figure 3-5 Products yields and  $M_w$  of DKLs at various substrate concentrations (wt.%) (Reaction temperature: 250 °C; Reaction time: 120 min; NaOH/lignin ratio  $\approx$ 0.27-0.28)

### 3.3.5 Characterization of depolymerized lignin/polyols

#### 3.3.5.1 FTIR

IR spectra's of KL and DKLs at various temperatures were analyzed while the other reaction conditions were fixed: 45 min reaction time, NaOH/lignin ratio of  $\approx$ 0.27- 0.28 (w/w) and 20 wt.% substrate concentration. FTIR can be used qualitatively for

monitoring the changes of functional groups (particularly, hydroxyl groups) in the substrate after depolymerization. All spectra of KL and DKL contained the broad absorption at 3200-3550  $\text{cm}^{-1}$  attributed to aromatic and aliphatic O-H stretching, as expected. IR absorbance at 1400-1700  $\text{cm}^{-1}$  was due to the aryl groups. The peaks at 1000-1300  $\text{cm}^{-1}$  correspond to C-O stretching of O-H, suggesting the presence of primary, secondary and tertiary alcohols, phenols, ethers and esters (Islam et al., 2005; Kubo and Kadla, 2005). The ether linkage at 1060-1160  $\text{cm}^{-1}$  was observable for KL while the IR spectra for DKLs showed almost no absorption, suggesting that during hydrolysis reaction most of the ether linkages were cleaved. The intensities of the aromatic absorptions at 1400-1700  $\text{cm}^{-1}$  in the DKLs obtained at various temperatures were almost the same as those in the original KL, suggesting that the hydrolytic process does not change lignin's aromaticity. Hence, it is meaningful to compare the relative intensities of hydroxyl group absorption in relation to the aromatic absorption for KL and DKLs. The results showed that relative intensities of -OH group are much higher in all DKLs compared to that of the KL, implying that the hydrolytic depolymerization could increase the amount of hydroxyl group in the DKL products.

### 3.3.5.2 $^1\text{H}$ NMR

Qualitative  $^1\text{H}$ -NMR analysis was conducted using the KL and DKLs without any modification. The  $^1\text{H}$ -NMR spectra of these samples showed broad peaks for most of the protons, typical of high molecular weight polymers with long relaxation times (Yuan et al., 2010), so the spectra are not included for simplification. However, the  $^1\text{H}$ -NMR spectra of the DKLs showed relatively sharper signals for most of the protons, suggesting smaller molecular weights in comparison of the untreated KL. Most of the peaks appearing at chemical shifts of 0.8-2.0 ppm were due to aliphatic methyl (C- $\text{CH}_3$ ) or methylene (C- $\text{CH}_2$ -C) protons (Duan and Savage, 2011). Peaks attributed to phenolic -OH and aliphatic -OH were observed at 8.5 ppm and 2.3 ppm, respectively. The peak corresponding to aliphatic -OH was relatively stronger in DKL than that in the original KL, consistent with the cleavage of ether linkages (e.g.,  $\alpha$ -O-4 and  $\beta$ -O-4) as a result of hydrolytic depolymerization. The protons signals associated with methoxy group (- $\text{OCH}_3$ ) directly connected to the benzene ring were detected at 3.5 ppm in KL and DKLs.

The qualitative NMR analysis thus indicates that the aliphatic and overall hydroxyl contents in the DKLs were increased during hydrolytic depolymerization of KL, which makes the DKLs a potential substitute for polyols for polyurethane production.

For quantitative  $^1\text{H-NMR}$  analysis, KL and DKL samples were acetylated to improve their solubility in *d*-chloroform.  $^1\text{H-NMR}$  spectra of both KL/DKL showed signal for internal standard (Dibromomethane) at 4.9 ppm. The signals associated with aliphatic acetates, phenolic acetates and methoxyl groups in KL and DKL were at 1.6-2.2 ppm, 2.2-2.6 ppm and 3.0-4.0 ppm respectively (El Mansouri et al., 2011). Aliphatic and phenolic acetate protons actually represent aliphatic and phenolic hydroxyls in their acetylated samples. Quantitative estimates of the various proton containing functional groups were made by the following step by step calculation. The signal area corresponding to internal standard was initially calibrated and then integrated to 1.0, followed by the integration of the regions related to aliphatic and phenolic acetate protons respectively, and the resulting values are shown in Table 3-2. The moles ( $M_{\text{DBM}}$ ) of internal standard were determined as  $W_{\text{DBM}}/173.83$ ; where  $W_{\text{DBM}}$  is the amount of the internal standard used in g and 173.83 is the formula weight of internal standard i.e., dibromomethane. In NMR spectra, integrated peak area of each signal is compared with that of internal standard, to obtain the relative concentration of respective peak. Then moles of total  $-\text{OH}$ , aliphatic and phenolic  $-\text{OH}$  groups per lignin unit were calculated using the following relation:

$$M_{\text{TOH}} = \frac{\frac{2}{3} \times I_{\text{TAC}} \times M_{\text{DBM}}}{[W_{\text{AC}} - (\frac{2}{3} \times I_{\text{TAC}} \times M_{\text{DBM}} \times 42)]/180} \quad (1)$$

where  $M_{\text{TOH}}$  are the moles of total  $-\text{OH}$  i.e., aliphatic and phenolic, per lignin unit; 2 and 3 are the number of protons of internal standard and acetyl groups respectively;  $I_{\text{TAC}}$  is the integration of protons of total acetate groups i.e., aliphatic and phenolic acetates;  $M_{\text{DBM}}$  are the moles of internal standard;  $W_{\text{AC}}$  is the weight of the acetylated samples of either KL or DKL/polyols; 42 is the formula weight of acetyl group minus one (43-1); 180 is

the average weight of one lignin unit. The determined value of  $M_{TOH}$  shows the available total number of moles of hydroxyl groups (aliphatic and phenolic) on single lignin unit. It was observed that with the increase in treatment severity moles of phenolic –OH increased and methoxyl groups decreased especially at higher temperature like 300 °C. These results suggested that methoxyl groups were hydrolyzed, similar was observed by [Beauchet et al., \(2012\)](#), at the said conditions and as a result the accessibility of –OH groups to lignin unit increased giving rise to higher total moles of phenolic –OH per lignin unit. Then the functionality ( $F$ ) of polyols i.e. number of reactive sites can be determined by the following relationship:

$$F = \frac{(M_w \text{ of polyols}) \times (\text{Mole of OH groups per lignin unit})}{180} \quad (2)$$

The hydroxyl number of produced DKL/polyols can be then determined by using the following relation between functionality and hydroxyl number:

$$\text{Hydroxyl number (mg KOH/g)} = \frac{56.1 \times 1000 \times F}{M_w} \quad (3)$$

The obtained hydroxyl numbers of polyols are given in Table 3-3. In the expression 56.1 represent the equivalent molecular weight of KOH, 1000 is the conversion of grams to mg. It can be observed from the data (Table 3-3) that all the DKLs/polyols produced have total hydroxyl number in the range of 678-819 g/mole where aliphatic hydroxyl number is varying in the range between 236-352 g/mole, greater than the original KL (128 mgKOH/g). It can also be observed from Table 3-3 that polyols/DKLs produced at both reaction temperatures 250 °C and 300 °C for longer reaction times aliphatic hydroxyl number reduced which could be due to the dehydration reactions become prominent at these conditions. The reported hydroxyl number of polyols produced via oxypropylation ranges between 300-800 ([Li and Ragauskas, 2012](#)). Also in some literature it's mentioned that the suitable hydroxyl number of polyols for their utilization in rigid PU varies between 250-1000 mgKOH/g ([Badri, 2012](#)). Thus, the above results show that direct

hydrolytic depolymerization of KL, at moderate operating conditions (temperature, pressure and reaction time) can be a viable route for the production of polyols for PU synthesis. Among all the conditions tested in this study, the best reaction conditions to get the bio-polyols with the highest aliphatic hydroxyl number or functionality appear to be 250 °C for 60 min with 20 wt.% substrate concentration and NaOH to lignin ratio  $\approx$  0.27-0.28 (w/w).

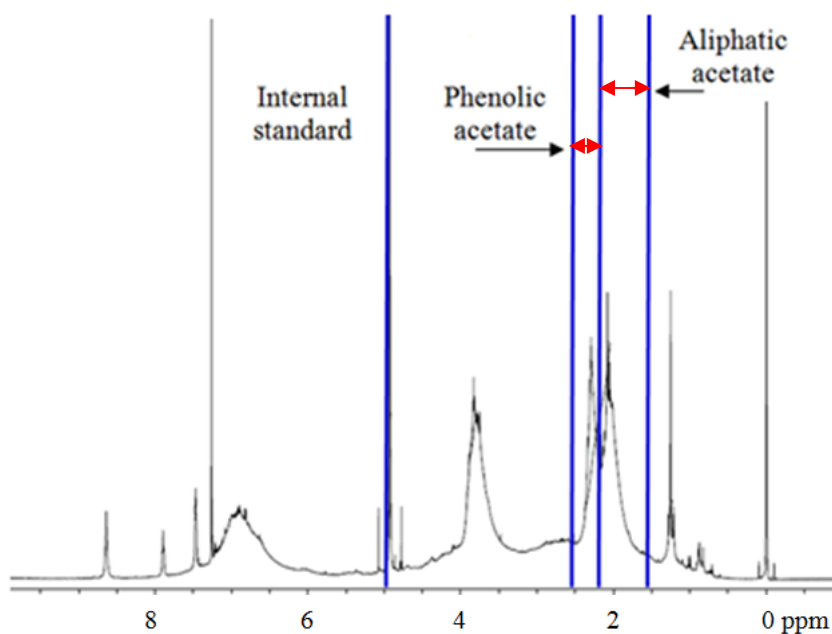


Figure 3-6  $^1\text{H}$  NMR spectra of acetylated KL

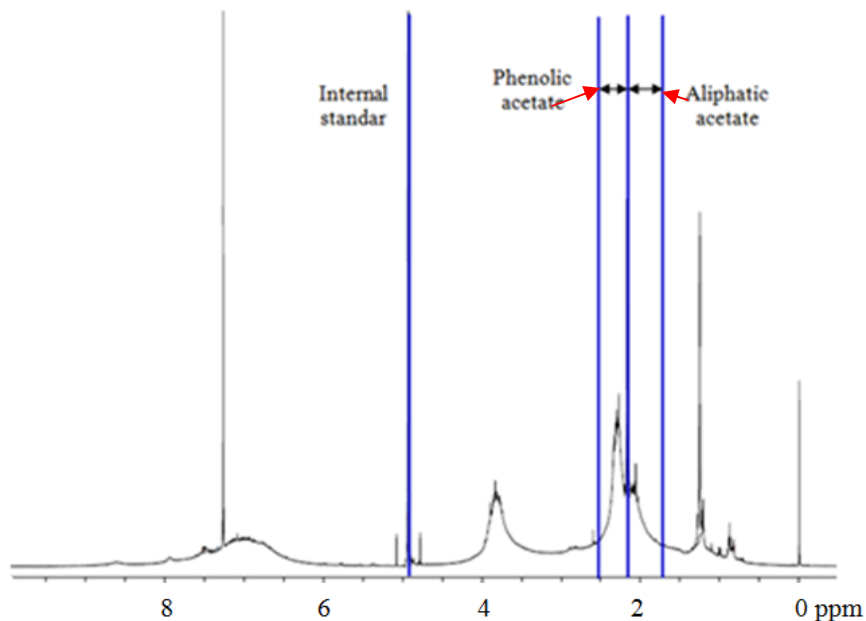


Figure 3-7  $^1\text{H}$  NMR spectra of acetylated DKL at 250 °C, 1h at 20 wt.% substrate concentration

Table 3-2 Relative integrals of  $^1\text{H}$ -NMR spectra signals of aliphatic/phenolic acetates in the acetylated KL and various DKLs (The DKLs were obtained from the experiments at 250 and 300 °C for various lengths of time) (Other experimental conditions are: NaOH/lignin mass ratio of  $\approx 0.27$ - $0.28$ , and 20 wt.% substrate concentration)

Acetylated Sample	Temp. (°C)	Time (min)	Aliphatic acetate (1.6-2.2 ppm)	Phenolic acetate (2.2-2.6 ppm)
KL	-	-	0.771	0.881
DL	250	60	1.499	1.387
		90	0.964	1.173
		120	1.264	1.750
	300	60	1.097	1.799
		90	0.960	1.880
		120	0.898	1.999

Table 3-3 Hydroxyl No. of the KL and various DKLs (The DKLs were obtained from the experiments at 250 and 300 °C for various lengths of time) (Other experimental conditions are: NaOH/lignin mass ratio of ~0.28, and 20 wt.% substrate concentration)

Sample	Temp. (°C)	Time (min)	Hydroxyl No. (based on Aliphatic -OH) (mg KOH/g)	Hydroxyl No. (based on total -OH) (mg KOH/g)
KL	-	-	128	275
DL	250	60	352	678
		90	307	681
		120	288	686
	300	60	310	819
		90	255	755
		120	236	761

### 3.3.5.3 Carbon balance

Elemental measurements were carried out to determine the CHNS contents of the KL and DKL samples, and to examine the overall carbon balance of the hydrolytic depolymerization experiments. In addition, the CHNS measurements can provide useful information on the fate of elements like N and S to address the environmental concerns related to the reaction process. Table 3-4 shows elemental compositions of the KL and two typical DKL products obtained at 250 °C/120 min and 300 °C/60min. The C and H contents of the DKL obtained at a lower temperature, even for a longer reaction time (250 °C/120 min), were not much varied when compared to that of the original KL, while the high temperature DKL product (300 °C/60 min) had a much higher C content (71.0 wt.% compared to 63.8 wt.%). N contents were neglected before and after depolymerization. The S contents are significantly lower in both DKLs, suggesting the catalytic hydrolytic treatment is very effective for de-sulfurization of Kraft lignin. The DKLs contained approximately 1% S, compared with 5.2 wt.% S in the original KL. The resulting DKL products have almost no odor, making them suitable for polyurethane synthesis.

Table 3-4 Elemental compositions of the KL and two typical DKL products obtained at 250 °C/120 min and 300 °C/60 min (Other reaction conditions: 20 wt.% substrate conc. and NaOH to lignin ratio of 0.28 (w/w))

Reaction conditions		Elements (% , d.a.f.) <sup>a</sup>				
T (°C)	t (min)	C	H	N	S	O <sup>b</sup>
KL	-	63.8	5.4	0.02	5.2	25.6
250	120	65.6	5.5	0.00	1.3	27.7
300	60	71.0	5.0	0.00	0.9	23.1

<sup>a</sup> Dry and ash-free basis; <sup>b</sup> Determined by difference.

TOC analysis was also carried out to determine the concentration of organic carbon in the filtrate or aqueous phase (Aq) to enable calculation of the overall carbon balance of the hydrolytic depolymerization experiments. At reaction conditions of 250 °C for 120 min, substrate concentration of 20 wt.% and NaOH-to-lignin mass ratio of 0.27-0.28, the percentage of organic carbon contained in the Aq is 2.0-2.5 wt.% of the total carbon in the reaction substrate. It should be noted that, in this work, the %carbon recovered in the SR was not available due to their very low yields. Calculated results based on % carbon recovered in the DKL, Aq and Gas products showed that the carbon balance for all tests was mostly in the range of 80-90 wt.%, which is a reasonable carbon balance considering the unavoidable errors in the experiments and product recovery and analysis. For a typical run at 250 °C, 120 min, 20 wt.% substrate concentration and NaOH/lignin mass ratio of ~0.27-0.28, the carbon distribution in the products was: ~0.50 wt.% in Aq., ~0.02 wt.% in gas, and ~90 wt.% in DKL, with a total percentage carbon recovery of ~91 wt.%.

### 3.4 Conclusions

Hydrolytic depolymerization was very effective for producing depolymerized lignin (DKL) from Kraft lignin (KL) at a yield of 80-90% at 250 °C/300 °C for 45-90 min. The DLs have  $M_w$  of 3000-5000 g/mol, significantly lower than that of the original KL (10,000 g/mol). All the DKLs produced had aliphatic-hydroxyl number in the range of 236-352 mgKOH/g, making them potential bio-polyols for PU foam synthesis. The best



operating conditions, from the perspective of yield and obtaining  $M_w$  suitable for PU polyols, appear to be 250 °C, 1 h, 20 wt.% substrate concentration, and NaOH/lignin ratio of  $\approx 0.28$  (w/w) for polyols.

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## Chapter 4

### 4 Production of polyols via direct hydrolysis of Kraft lignin: Optimization of process parameters

#### Abstract

Polyols were produced via alkaline hydrolysis of softwood Kraft lignin (KL) without employing any organic solvent/capping agent. Optimum reaction conditions for producing polyols with characteristics suitable for polyurethane synthesis were determined using response surface methodology with a central composite design. The optimization was constrained by requirements that a polyol should fulfill for use in polyurethane synthesis: aliphatic-hydroxyl number  $\geq 300$ -500 mgKOH/g, weight-average molecular weight  $< 2000$  g/mole and moderately high yield. The optimum conditions identified were 250 °C, 120 min and 10 wt.% substrate concentration. The polyol produced under these conditions had an aliphatic-hydroxyl number  $\approx 365$  mgKOH/g,  $M_w \approx 1700$  g/mole and 77 wt.% yield. The predicted and experimental results were in good agreement ( $R^2$  values are 0.90, 0.82 and 0.98 for yield,  $M_w$  and aliphatic-hydroxyl number, respectively). Temperature was the most significant parameter.

**Keywords:** Process optimization, hydrolytic de-polymerization, Kraft lignin, polyols, polyurethanes.

## 4.1 Introduction

Rising and volatile petroleum prices has increased concerns about the environmental footprint of industrial processes and generated much interest in the use of forestry and agricultural residues as raw materials for bio-based products/chemicals (Maache-Rezzoug et al., 2008).

The major residual stream from the Kraft pulping process is black liquor, which contains 30-34 wt.% lignin. Black liquor is burned to recover pulping chemicals and to generate steam and electricity for mill operations (Font et al., 2003). Although most Kraft lignin is not available for isolation, 60-70% of North American Kraft mills experience production bottlenecks due to the thermal capacity of their recovery boilers. A moderate-capital solution to this problem is to precipitate some portion of Kraft lignin from the black liquor, which would increase incremental pulp production and provide an additional revenue stream from sale of the Kraft lignin.

While worldwide 1-1.5 million tons/year of lignin are employed for a wide range of applications (Lora and Glasser, 2002), almost all of this is lignosulfonates from sulfite pulping. This water-soluble, highly sulfonated substance is quite different from Kraft lignin. Until recently, the only commercial source of Kraft lignin has been from Mead-Westvaco, which produces approximately 20,000 metric tons/year of Kraft lignin under the trade name Indulin from a plant in South Carolina. However, in the first half of 2013, Domtar has begun operation of a 75 m ton/day Kraft lignin plant at its mill in Plymouth, North Carolina.

Lignin, a branched phenolic natural biopolymer, can be used for producing value-added bio-based products such as phenol substitutes and polyols (Wang et al., 2012).

Polyols, with a suitable weight-average molecular weight ( $M_w$ ) and aliphatic-hydroxyl number, are one of the essential raw materials for polyurethanes (PU) (Demharter, 1997). Bio-based polyols can be produced from lignin which contains aliphatic and phenolic hydroxyls in its structure. Conventionally, polyols employed for PU synthesis are petroleum derived with varying hydroxyl number (300-500 mgKOH/g) (Luo et al., 2008)

and relatively low molecular weights. Recent high prices for petroleum derived polyols have renewed interest in bio-based polyols. Lignin-based polyols with suitable characteristics have already been produced via oxidation (Borges da Silva et al., 2009), oxypropylation (Li and Ragauskas, 2012; Cateto et al., 2008) and hydrolytic degradation in an organic solvent using phenol as a capping agent (Yuan et al., 2010). Oxypropylation has been recognized as a promising route to derive liquid polyols (Li and Ragauskas, 2012; Matos et al., 2010) and optimization studies have already been conducted (Cateto et al., 2009) for getting polyols for PU synthesis using different types of lignin (Alcell, Indulin AT, Curan 27-11P and Sarkanda).

Hydrothermal degradation/de-polymerization of lignin was studied in the past using alcohols/capping agents/alkaline or acidic catalysts, with major emphasis on determining the best operating conditions to obtain the maximal yield of phenolic monomers. The studies on hydrothermal degradation of lignin alone are not as common as studies on cellulose (Ye et al., 2012). Hydrolytic de-polymerization of lignin produces polyols via selective cleavage of  $\beta$ -aryl ether linkages by water molecules or  $[H^+]/[OH^-]$  which makes hydroxyl groups more accessible in PU synthesis (Fang et al., 2008). However, during lignin hydrolysis there is competition between depolymerization and condensation/repolymerization of reaction intermediates, which makes it difficult to consistently produce polyols with the desired hydroxyl number, molecular weights and a satisfactory yield (Kleinert et al., 2009). The desired characteristics of polyols can be controlled via process optimization of reaction conditions and this can be achieved by performing a smaller number of experiments under suitable constraints by using surface response methodology (SRM) (Abnisa et al., 2011). Optimum reaction conditions for producing polyols of desired characteristics via direct hydrolysis for their utilization in polyurethane synthesis have not yet been studied.

The objective of this present study is to determine the optimum reaction conditions for hydrolytic de-polymerization of Kraft lignin under alkaline conditions for obtaining polyols of suitable characteristics for PU synthesis, i.e., high-aliphatic hydroxyl number, lowest possible  $M_w$  and moderately high yield. The effects of three input variables, reaction temperature, time and substrate concentration were studied using SRM with a



rotatable central composite design. Synthesis of PU foam using the produced polyols will be reported in future work.

## 4.2 Experimental

### 4.2.1 Materials

Kraft lignin (KL) used in this study was provided by FPIinnovations, produced using the proprietary LignoForce process in its pilot plant in Thunder Bay, Ontario (Kouisni, 2012) from commercial softwood black liquor. The black liquor was produced by a modified continuous cooking of softwood chips (spruce/fir) in a Kamyr digester. Effective alkali was 15% on wood and the alkali addition was split 90/10 between the top of the digester and the wash zone. The  $M_w$  of KL is 10,000 g/mol (polydispersity index  $\approx 2.0$ ) based on GPC-UV analysis. The dried sample contains 0.11 wt.% ash and 63.8 wt.% C, 5.4 wt.% H, 0.02 wt.% N and 5.2 wt.% sulfur (on dry and ash free basis). Other chemicals used in this study, including NaOH (96%), sulfuric acid (99%), acetone (99.5%), *d*-chloroform, tetrahydrofuran (THF, HPLC grade), pyridine, acetic anhydride and dibromomethane, are all CAS reagent grade chemicals purchased from Sigma-Aldrich and were used as received.

### 4.2.2 Hydrolysis of Kraft lignin (KL)

In a typical hydrolysis run, 6-12 g KL, 33-40 g NaOH (10 wt.%) solution and 15 g of distilled water were loaded into the reactor. The reactor was closed, tightened, purged thrice with  $N_2$  and then pressurized with 2 MPa  $N_2$ . The reactor was then heated up at approximately 10 °C/min under stirring (285 rpm) to the specified reaction temperature and soaked for a pre-specified length of time after the reactor reached the temperature. At the end of the reaction, the reactor was immediately quenched with water. The gases were released in the fume hood, the reactor contents were washed into a beaker using water and the pH was adjusted to  $\approx 2.0$  using 1M sulfuric acid. The acidified mixture was filtered and the solid cake left after filtration was dissolved in acetone. The solid residues were separated from the acetone solution of degraded lignin (DKL)/polyols by filtration and dried in an oven (at 105 °C for 24 h). The depolymerized lignin was recovered using a rotary evaporator under vacuum at 60-65 °C to remove acetone. The polyol yield (i.e., the

depolymerized lignin) was determined based on the dry weight of KL used in each experiment.

### 4.2.3 Statistical experimental design

Statistically designed experiments were conceived using response surface methodology (RSM) with central composite design (CCD) in order to study the effects of three independent variables (reaction temperature, reaction time and substrate concentration) on aliphatic-hydroxyl number,  $M_w$  and yield of DKL/polyols, which subsequently provided a basis for determining the optimized process conditions. A total of 20 experiments ( $N=2^k+2k+n_0=8+6+6=20$ ) were performed. The optimization was subjected to the following constraints; (a) aliphatic-hydroxyl number  $\geq 300$ -500 mgKOH/g, (b) lowest possible  $M_w$  (<2000 g/mole) and (c) moderate to high yield of polyols ( $\geq 75\%$ ). The total numbers of experiments along with their different levels are given in Table 1. A full second-order polynomial model for three factors ( $k=3$ ) by using Minitab 16.0 was adopted to describe the response surface. Coding of the independent variables was done with the aid of the transformation:  $X_i = (x_i - x_{i0}) / (\Delta/2)$  where;  $X_i$  is the coded value of the factor,  $x_i$  is the natural value of the factor,  $x_{i0}$  is the natural value of factor at its basic level,  $\Delta$  is variation/range/step change interval and  $i$  is the number of the independent factor. The mathematical relationship of the predicted responses as a function of variables ( $X_1$ ,  $X_2$  and  $X_3$ ) can be approximated by a quadratic or 2<sup>nd</sup> degree polynomial equation as shown in the following equation (1);

$$Y = b_0 + b_1 X_1 + b_2 X_2 + b_3 X_3 + b_{12} X_1 X_2 + b_{13} X_1 X_3 + b_{23} X_2 X_3 + b_{11} X_1^2 + b_{22} X_2^2 + b_{33} X_3^2 \quad (1)$$

where,  $b_0$  is the constant,  $b_1$ ,  $b_2$  and  $b_3$  are the linear coefficients  $b_{12}$ ,  $b_{13}$  and  $b_{23}$  are the interaction coefficients, and  $b_{11}$ ,  $b_{22}$  and  $b_{33}$  are the quadratic coefficients.

### 4.2.4 Analysis/characterization of polyols/DKL

The aliphatic-hydroxyl numbers of the KL/DKL were quantitatively analyzed by proton-nuclear magnetic resonance ( $^1\text{H-NMR}$ ) of acetylated samples, employing *d*-chloroform as a solvent and dibromomethane ( $\text{CH}_2\text{Br}_2$ ) as an internal standard. All the spectra were

acquired at 25 °C using a Varian Inova 600 NMR spectrometer equipped with a Varian 5mm triple-resonance indirect-detection HCX probe. A total of 16-32 scans were accumulated using a 2s recycle delay, 3.6s acquisition time, a 45-degree tip angle (pw=4.8 us), and a spectral width from -2 ppm to 14 ppm (sw=9000.9 Hz). The relative molecular weight distributions ( $M_w$  and  $M_n$ ) of DLs were measured with a Waters Breeze GPC-HPLC instrument (1525 binary pump, UV detector set at 270 nm, Waters Styragel HR1 column at 40 °C) using THF as the eluent at a flow rate of 1 ml/min with linear polystyrene standards for the molecular weight calibration curve). Elemental analysis of the DLs was obtained using a CHNS-O Flash Elemental Analyzer 1112 series (Thermo) for determining the contents of CHNS (carbon, hydrogen, nitrogen and sulfur) in the samples. The ash contents of KL and DKLs were obtained by combustion of 1-2 g of the pre-dried sample of KL or DKLs in a crucible in a muffle furnace at 700 °C for 4 hours.

## 4.3 Results and discussions

### 4.3.1 Single factor analysis at a time

In the first stage of this study, effects of reaction temperature (200-350 °C), reaction time (30-240 min), initial substrate (KL) concentration (15-30 wt.%), NaOH/lignin ratio (0.22-0.33 w/w) and atmosphere ( $N_2/H_2$ ) on the yield,  $M_w$  and aliphatic-hydroxyl number of polyols/DKL were investigated using single factor analysis at a time and the results were given in details elsewhere ([Mahmood et al., 2013](#)). In brief, effects of atmosphere and NaOH/lignin ratio ( $\geq 0.25$ ) had negligible effects on the yields and characteristics of the polyol products. Also, substrate concentration  $<20$  wt.% was desirable to obtain low  $M_w$  polyols. Although increasing temperature (350 °C) reduced  $M_w$ , it also reduced the yield of polyols with increased production of char/ash/solid residues (SR) due to excessive cross-linking and repolymerization reactions. Lower temperatures (200-220 °C) did not affect the  $M_w$  much, but gave a low yield of DKL. Aliphatic-hydroxyl numbers could be greatly reduced with increasing the treatment severity especially at higher temperatures. With the above preliminary results obtained, experiments in this study were further designed using CCD for optimization of reaction conditions.

### 4.3.2 Response surface experiments using rotatable central composite design (CCD)

The 20 designed experiments were carried in accordance with Table 4-1, at a fixed NaOH/lignin ratio (0.28-0.30 (w/w)) and a cold pressure of 2 MPa N<sub>2</sub>. Table 4-2 shows all three experimental variables along with the actual and predicted values. The regression equations provided in Table 4-3 were obtained from response surface analysis of variance (ANOVA). The actual and predicted values for all three responses were in good agreement and are shown in Figures 4-3 (a, b, c). Since the linear tendencies were obtained with regression fit, therefore model itself is depicting that the experimental range was studied quite adequately.

Table 4-1 Experimental levels of both coded/actual values of independent variables

Coded variables	Experimental variables	Levels				
		-1.682	-1	0	1	+1.682
$X_1$	Reaction temperature (°C)	240	250	265	280	290
$X_2$	Reaction time (min)	40	60	90	120	140
$X_3$	Substrate conc. (wt.%)	7	10	15	20	23

Table 4-2 The 2<sup>3</sup> full factorial and central composite design for experiments along with actual/predicted responses

No.	Variables in coded units			Variables in uncoded/original units								
	$X_1$	$X_2$	$X_3$	$X_1$	$X_2$	$X_3$	$Y_1$		$Y_2$		$Y_3$	
				Temp (°C)	Time (min)	Sub. conc. (wt.%)	yield of DKL (wt.%)		$M_w$ (g/mole)		Aliphatic-hydroxyl No. of DL (mgKOH/g)	
							Actual	Predicted	Actual	Predicted	Actual	Predicted
1	-1	-1	-1	250	60	10	86	86	1940	1931	411	410
2	1	-1	-1	280	60	10	69	74	1870	1786	299	295
3	-1	1	-1	250	120	10	77	75	1700	1825	365	353
4	1	1	-1	280	120	10	57	56	1780	1945	NA	254
5	-1	-1	1	250	60	20	84	87	3020	2813	382	374
6	1	-1	1	280	60	20	72	76	2300	2133	268	272
7	-1	1	1	250	120	20	92	89	2190	2232	338	335
8	1	1	1	280	120	20	70	72	1850	1817	256	250
9	-1.682	0	0	240	90	15	84	86	2480	2490	378	389
10	1.682	0	0	290	90	15	66	61	1970	2020	NA	221
11	0	-1.682	0	265	40	15	90	84	1900	2157	367	369
12	0	1.682	0	265	140	15	69	72	2000	1802	292	301

13	0	0	-1.682	265	90	7	74	73	1770	1633	320	327
14	0	0	1.682	265	90	23	89	87	2070	2267	289	293
15	0	0	0	265	90	15	83	81	2110	2080	300	299
16	0	0	0	265	90	15	80	81	2050	2080	NA	-
17	0	0	0	265	90	15	81	81	2080	2080	NA	-
18	0	0	0	265	90	15	80	81	2060	2080	NA	-
19	0	0	0	265	90	15	84	81	2100	2080	NA	-
20	0	0	0	265	90	15	80	81	2090	2080	NA	-

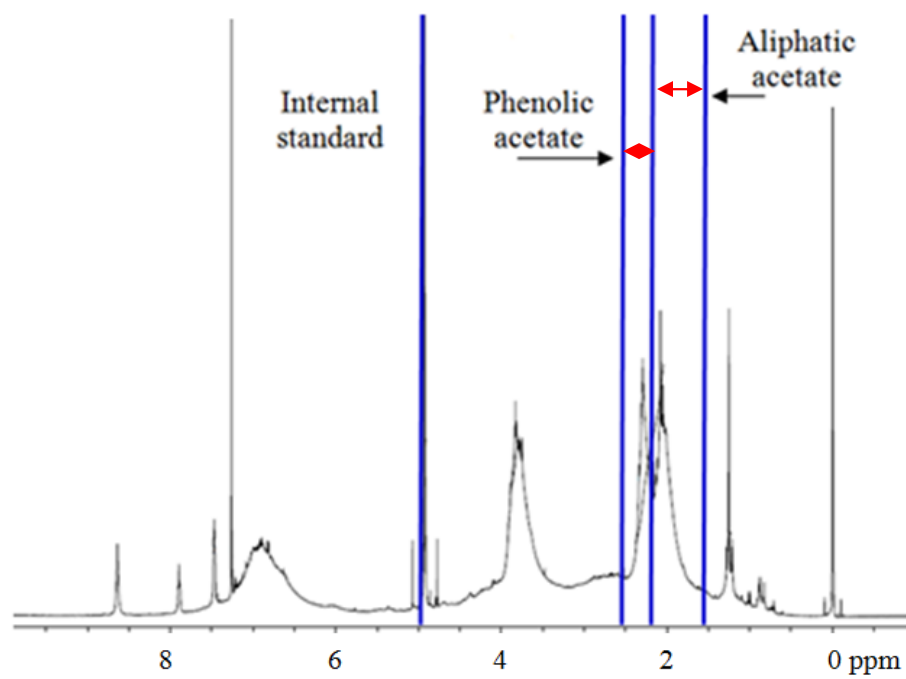


Figure 4-1  $^1\text{H}$  NMR spectra of acetylated KL

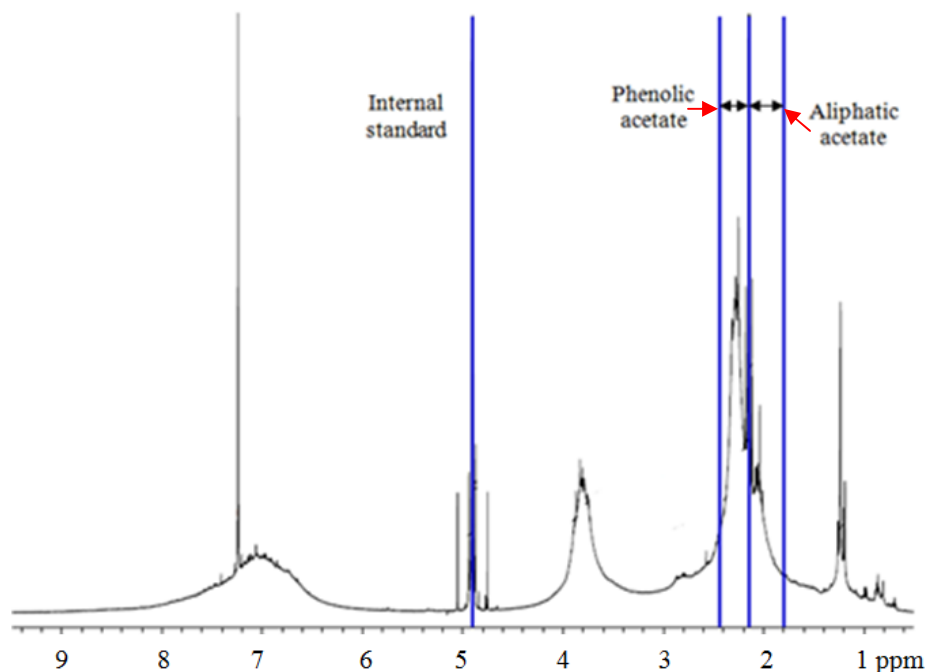


Figure 4-2  $^1\text{H}$  NMR spectra of acetylated DKL (250  $^\circ\text{C}$ , 120 min and 10 wt.% KL concentration)

Table 4-3 Regression equations obtained for responses  $Y_1$ ,  $Y_2$  and  $Y_3$

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Regression equations

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In un-coded units

$$Y_1 = 81.19 - 7.42 X_1 - 3.6844 X_2 + 3.97 X_3 - 1.62 X_1 X_2 + 0.37 X_1 X_3 + 3.38 X_2 X_3 - 2.72 X_1^2 - 1.13 X_2^2 - 0.42 X_3^2$$

$$Y_2 = 2079.97 - 139.69 X_1 - 105.57 X_2 + 188.52 X_3 + 66.25 X_1 X_2 - 133.75 X_1 X_3 - 118.75 X_2 X_3 + 61.78 X_1^2 - 35.45 X_2^2 - 46.05 X_3^2$$

$$Y_3 = 299.05 - 50.00 X_1 - 19.97 X_2 - 10.06 X_3 + 4.17 X_1 X_2 + 3.33 X_1 X_3 + 4.33 X_2 X_3 + 2.09 X_1^2 + 12.72 X_2^2 + 3.88 X_3^2$$


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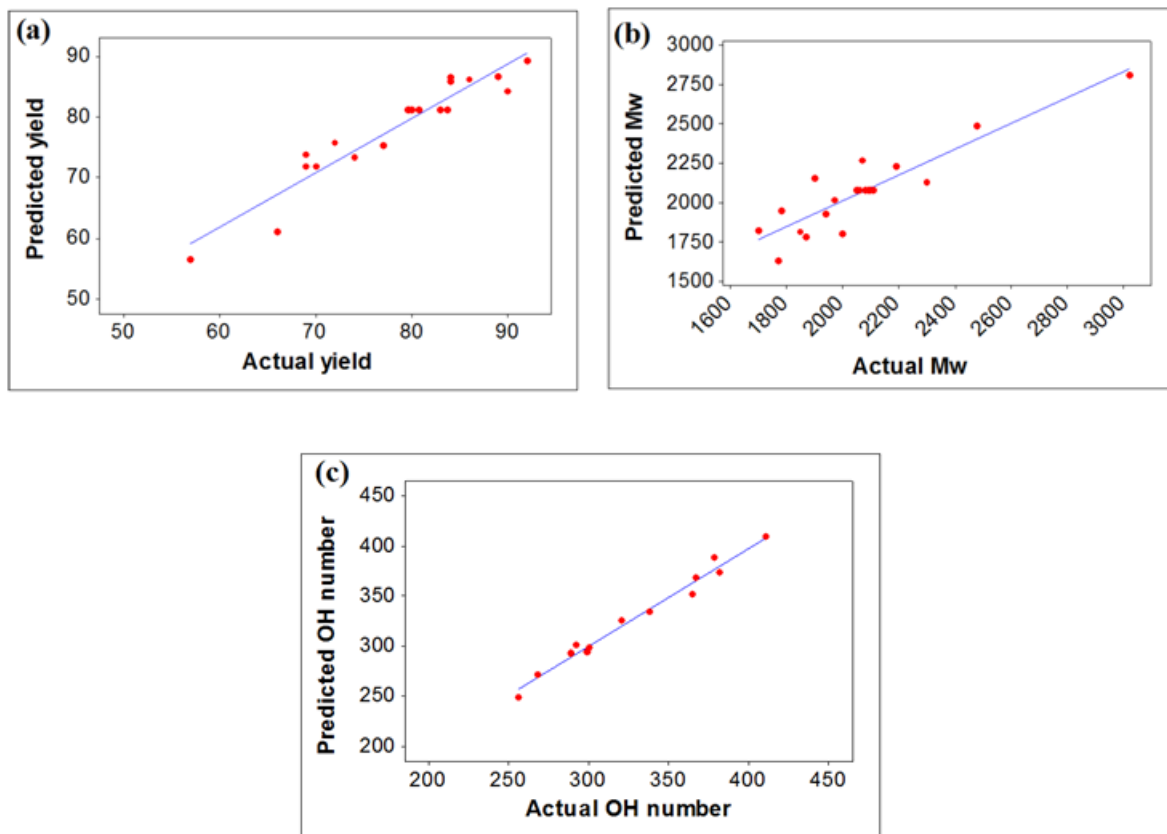


Figure 4-3 Actual vs predicted values of (a)  $Y_1$  (%yield of DKL/polyols), (b)  $Y_2$  ( $M_w$  of polyols) and (c)  $Y_3$  (aliphatic-hydroxyl number of polyols)

### 4.3.3 Main effect plots

Figures 4-4 (a, b, c) represent the main effects plots of three independent variables on responses. Figure 4-4a shows that the yield of polyols almost remains same with the increase in temperature from 240 °C to 250 °C. However, on further increasing  $X_1$  (reaction temperature) above 250 °C lead to significant decline in the yield of polyols due to the occurrence of repolymerization/condensation reactions. Similarly the  $X_2$  (reaction time) was also found to have a negative impact on the polyol yield especially for longer reaction times. Slow lignin depolymerization was also observed at temperature <220 °C (Yuan et al., 2010; Mahmood et al., 2013), but the low yield of polyols at a higher temperature or longer reaction time was believed a result of enhanced repolymerization/condensation/crosslinking reactions (Mahmood et al., 2013; Knežević, 2009), as evidenced by the increased char/SR yield under these conditions.

The yield of polyols/DKL increased with increasing  $X_3$  (substrate concentration) up to 23 wt.%, while a higher  $X_3$  led to larger  $M_w$  for the polyol/DKL products (Figure 4-4b). In our previous study (Mahmood et al., 2013) we found that at  $X_3$  up to 30 wt.%, polyols and SR yields remained unchanged, but the corresponding  $M_w$  increased due to the enhanced crosslinking reactions.

On the other hand,  $M_w$  of polyols/DKL (Figure 4-4b) decreases with the increasing  $X_1$  likely attributing to enough energy available to break lignin polymer structure (alkyl-aryl ether linkages). Increasing  $X_2$  above 60 min led to a low  $M_w$ , however  $M_w$  increased significantly at reaction times above 120 min. This is likely due to the enhanced repolymerization/condensation reactions at these conditions (Mahmood et al., 2013). Lower values of  $X_3$  (e.g. 10 wt.%) appeared to be more promising for producing polyols of a lower  $M_w$ .

Aliphatic hydroxyl content ( $Y_3$ ) decreased with increasing temperature, reaction time or substrate concentration. These results could be attributed to the enhanced dehydration reactions of lignin or the reaction intermediates with increasing reaction severity (Arami-Niya et al., 2012; Xu et al., 2008).

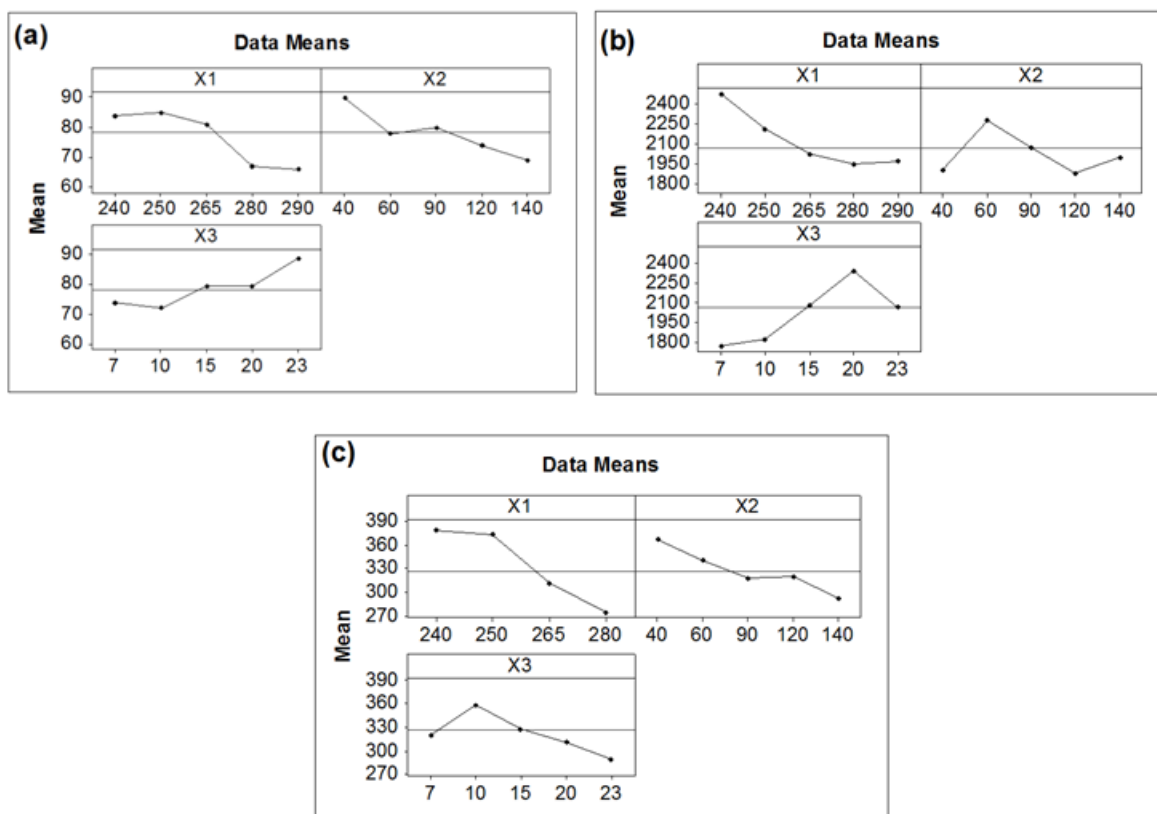


Figure 4-4 Main effect plots for (a) % yield, (b)  $M_w$  and, (c) aliphatic-hydroxyl number in actual units

#### 4.3.4 Analysis of variance (ANOVA) and response surface/contour plots

ANOVA was performed using Minitab 16.0 to explain the effects of the input variables ( $X_1$ ,  $X_2$  and  $X_3$ ) on the response variables at a predefined confidence interval (CI) in terms of their linear, 2-factor interactions (2fi) and quadratic contributions. ANOVA can also help identify the most significant parameters in terms of their p-value. The analysis was done at 95%CI (or  $\alpha = 0.05$ ) where  $\alpha$  is the level of significance. The models for all responses were significant (p-value <  $\alpha$ ) at 95% CI, as shown in Table 4-4. Linear contributions to all responses had a more significant effect than the interaction/quadratic contributions over the studied range of the parameters in our experiments (Table 4-4).

Table 4-4 ANOVA for responses ( $Y_1$ ,  $Y_2$  and  $Y_3$ ) at 95% CI

Source of variance	Responses					
	$Y_1$		$Y_2$		$Y_3$	
	F-value	p-value	F-value	p-value	F-value	p-value
Model	10.17	0.001	4.99	0.010	21.66	0.005
Linear contribution	25.41	0.000	10.34	0.002	45.66	0.001
Interaction contribution	2.50	0.119	3.33	0.062	3.36	0.136
Quadratic contribution	2.59	0.111	1.31	0.325	0.81	0.551

#### 4.3.4.1 Yields of Polyols

The fitted model for polyol yield is significant with  $R^2 = 0.902$  and p-value of  $0.001 \ll \alpha$ . All the linear terms had a significant effect on the polyol yield, with  $X_1$  (temperature) being more significant than other two parameters as shown in Table 4-5. The quadratic effect of  $X_1$  is less significant (p-value: 0.024) than its linear term, which suggests a dominantly linear relationship between the variable and  $Y_1$ . The model representing polyol yield after excluding the insignificant terms is shown in Eq. (2);

$$Y_1 = 81.1965 - 7.4155X_1 - 3.6844X_2 + 3.9707X_3 + 3.3750X_2X_3 - 2.7184X_1^2 \quad (2)$$

It can be observed from Eq. (2) that  $X_1$  and  $X_2$  both showed negative effects on  $Y_1$ , while  $X_3$  has a positive effect on  $Y_1$ , i.e., increasing substrate concentration ( $X_3$ ) promoting the yield of polyols. However, in our previous study we found that at the substrate concentration  $>20$  wt.%, the yield of polyols remained almost the same (Mahmood et al., 2013).

Table 4-5 ANOVA for response surface quadratic model at 95% CI for polyol's yield

%Yield of polyols					
Source	DOF	SS	MS	F-value	p-value
Model	9	1382.34	153.59	10.17	0.001
$X_1$	1	750.98	750.98	49.71	0.000
$X_2$	1	185.39	185.39	12.27	0.006

$X_3$	1	215.32	215.32	14.25	0.004
$X_1 X_2$	1	21.13	21.12	1.40	0.264
$X_1 X_3$	1	1.12	1.12	0.07	0.790
$X_2 X_3$	1	91.12	91.12	6.03	0.034
$X_1^2$	1	97.58	106.49	7.05	0.024
$X_2^2$	1	17.16	18.32	1.21	0.297
$X_3^2$	1	2.55	2.54	0.17	0.690
Residual error	10	151.07	15.11	-	-
Lack of fit	5	135.12	27.02	8.47	0.017
Pure error	5	15.95	3.19		
Total	19	1533.42			
$R^2$	0.902				

Response surface/contour plots collectively helped to evaluate the relationship between input/output variables. Since the model has more than two factors, one factor is held constant in each response surface diagram. We kept the third variable fixed at its respective zero level (middle value). Figures 4-5a and 4-5b represent the surface/contour plots for %yield of DKL/polyols ( $Y_1$ ). The contour plot of  $X_2 * X_1$  at  $X_3 = 0$ , showed that all the values are uniformly distributed over the studied range and that  $Y_1$  increases as  $X_2 * X_1$  moves from the right upper corner to the left side of the plot. This suggests that the high yield could be obtained at low temperature with longer reaction time or vice versa. At the fixed value of  $X_2 = 0$ , a mound-shaped response surface and nearly elliptical shaped contours were generated, which suggests that we were operating close to the maximum point of  $Y_1$ . When  $X_1 = 0$ , contours of  $X_3 * X_2$  are of elliptical shape, representing that there is a significant interaction between the corresponding variables and we are operating close to the stationary points (maxima).

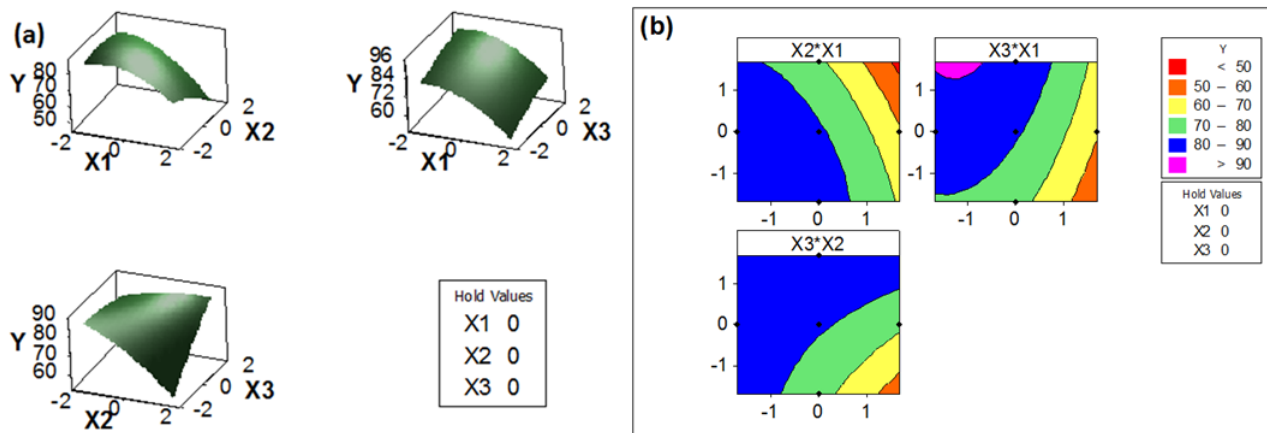


Figure 4-5 Surface (a) and contour (b) plots of % yield of DKL/polyols

#### 4.3.4.2 $M_w$ of polyols

The fitted model for  $M_w$  of polyols is also significant with  $R^2 = 0.82$  and a p-value of  $0.010 < \alpha$ . As shown in Table 4-6, only the linear terms showed significant effect (p-values  $< \alpha$ ), therefore the model equation may be simplified to show the linear terms only.

Table 4-6 ANOVA for response surface quadratic model at 95% CI for  $M_w$  of polyols

Source	DOF	SS	MS	F-value	p-value
Model	9	1309679	145520	4.99	0.010
$X_1$	1	266487	266487	9.14	0.013
$X_2$	1	152220	152220	5.22	0.045
$X_3$	1	485342	485342	16.65	0.002
$X_1 X_2$	1	35113	35112	1.20	0.298
$X_1 X_3$	1	143112	143112	4.91	0.051
$X_2 X_3$	1	112812	112812	3.87	0.078
$X_1^2$	1	70151	55003	1.89	0.200
$X_2^2$	1	13875	18109	0.62	0.449
$X_3^2$	1	30567	30567	1.05	0.330
Residual error	10	291576	29158	-	-

Lack of fit	5	288893	57779	107.66	0.000
Pure error	5	2683	537		
Total	19	1601255			
$R^2$	0.82				

The response surface and contour plots are shown in Figures 4-6a and 4-6b, respectively. At  $X_3 = 0$ , the plots show a saddle behavior, suggesting that the lowest  $M_w$  can be obtained at either a higher temperature with a low reaction time or at a moderately low temperature with a longer reaction time. At  $X_2 = 0$ , rising ridge behavior was observed, showing that the lowest possible  $M_w$  can be obtained at low substrate concentration with moderate to high temperature conditions. Finally,  $X_1 = 0$  (rising ridge) the lowest  $M_w$  can be obtained at the lowest reaction time and lowest substrate concentration.

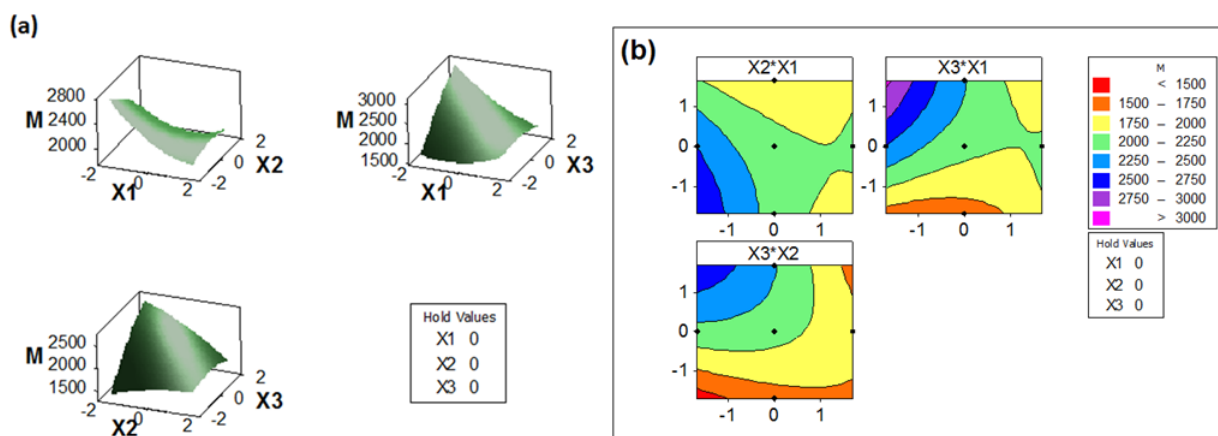


Figure 4-6 Surface (a) and contour (b) plots of  $M_w$  (g/mole) of DKL/polyols

#### 4.3.4.3 Aliphatic-hydroxyl number of polyols

The fitted model for aliphatic-hydroxyl number of polyols ( $Y_3$ ) is highly significant, with  $R^2 = 0.98$  and a p-value of  $0.005 < \alpha$ . The linear terms in  $X_1$  and  $X_2$  and the quadratic term in  $X_2$  were significant. The model equation for  $Y_3$  after dropping the insignificant terms can be given simply in Eq. (3):

$$Y_3 = 299.050 - 50.004 X_1 - 19.974 X_2 + 12.723 X_2^2 \quad (3)$$

Table 4-7 ANOVA for response surface quadratic model at 95% CI for aliphatic-hydroxyl number of polyols

Source	DOF	SS	MS	F-value	p-value
Model	9	28727.3	3191.9	21.66	0.005
$X_1$	1	20245.7	13275.8	90.07	0.001
$X_2$	1	5296.5	4152.8	28.17	0.006
$X_3$	1	1338.9	1054.9	7.16	0.056
$X_1 X_2$	1	240.1	90.7	0.62	0.477
$X_1 X_3$	1	19.8	57.9	0.39	0.565
$X_2 X_3$	1	97.9	97.9	0.66	0.461
$X_1^2$	1	3.2	22.6	0.15	0.715
$X_2^2$	1	1347.4	1437.7	0.75	0.035
$X_3^2$	1	137.8	134.0	0.91	0.394
Residual error	4	589.6	147.4		
Lack of fit	3	589.6	196.5		
Pure error	1	0.0	0.0		
Total	13	29316.9			
$R^2$	0.98				

Surface/contour plots for the aliphatic hydroxyl content are shown in Figure 4-7. These show that an increase in the treatment severity – either by increasing reaction temperature at fixed reaction time or by increasing reaction time at a fixed reaction temperature reduces the aliphatic-hydroxyl number. This may be due to the fact that under severe conditions dehydration reactions become more dominant than hydration (Arami-Niya et al., 2012; Xu et al., 2008).

At  $X_3$  (substrate concentration) = 0, the contours are elliptical, suggesting that at fixed substrate concentration the other two variables significantly affect the response. Aliphatic-hydroxyl number increases as we move from low to moderate reaction



temperatures with the combination of lower reaction times showing near to stationary point behavior towards maxima.

At  $X_2$  (reaction time) = 0, moderate to high aliphatic-hydroxyl number can be obtained at low to moderate temperature in combination with low to moderate substrate concentrations. At  $X_1$  (temperature) = 0, elliptical contours were generated, which indicates that the maximum response can be predicted in the surface confined in the smallest ellipse within the contour diagram (Lan et al., 2005).

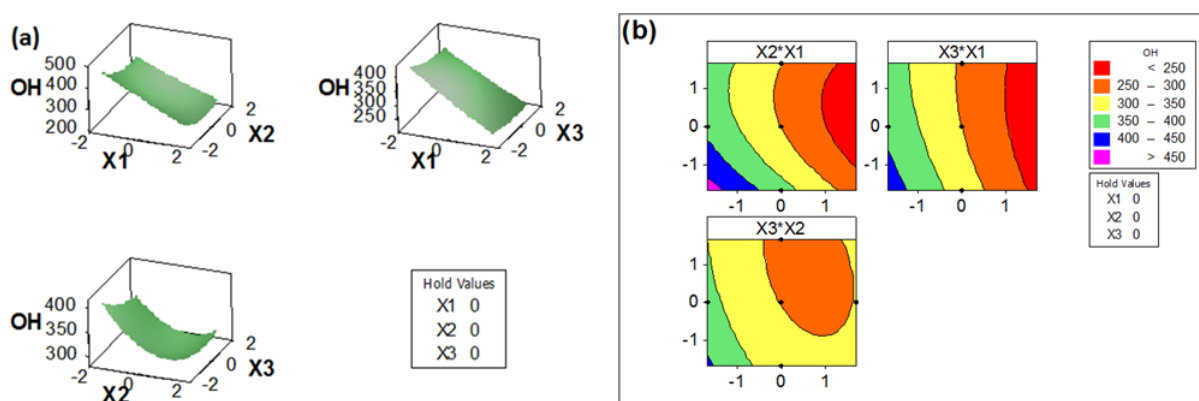


Figure 4-7 Surface (a) and contour (b) plots of aliphatic-hydroxyl number (mgKOH/g) of DKL/polyols

#### 4.3.5 Optimized process conditions

The ANOVA of our design model indicates that it is not possible to differentiate local minima or maxima in the responses of interest (yield,  $M_w$ , aliphatic hydroxyl content), since the quadratic terms of the input variables were not significant. Thus, to achieve the goal of process optimization, we used a combination of parallel charts, overlaid contour plots and a response optimizer (available within Minitab 16.0) as shown in Figure 4-8. The most feasible conditions can be obtained from D-optimality aimed to get the response with minimized variance and the overlaid contours. The optimum reaction conditions to produce DKL/polyols from KL suitable for PU synthesis were: 250 °C, 120 min with 10 wt.% substrate concentration. The predicted results are compared with the experimental data in Table 4-8, revealing satisfactory agreement.

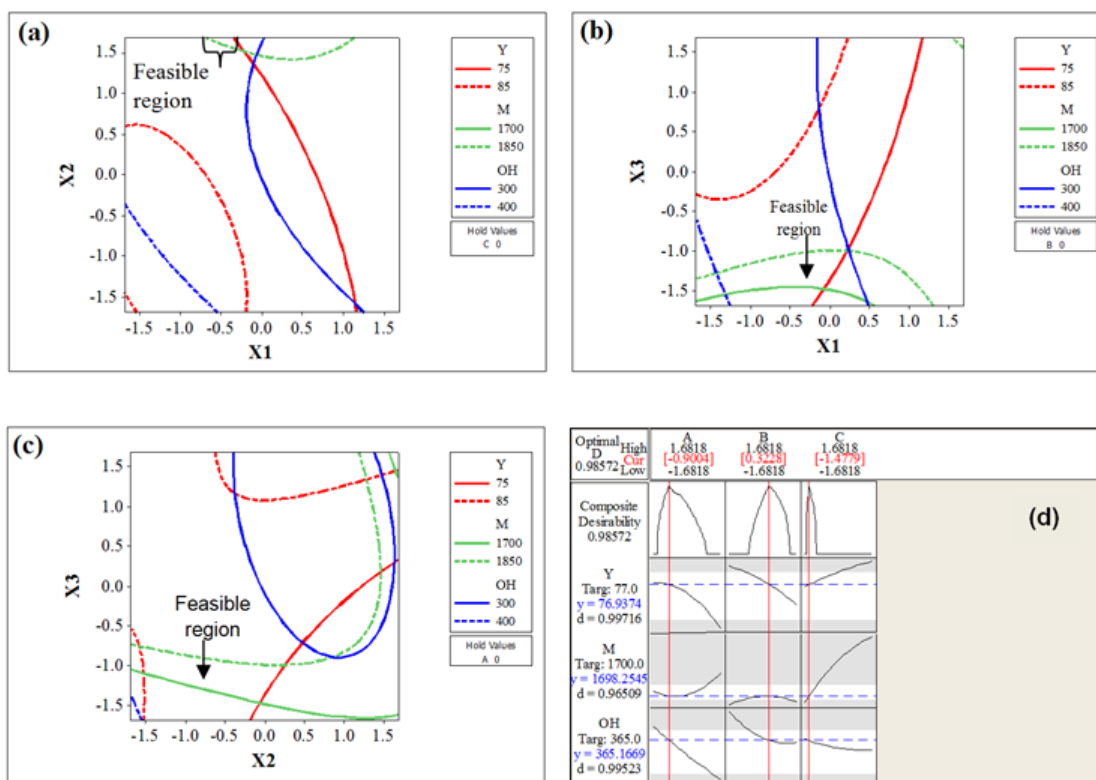


Figure 4-8 (a, b, c) Overlaid contour plots; (d) response optimizer plot

Table 4-8 Comparison of predicted and experimental values of responses ( $Y_1$ ,  $Y_2$  and  $Y_3$ )

Condition	Predicted response values	Experimental response values
$X_1 = 250\text{ }^\circ\text{C}$	$Y_1 \approx 75\text{ wt.}\%$	$Y_1 = 77\text{ wt.}\%$
$X_2 = 120\text{ min}$	$Y_2 \approx 1825\text{ g/mole}$	$Y_2 = 1700\text{ g/mole}$
$X_3 = 10\text{ wt.}\%$	$Y_3 \approx 353\text{ mgKOH/g}$	$Y_3 = 365\text{ mgKOH/g}$

## 4.4 Conclusions

Optimum reaction conditions for producing polyols suitable for PU synthesis (a high aliphatic-hydroxyl number, a low  $M_w$  with a moderately high yield) via direct hydrolysis of KL were investigated using a central composite design. The optimal reaction

conditions were 250 °C, 120 min and 10 wt.% substrate concentration, which gave a lignin polyol with aliphatic-hydroxyl number  $\approx 365$  mgKOH/g,  $M_w \approx 1700$  g/mole at  $\approx 77$  wt.% yield). Temperature was the most significant parameter affecting the desired characteristics of polyols.

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## Chapter 5

### 5 Preparation of bio-based rigid polyurethane foam using hydrolytically depolymerized Kraft lignin (DKL) via direct replacement or oxypropylation

#### Abstract

Bio-based rigid polyurethane (BRPU) foams of densities 54-105 kg/m<sup>3</sup> were successfully produced using hydrolytically depolymerized Kraft lignin (DKL, with  $M_w$  ~1700 g/mole, aliphatic hydroxyl number ~365 mgKOH/g and total hydroxyl number ~671 mgKOH/g) as bio-polyols replacing 50 wt.% of petroleum-based polyol. Three types of BRPU foams were prepared with different routes i.e., replacing PPG400 directly with DKL, substituting sucrose polyol directly with DKL, and oxypropylation of DKL. All three BRPU foams along with the PPG400 and sucrose polyol reference foams were characterized and compared in terms of their physical, mechanical and thermal properties. All BRPU foams exhibit good compressive strengths, compared with the reference foams, and showed the following sequence for decreasing compression modulus: BRPU foam with oxypropylated DKL (10986.0 kPa)>BRPU foam with 50 wt.% sucrose polyol and 50 wt.% DKL (5152.0 kPa)>sucrose polyol reference foam (2086.0 kPa)>BRPU foam with 50 wt.% PPG 400 and 50 wt.% DKL (1016.0 kPa)>PPG 400 reference foam (789.1 kPa). Thermal conductivity of all the prepared foams varied between 0.029 W/mK to 0.04 W/mK. All BRPU foams also possess better thermal insulation properties than reference foams, with lower thermal conductivity, among which the BRPU foam with oxypropylated DKL has the lowest thermal conductivity (0.029 W/mK), making it suitable for utilization as an insulation material.

**KEYWORDS:** Kraft lignin, depolymerization, bio-polyols, PPG 400, sucrose polyol, rigid polyurethane foam, oxypropylation.

## 5.1 Introduction

Rigid polyurethane (PU) foams are widely used for many engineering applications, such as insulation materials, automotive parts, and structural materials (Narine et al., 2007). The production of PU foams is realized through the reaction of isocyanates with polyols. Currently, both isocyanate and polyols are mostly derived from petrochemical resources. With the increasing concerns over the depletion of fossil fuels and their environmental impact, there is a growing interest in exploring renewable feedstock to replace petroleum derived polyols either partially or completely for the production of bio-based PU foams (Zhao et al., 2012), without sacrificing the physical, mechanical and thermal characteristics of the material.

Lignin, a natural aromatic high molecular weight biopolymer, composed of phenyl propanol units (Tejado et al., 2007). It can be a potential candidate for the production of fuels, chemicals and bio-based materials. All native lignin products are heterogenous in nature and their molecules mainly consist of two types of linkages: condensed linkages (e.g., 5-5 and  $\beta$ -1 linkages) and ether linkages (e.g.,  $\alpha$ -O-4 and  $\beta$ -O-4) (Chakar and Ragauskas, 2004). Aryl ether linkages can be more easily cleaved than the stable C-C linkages which are resistant to chemical depolymerization. Large quantities of lignin are available from pulp and paper mills or cellulosic ethanol plants. It was estimated that the pulp and paper industry generates 50 million tons of lignin in 2010, mainly utilized as a low-value fuel for recovery boilers in pulp/paper mills for heat and power generation (Borges da Silva et al., 2009), but only approximately 2% (1 million tonnes) has been commercialized for other value-added industrial applications. Recently, lignin has gained increasing attention for its potential utilizations either directly or after chemical modification as a renewable feedstock for chemicals such as bio-polyols in the preparation of polyurethane (PU) foams (Cateto et al., 2011).

Crude lignin has much lower reactivity (Cheng et al., 2012), however, due to its larger molecular weight and steric hindrance effect, so it could only replace less than 30% of polyols in the preparation of PU foams. Hydrolytic depolymerization of Kraft lignin (KL) employing water alone as a solvent under alkaline conditions was found a promising approach to convert KL of a very high molecular weight into low molecular weight



depolymerized KL (DKL) (Mahmood et al., 2013). After depolymerization the resulted DKLs has lower molecular weights and more functionality such as higher hydroxyl numbers (Mahmood et al., 2013), Which could substitute petroleum-based polyols as reactive bio-polyols at a larger replacement ratios for the manufacture of rigid PU foams, one of the most widely used polymeric foam materials, particularly in the construction industry as insulating material .

The objective of this study is to prepare bio-based rigid polyurethane (BRPU) foams with hydrolytically depolymerized KL (DKL) as bio-polyols to substitute petroleum-based polyols at a high replacement ratio, i.e., 50 wt.%. Three preparation routes that differ in the methods of how to incorporate DKL into the PU foams were employed in the preparation of BRPU foams, i.e., (1) partially replacing PPG 400 with DKL, (2) partially replacing sucrose polyol with DKL, and (3) oxypropylation of DKL. The obtained BRPU foams were characterized and compared in terms of their physical, mechanical and thermal properties for potential utilization as insulation materials.

## 5.2 Experimental

### 5.2.1 Materials

Kraft lignin (KL) used in this study was provided by FPIInnovations, produced using the proprietary LignoForce process (Kouisni, 2012) in its pilot plant in Thunder Bay, Ontario. The KL has a weight-average molecular weight ( $M_w \sim 10,000$  g/mole) based on GPC-UV analysis, and the dried KL sample contains 0.57 wt.% ash and 5.2 wt.% sulfur (on dry ash free basis). Other chemicals used in this work are all CAS reagent grade chemicals, purchased from Sigma-Aldrich and used without further purification, including NaOH, acetone, pyridine, acetic anhydride, sulfuric acid, HCl, dibromomethane, PPG400, polymeric MDI, sucrose polyol (JEFFOL SD-361), triethanolamine (co-catalys), triethylene diamine (1,4-Diazabicyclo [2.2.2] octane), dibutyltin diluarate, silicon oil, glycerol etc. The physical characteristics of all chemicals used in the foam preparation are given in Table 5-1.

Table 5-1 Physical characteristics of all chemicals used

Ingredients	Functionality	Equivalent weight (g/mol)	-OH # (mgKOH/g)	Comments
PMDI	2.7	135.0	-	NCO contents: 31.2%
PPG400	2.0	200.0	280.5	Petroleum polyol
Glycerol	3.0	30.7	1829.4	Crosslinking agent
Sucrose polyol	8.0	155.8	360.0	Reference polyol
Water	2.0	9.0	6233.3	Chemical blowing agent
Acetone	-	-	-	Physical blowing agent
Poly(siloxane ether)	-	-	-	Silicon surfactant
Triethylene diamine	-	-	-	Foaming catalyst
Dibutyltin dilaurate	-	-	-	Gelation catalyst
Triethanol amine	3.0	49.73	1128.1	Co-catalys

### 5.2.2 Depolymerization of KL

Briefly, in a typical run, 25 g KL, 7 g NaOH and 218 g of distilled water were loaded into a 500 mL autoclave reactor. The reactor was sealed, purged thrice with N<sub>2</sub> and then finally pressurized with 2 MPa N<sub>2</sub>, and finally heated up 250 °C under stirring for 2 h after the reactor reached the temperature. At the end of the reaction, the reactor was immediately quenched in an ice water bath. The gases inside the reactor vented in the fume hood, and the reactor contents were washed into a beaker using distilled water and the pH was adjusted to  $\approx$ 2.0 using 1M sulfuric acid to precipitate the DKL products. The acidified mixture was filtered and the solid cake left after filtration was dissolved in acetone. The solid residues (SRs) remained on the filter paper were separated and dried in an oven (at 105 °C for 24 h). The depolymerized Kraft lignin (DKL) in the acetone solution was recovered by rotary evaporation at 40-65 °C under reduced pressure. The yield of DKL was determined to be  $\sim$ 77 wt.%, based on the dry weight of KL used in each run.

### 5.2.3 Oxypropylation of DKL

Oxypropylation of DKL with 50 wt.% bio-contents was carried out in a 100 mL Parr autoclave reactor. In a typical run, 18.9 g of DKL, 21.21 g propylene oxide (PO), 2.31 g of glycerol and KOH mixture with 16.8 g of acetone were loaded to the reactor; the reactor was sealed under atmospheric pressure (1 atm-g), and heated up to 150 °C under atmospheric pressure (1 atm-g). Initially the pressure increased slightly but after a while it restored to the initial start-up pressure (atmospheric pressure) implying complete consumption of PO by the oxypropylation reactions. After cooling, the oxypropylated DKL in the reactor was washed using acetone and vacuum filtrated. The filtrate was evaporated via rotary evaporation under reduced pressure to completely remove all acetone and any unused PO if any. The weight of the oxypropylated product was approximately equal to the total weight of DKL, PO and glycerol.

### 5.2.4 Preparation of DKL based BRPU foam

All DKL based BRPU foams were prepared in 455-ml plastic cups using one shot method. For the BRPU foams prepared by replacing PPG400 or sucrose polyols directly with, DKL was pre-dissolved in acetone before the foam preparation. Whereas, oxypropylated sample was in liquid form, so it can be used directly for foaming. In formulation of the DKL based BRPU foams (as well as the reference foams) glycerol at 10% (w/w) was added as a cross-linking agent to the polyol (or bio-based polyol). The reference foams were prepared with PPG400 and sucrose polyols, respectively. The formulation also includes a physical blowing agent (acetone at 20% (w/w)), a catalyst (combined mixture of equal amounts of dibutyltin diluarate and triethylene diamine) at 2% (w/w), surfactant at 2% (w/w) and water at 2% (w/w). The weight amounts of the blowing agent, catalyst, surfactant and water were determined with respect to the total weight of polyol (s). PMDI was added at a NCO/OH ratio of 1.1. Overall, the foaming procedure employed is comprised of the following steps: (1) desired amounts of polyols, catalysts and blowing agents were all weighed in the cup, followed by premixing the ingredients at a speed of 550 rpm for 10-12 s to obtain a homogeneous mixture, (2) pre-calculated polymeric MDI was then transferred into the cup and the mixture was stirred vigorously for another 12-15s at ambient temperature ( $23\pm 2$  °C), and (3) the mixture was

placed on a leveled surface in a fume hood and let the foam rise owing to the self-generated heat. All the foams were left in the fume hood for 24-48 h for curing prior to analysis. The foam shrinkage, structural uniformity, stability and cells appearance were observed at this point. Prior to further characterization, the foam samples were conditioned for a minimum of 24 h to max of 1 week, depending on the testing requirements.

### 5.2.5 Characterizations of DKL, oxypropylated DKL and BRPU foams

Hydroxyl number of powdered DKL after acetylation was determined by  $^1\text{H}$  NMR spectra analysis. Hydroxyl number of the oxypropylated sample was measured using a Potentiometric Titrator (Titroline 7000 Titrator) in accordance to ASTM D4274-99 standard. The viscosity of the oxypropylated DKL sample was determined using BROOKFELD CAP 2000+VISCOMETER at 80 °C. Functional groups of the bio-polyol feedstock and the foam products were investigated using IR analysis and the molecular weight distributions of the DKL and oxypropylated DKL were measured on a GPC-HPLC instrument (1525 binary pump, UV detector set at 270 nm, Waters Styragel HR1 column at 40 °C) using THF as the eluent at a flow rate of 1 ml/min, calibrated with polystyrene standards.

The apparent density of foam samples was measured according to ASTM D1622-03 with the sample size of 16.4 cm<sup>3</sup>. The mechanical properties of PUF samples were measured at ambient conditions with an ADMET UTM (Model SM-1000-38). Modulus of elasticity (Young's modulus/compressive modulus) and compressive strength at 10% and 20% deformation were determined according to ASTM D 1621-00 standard. Thermal conductivity of the foam samples was measured using KD2 PRO thermal properties analyzer with SH-1 dual needle sensor (1.3 mm diameter, 3 cm long, and 6 mm spacing) capable of measuring thermal conductivity in the range of 0.02 and 2.00 W/mK. The specimen size used was ~ 50 mm × 50 mm × 30 mm. Water absorption capacity of the foam samples was determined according to modified ASTM C272 standard using the specimen size of ~ 50 mm × 50 mm × 30 m. Initially, a dry foam sample was weighed and then placed into a beaker filled with de-ionized water (250 mL) for 24 h at room

temperature. The specimen was then taken out of water, removed the excess water and weighed it. Water absorption was then reported as percentage of weight gain. Thermal stability of the foams was measured by *Pyris<sup>TM</sup>* Diamond, Perkin–Elmer Thermogravimetric analyzer (TGA), under a N<sub>2</sub> flow (20 ml/min) from 40 °C to 800 °C at 10 °C/min. Glass transition temperature ( $T_g$ ) of foam samples was determined using DSC (differential scanning calorimeter: Mettler Toledo DSC 1) under a N<sub>2</sub> flow (50-60 mL/min) where the sample was heated at a heating rate of 10 °C/min from 50-350 °C. Morphology of the foams was observed by Hitachi S-4500 field emission cross beam scanning electron microscope (SEM). After examination by SEM, selected locations on the foam surface were subjected to a cross-sectional cut and the sample was coated with osmium, and imaged using a focused ion beam LEO (Zeiss, Thornwood, NY, USA) 1540XB SEM.

### 5.3 Results and discussions

Table 5-2 summarizes  $M_w$ , hydroxyl numbers and viscosity of the bio-polyols feedstock including the original KL, DKL and oxypropylated samples. As shown in the Table, both KL and DKL are in solid powder form, while the oxypropylated DKL is in viscous liquid state (with viscosity of 0.61 Pa.s at 80 °C). As clearly shown in the Table, the DKL and oxypropylated DKL have much higher total hydroxyl numbers (671 mgKOH/g and 350 mgKOH/g, respectively), as compared with that of original KL (275 mgKOH/g). In addition to the total hydroxyl numbers, the other most relevant physico-chemical property for a polyol is viscosity. For a polyol (such as KL or DKL) if in solid powder state, it is critically important to convert it into liquid form for the preparation of BRPU foams. This conversion can be achieved either via oxypropylation or by dissolving DKL in an organic solvent (such as acetone in this study) prior to its addition in the foaming reaction mixture. Figure 5-1, 5-2 and 5-3 shows the <sup>1</sup>H NMR spectra of acetylated KL, DKL and oxypropylated DKL. It can be seen clearly from the Figure 5-1 and Figure 5-2 that original KL and DKL both have aliphatic and phenolic –OH groups shown in terms of aliphatic and phenolic acetates. However, oxypropylation converted all phenolic –OH groups into aliphatic –OH groups (shown as a one signal) via oxypropylation reaction.

Table 5-2  $M_w$ , hydroxyl numbers and viscosity of the bio-polyols feedstock

Sample ID	$M_w$ (g/mole)	Aliphatic hydroxyl number (mgKOH/g)	Total hydroxyl number (mgKOH/g)	Viscosity at 80 °C (Pa.s)	State of product
KL	10,000	128	275	-	Powder
DKL	1700	365	671	-	Powder
DKL50PO50	3600	-	350	0.61	Viscous liquid

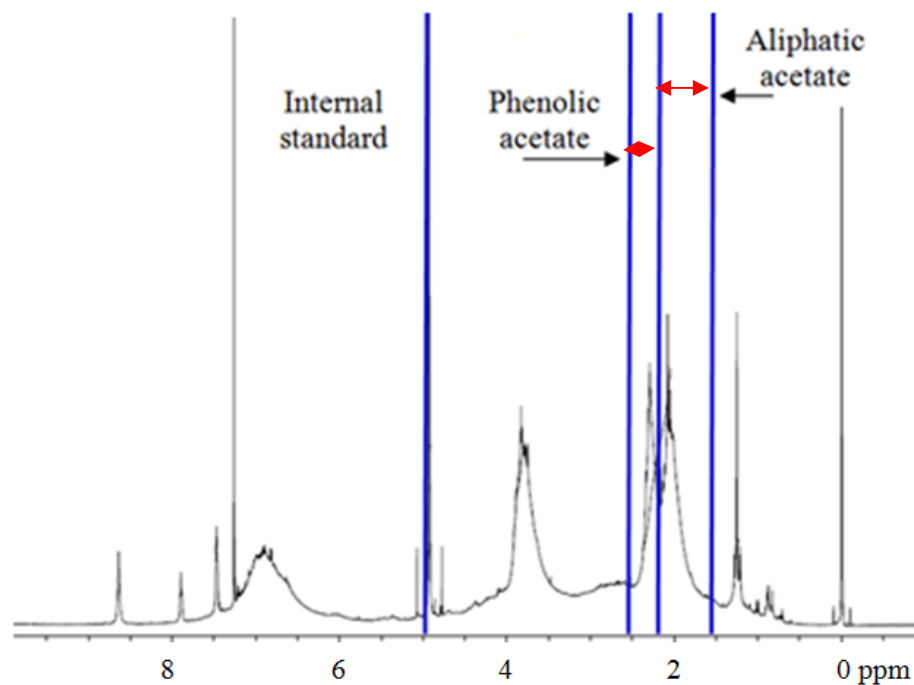
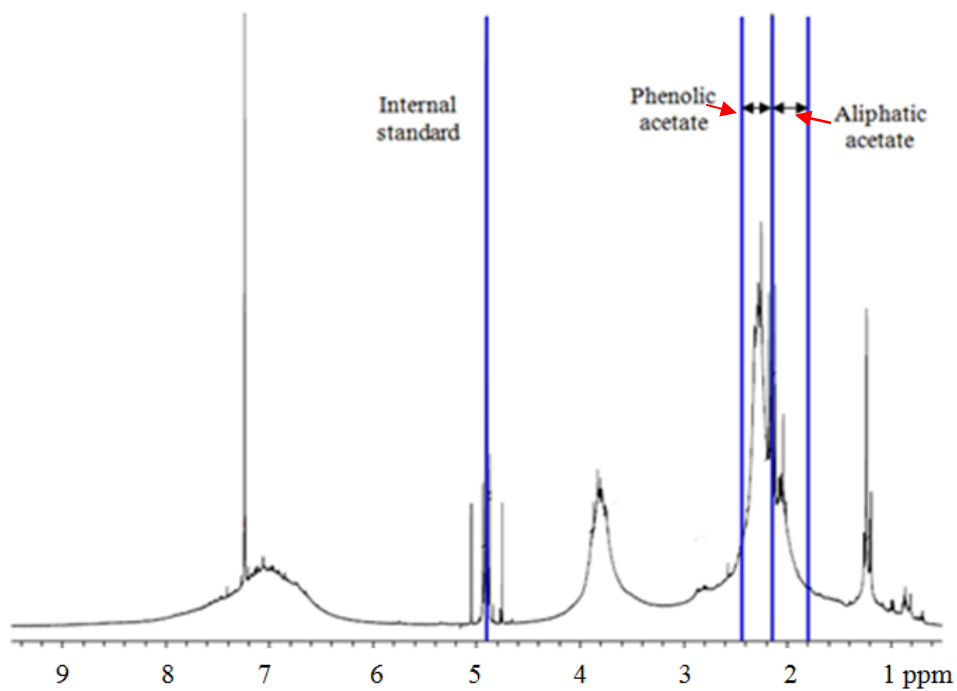
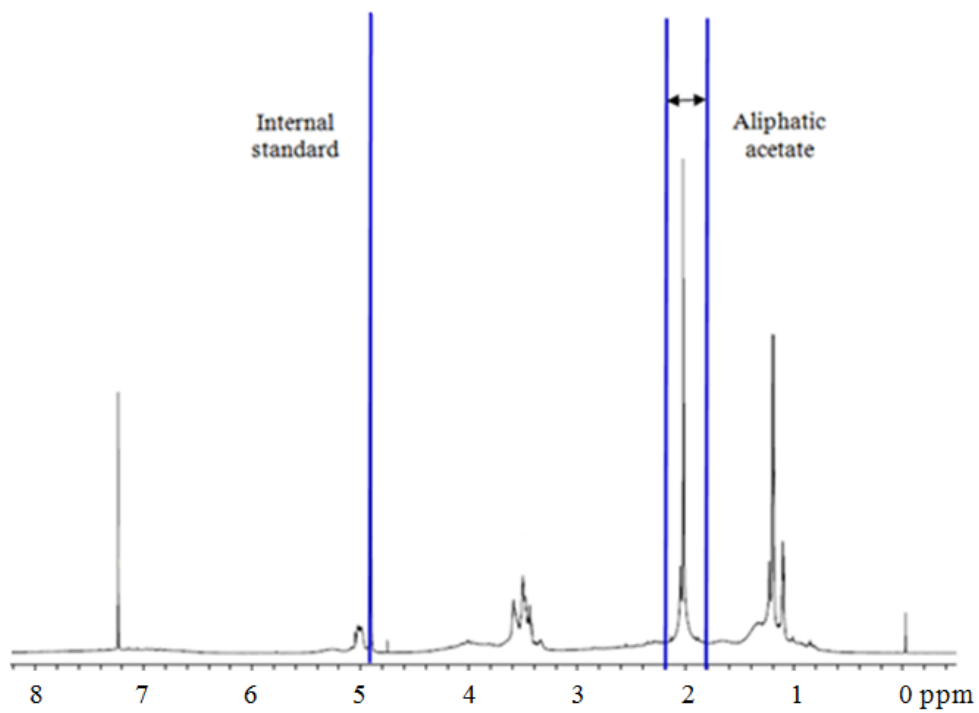


Figure 5-1  $^1\text{H}$  NMR spectra of acetylated KL

Figure 5-2  $^1\text{H}$  NMR spectra of acetylated DKLFigure 5-3  $^1\text{H}$  NMR spectra of acetylated oxypropylated DKL

### 5.3.1 Physical properties

Physical properties of all foams, including 2 reference foams and 3 DKL-based BRPU foams, were measured and reported in Table 5-3, in which the foam density, rigidity, structural uniformity, structural stability or shrinkage, etc. are presented. It was found that the incorporation of the lignin-derived bio-polyols to the rigid foams could positively contribute towards overall improvement of the foam's rigidity, owing to the also introduction of hard segments by the bio-polyols. In this study, PPG400 and sucrose polyols, whose physical characteristics are shown previously in Table 5-1, were selected as reference polyols since they have different functionalities and structure. PPG400 is a di-functional polyol with linear long chain structure, while sucrose polyol has multiple branched short chain structure. As shown in Table 5-3, densities of the reference foams from PPG 400 and sucrose polyols are similar i.e.,  $55(\pm 1)$  kg/m<sup>3</sup>. However, the DKL-based BRPU foams prepared by directly replacing 50 wt.% of PPG 400 or sucrose polyol have higher densities of  $104(\pm 2)$  kg/m<sup>3</sup>. A possible reason for such greatly increased foam density by direct incorporation of DKL in the BRPU formula is that DKL has relatively lower reactivity, which hence causes a slower gelation reaction rate. A slower gelation reaction rate would lead to more gases to escape from the foam structure and hence smaller void volumes and higher foam densities. It shall be noted that, density of the DKL-based BRPU foams could be tuned by varying the additional amount of physical blowing agent. Interestingly, the density of BRPU foam prepared with the oxypropylated DKL ( $55.3$  kg/m<sup>3</sup>) is very close to that of the reference foams, likely because the oxypropylated DKL has similar molecular structure and hence similar reactivity as the reference polyols, as evidenced by the FTIR analysis of all the polyols to be discussed in the later part of this section.

Table 5-3 Physical characteristics of 2 reference and 3 DKL-based BRPU foams

Foam ID	Density (kg/m <sup>3</sup> )	Structural uniformity	Shrinkage	Stability before/after conditioning	Water absorption (wt.%)
PPG400 (Ref foam)	56.0±1.0	0.5	0	1	31.5±0.20
DKL50-PPG40050	105.0±2.0	0	1	0	21.3±0.50



Sucrose polyol (Ref foam)	54.0±1.5	1	0	1	5.8±0.35
DKL50-Sucrose50	104.3±1.0	1	0	1	4.3±0.50
DKL50-PO50	55.3±1.0	1	0	1	11.8±0.50

Note: “1” and “0” denotes “Yes” and “No”, respectively.

Water uptake after 24 h in water exposure at room temperature was 31.5 wt.% for the PPG400 based reference foam. However, replacing PPG400 polyols directly with DKL at 50 wt.%, the water absorption for the BRPU foam was reduced markedly by 10%. On the other hand, sucrose polyol-based RPU foam showed superb water resistance property, and it absorbed only 5 wt.% water, which was further reduced to 4.3 wt.% replacing sucrose polyol with DKL at 50 wt.%. The BRPU foam prepared from oxypropylated DKL absorbed 11.8 wt.% water, which could result from the rupture of foam's cell windows due to the hydraulic pressure of water, causing water to penetrate inside the foam (Mondal and Khakhar, 2004). It was suggested that increasing MDI contents could reduce the water absorption capacity of the foam, due to the formation of more closely packed small pores Kumar and Kaur (2013).

As discussed above, the density of BRPU foam prepared with the oxypropylated DKL is very close to that of the reference foams. To account for this, a possible reason was proposed, i.e., the oxypropylated DKL has similar structure and hence similar reactivity as the reference polyols. To provide some evidence, FTIR analysis was carried out on all the polyols including KL, DKL, the oxypropylated DKL and the two reference polyols (PPG400 polyol and sucrose polyol). The FTIR spectra of all these polyols are illustrated in Figure 5-4. All spectra contain a broad absorption peak at 3200-3550  $\text{cm}^{-1}$  attributed to aromatic and aliphatic O-H stretching, as expected. For all lignin related samples, there are strong peaks at 1400-1700  $\text{cm}^{-1}$  attributed to IR absorbance by aryl groups. In all samples, the peaks at 1000-1300  $\text{cm}^{-1}$  correspond to C-O stretching of C-O-H, suggesting the presence of primary, secondary and tertiary alcohols, phenols, ethers and esters (Islam et al., 2005; Kubo and Kadla, 2005). The C-O ether linkage at 1000-1100  $\text{cm}^{-1}$  was observable in KL while the IR spectra of DKL show almost no absorption, suggesting that during hydrolytic depolymerization treatment most of the ether linkages were effectively cleaved. The intensities of the aromatic absorptions at 1400-1700  $\text{cm}^{-1}$  in DKL

sample are almost the same as those in the original KL, suggesting that the hydrolytic depolymerization treatment did not change lignin's aromaticity. The oxypropylation and occurrence of PO grafting on lignins can be evidenced by following FTIR observations: (a) an increase in the bands at 2971-2870  $\text{cm}^{-1}$  attributed to the stretching of  $\text{CH}_3$ ,  $\text{CH}_2$  and  $\text{CH}$  aliphatic groups; (b) reduction in the intensity of the carbonyl peak at 1714  $\text{cm}^{-1}$ ; (c) a marked increase of the absorption bands in the ether C-O stretching region (1000-1100  $\text{cm}^{-1}$ ); and (d) an increase in the band at 1371  $\text{cm}^{-1}$  confirming the introduction of  $\text{CH}_3$  groups (Cateto et al., 2009). More importantly, from Figure 5-4, the FTIR spectrum of the oxypropylated DKL is similar to the spectra of the two reference polyols (PPG400 polyols and sucrose polyol), suggesting that the oxypropylated DKL has similar molecular structure and hence similar reactivity as the reference polyols used in this work. This explains that the BRPU foams prepared from oxypropylated DKL has similar properties (e.g., density as shown in Table 5-3).

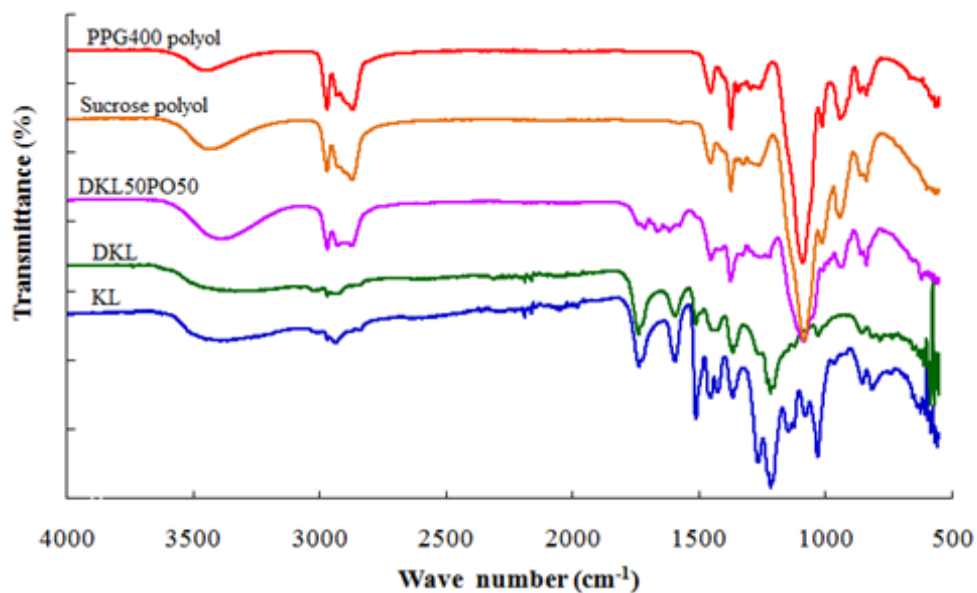


Figure 5-4 FTIR spectra of KL, DKL, the oxypropylated-DKL and the reference polyols (PPG400 polyols and sucrose polyols)

### 5.3.2 Mechanical properties

Mechanical properties of the reference and BRPU foams were measured as shown in Table 5-4. It can be seen clearly from Table 5-4 that the PPG400-based reference foam has the lowest compression modulus (789.1 kPa) and strengths (101.2 kPa and 113.7 kPa at 10% and 20% deformations respectively) which could result from a lower crosslinking density due to its bi-functional nature. On the other hand, sucrose based reference foam has a high compression modulus (2086.0 kPa) and high strengths (327.0 kPa and 342.8 kPa at 10% and 20% deformation respectively) attributed to higher crosslinking density in the resulting foam. When comparing the BRPU foams prepared with 50 wt.% partial substitution of PPG400 polyols or sucrose polyol with DKL, as clearly shown in Table 5-4, the sucrose-based BRPU has higher modulus and strengths than the PPG400-based BRPU foam. This is again due to the bi-functional structure of PPG400, causing lower crosslink density of the resulting foams. Interestingly, the BRPU foam prepared with the oxypropylated DKL has high compression modulus of 10986.0 kPa and strength of 515.0 kPa and 578.0 kPa at 10% and 20% deformation, respectively. The mechanical properties of the oxypropylated DKL-based BRPU foam are the best among all the foams, even better than the BRPU foam prepared with 50 wt.% sucrose polyols and 50 wt.% DKL. The reason that accounts for the superior mechanical properties for the oxypropylated DKL-based BRPU foam could be: oxypropylation converted all phenolic OH to aliphatic OH, transforming the DKL to highly branch and highly functionalized polyol.

Table 5-4 Mechanical properties of all RPU foams

Foam ID	Modulus of elasticity (kPa)	Compression strength at 10% displacement (kPa)	Compression strength at 20% displacement (kPa)	Max. stress (kPa)
PPG400 (Ref foam 1)	789.1±100.0	101.2±80.0	113.7±75.0	123.8
DKL50-PPG40050	1016.0±90.0	216.0±45.0	227.2±60.0	238.7
Sucrose polyol (Ref foam 2)	2086.0±100.0	327.0±68.0	342.8±70.0	361.5
DKL50-Sucrose50	5152.0±80.0	374.0±42.0	506.0±70.0	526.0
DKL50-PO50	10986.0±55.0	515.0±50.0	578.0±35.0	611.0

### 5.3.3 Thermal properties

Thermal conductivity is the key thermal property that governs insulation applications for rigid PU foams, and it is closely related to the foam density and cell morphology. Low thermal conductivity values for RPU foams results from a small average cell size and high contents of closed cell. For better insulation performance rigid PU foams shall have closed cell contents as high as possible. The thermal conductivities for all prepared foam samples were measured and comparatively given in Table 5-5. In this work thermal conductivities of the RPU foam samples either prepared by 50 wt.% replacement of PPG400 or sucrose polyol with DKL. The foam using oxypropylated DKL (DKL50-PO50) as a bio-polyols has the lowest thermal conductivity, 0.029 W/mK, which is towards the higher limits of common PU construction foams (thermal conductivities between 0.020 to 0.030 W/mK for densities ranging from 30-100 kg/m<sup>3</sup>) (Ribeiro da Silva et al., 2013). The obtained thermal conductivity results are also in a good agreement to the reported results of thermal conductivity (0.0257- 0.0329 W/mK) of rigid PU foams prepared from various types of lignins (Alcell, Indulin, Curan and Sarkanda) at different ratios (Cateto et al., 2010). It was also reported that the thermal conductivities of most common RPU foams lies between 0.02 W/mK and 0.05 W/mK (BING, 2006).

Table 5-5 Thermal conductivity of all RPU foams

Foam samples	Thermal conductivity (W/mK)
PPG400 (Reference foam 1)	0.040±0.001
DKL50-PPG40050	0.038±0.001
Sucrose polyol (Reference foam 2)	0.033±0.001
DKL50-Sucrose50	0.032±0.001
DKL50-PO50	0.029±0.001

Glass transition temperature ( $T_g$ ) was determined by DSC for the BRPU foam with the oxypropylated DKL in 50 mL/min N<sub>2</sub> flow heated from 50 °C temperature to 350 °C at 10 °C/min. The DSC profile is illustrated in Figure 5-5, from which  $T_g$  was determined to be ~300 °C. Thermal Stability of the oxypropylated DKL-based BRPU foam was

investigated by TGA in 20 mL/min N<sub>2</sub> flow heated from room temperature to 800 °C at 10 °C/min. Figure 5-6 displays the TGA profiles of all RPU foams. As shown in the Figure 5-6, all the foams were thermally stable to 200 °C, but after that degradation started. It was generally believed that the first stage of thermal degradation is related to the urethane bond decomposition, through dissociation to form isocyanate and alcohol followed by the thermal decomposition leading to the formation of amines, small transition components and carbon dioxide (Ribeiro da Silva et al., 2013; Zhao et al., 2012).

The area below 150 °C is considered to be due to the evaporation of water. Pyrolysis of PU foam under nitrogen atmosphere starts at ~170 °C and intensified at ~200 °C. Main decomposition range of RPU foams took place between 200-450 °C. Where, around 350 °C the decomposition of polyurethane start releasing components like diisocyanates and polyols along with other decomposition products like amines, olefins and carbon dioxide because of the destruction of polymer chain (Manocha et al., 2010). For bio-based foams after 600 °C, weight loss is negligible. For all the BRPU foams there is not much difference between their thermal stability.

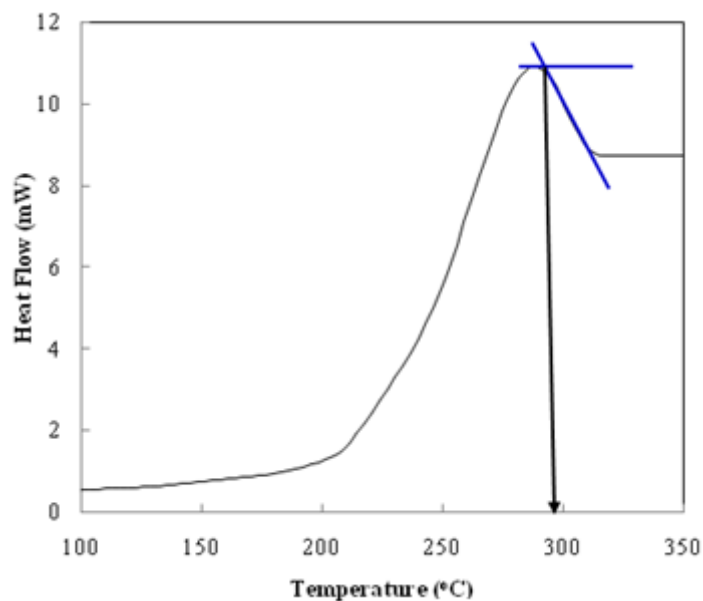


Figure 5-5 DSC profile for the oxypropylated DKL-based BRPU foam

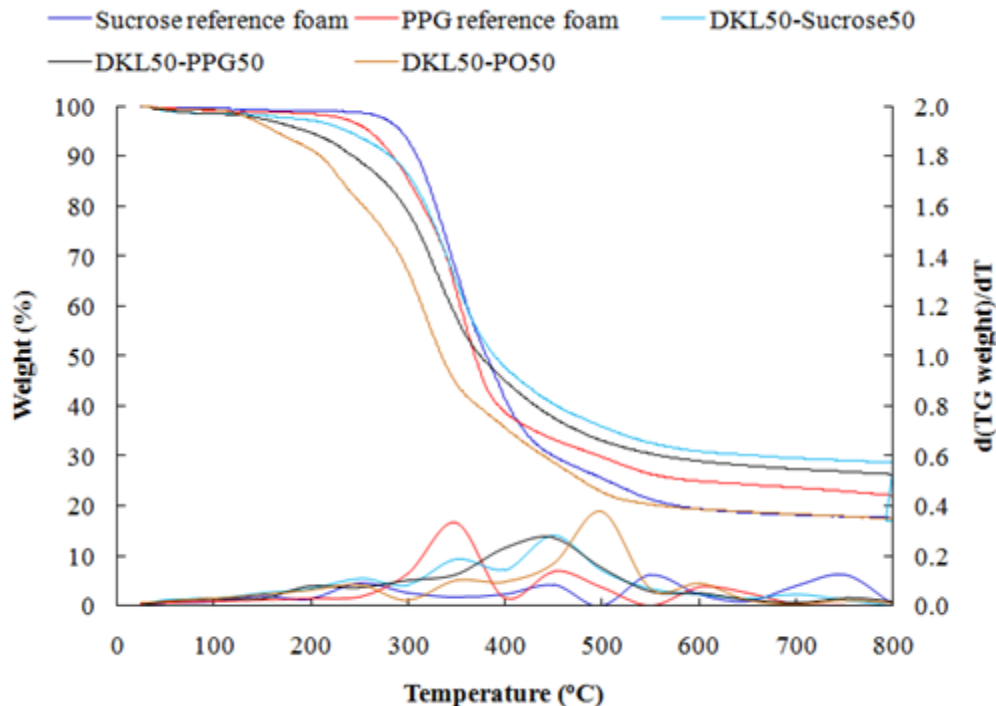


Figure 5-6 TGA and DTG of reference and BRPU foams

### 5.3.4 Morphology

In general, the physical properties of foams are not only dependent on the rigidity of the polymer matrix, but are related to the morphology of the foam cell. Thus, it is of interest to observe the cell structure of the foam using SEM. Figure 5-7, shows SEM images of the reference foams from sucrose and PPG400 polyols. As shown in Figure 5-7, the reference foam from sucrose polyol (Figure 5-7A) shows an average cell size  $\sim 780 \mu\text{m}$ , compared to  $\sim 500 \mu\text{m}$  for the cells for the PPG400-based reference foam. With the incorporation of bio-based polyols cellular shape become more homogeneous and less regular. The alteration in the cell morphology was probably due to the fact that the DKL may affect the process of cell nucleation in preparation of PU foam (Xue et al., 2014). SEM of all BRPU foams showed some broken cells, and some cells have distorted structure. The mechanism of cell growth was dominated by the stiffness of gas/polymer

matrix, the rate of gas diffusion, and the amount of gas loss (Zhao et al., 2012). For the BRPU foams with 50 wt.% DKL and 50 wt.% sucrose polyol or PPG400 polyol have less uniform cells, because the polyol's mixture is less expandable and leads to a bit faster foaming reaction, and hence the evolution of gas via ruptured cells. Bio-based rigid PU foams prepared with polyols containing 50% DKL have density 104-105 kg/m<sup>3</sup> which lead to more smaller cells even difficult to recognize on irregular foam surface.

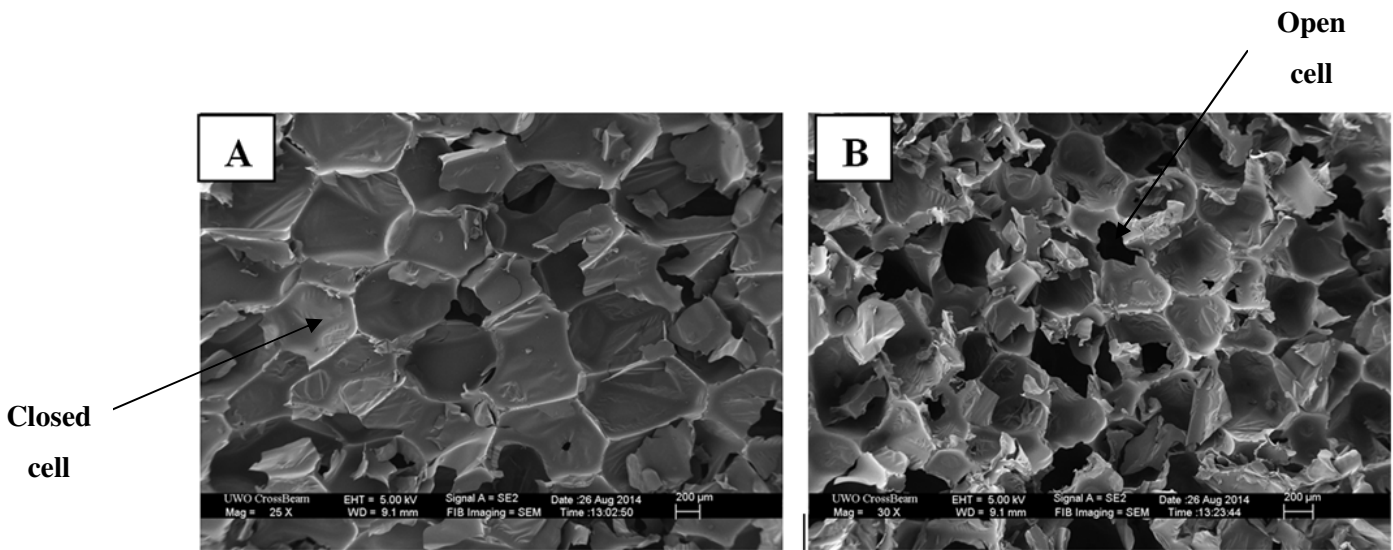


Figure 5-7 SEM images of sucrose (A) and PPG400 (B) derived reference foams

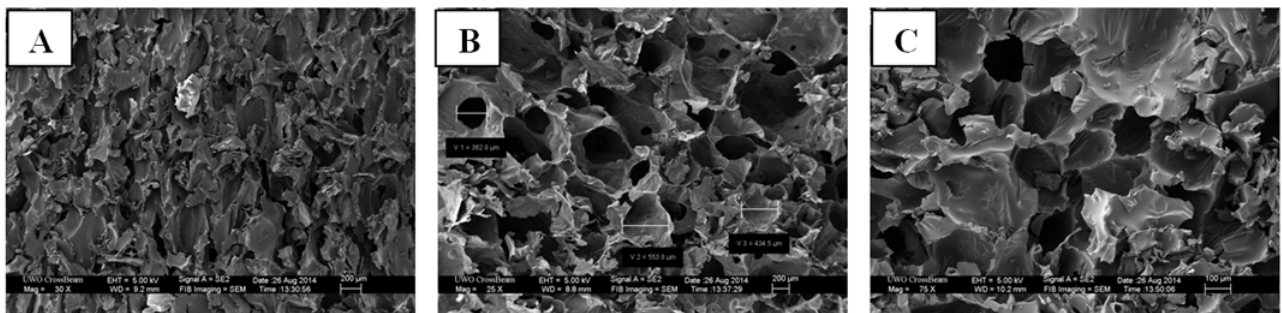


Figure 5-8 SEM images of bio-based rigid PU foams (DKL-sucrose-50, (B) DKL-PPG-50 and, (C) DKL50-PO50

As a summary, the reference RPU foams with the sucrose polyol or PPG400 polyol showed more closed cell structure than the BRPU foams prepared by partially replacing either PPG400 or sucrose polyols with DKL or using oxypropylated DKL. Therefore, the production of BRPU foams from DKL needs further optimization of surfactant, catalysts and blowing agents to improve the foam's microstructure.

## 5.4 Conclusions

Bio-based rigid polyurethane (BRPU) foams were prepared with depolymerized Kraft lignin (DKL) substituting 50 wt.% of petroleum-based polyols via three routes: directly replacing 50 wt.% of PPG400, directly replacing 50 wt.% of sucrose polyol, and using oxypropylated DKL as a single polyol feedstock. All foams were characterized in terms of physical, mechanical, and thermal properties as well as their morphology, and their properties were found to be strongly dependent on the DKL incorporation routes. The foams showed the following order in terms of their compression modulus: Oxypropylated DKL-based BRPU foam (10986.0 kPa) > BRPU foam with 50 wt.% sucrose polyol and 50 wt.% DKL (5152.0 kPa) > sucrose polyol based reference foam (2086.0 kPa) > BRPU foam with 50 wt.% PPG400 polyol and 50 wt.% DKL (1016.0 kPa) > PPG 400 based reference foam (789.1 kPa). The similar trend was observed for the compression strengths of the foams at 10% and 20% deformations. The lower modulus of PPG400 based RPU foams was believed due to its bi-functional long chain structure which leads to lower crosslinking density when compared to the multifunctional short chain structure sucrose polyol. All the foams showed thermal conductivity between 0.029 W/mK to 0.040 W/mK. Among three routes investigated for the preparation of BRPU foams, the oxypropylated DKL-based BRPU foam showed superior combination of physical, mechanical and thermal properties. All BRPU foams are thermally stable up to approximately 200°C.



## 5.5 References

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## Chapter 6

### 6 Hydrolytic depolymerization of hydrolysis lignin: Effects of catalysts and solvents

#### Abstract

Hydrolytic depolymerization of hydrolysis lignin (HL) in water and water-ethanol co-solvent was investigated at 250 °C for 1 h with 20% (w/v) HL substrate concentration with or without catalyst (H<sub>2</sub>SO<sub>4</sub> or NaOH). The obtained depolymerized HLs (DHLs) were characterized with GPC-UV, FTIR, GC-MS, <sup>1</sup>H NMR and elemental analyzer. HL was efficiently depolymerized employing water alone as a solvent without catalyst, producing 68 wt.% yield of DHL with a weight average molecular weight ( $M_w$ ) of ~2030 g/mole, and 4.8 wt.% yield of SRs. While introducing sulfuric acid (2%, w/w) as a catalyst in water,  $M_w$  reduced to ~1110 g/mole however, DHL yield was very low i.e., 32.8 wt.% with high SR's yield ~39.4 wt.%. No effective depolymerization of HL was observed when employing NaOH as a catalyst from 2%-5% (w/w). However, with increasing NaOH loading to 10% (w/w), HL was successfully depolymerized and DHL with yield of ~55.6 wt.% (SR's yield of 30.7 wt.%) was obtained with lower  $M_w$  ~850 g/mole. When water-ethanol mixture was employed without catalyst, DHL yield was improved to 70.5 wt.% (SR yield of ~ 9.8 wt.%) with  $M_w$  as low as ~1000 g/mole. Employing acid as a catalyst in water-ethanol mixture, the yield of DHL was improved to ~75.2 wt.% with a lower SR yield (~1.8 wt.%). However, the  $M_w$  of the DHL produced was slightly increased (1660 g/mole). NaOH in combination with water-ethanol mixture gave DHL yield ~66.5 wt.% (SR yield 20.9 wt.%) with high  $M_w$  (4710 g/mole). In view of the utilization of DHL for the preparation of rigid polyurethane foams/resins, uncatalyzed depolymerization of HL in water-ethanol mixture appeared to be the best route with a suitable aliphatic (227.1 mgKOH/g) and phenolic (215 mgKOH/g) hydroxyl numbers.

**Key words:** Hydrolysis lignin, depolymerization, water solvent, water-ethanol mixture, acid, base.

## 6.1 Introduction

Hydrothermal depolymerization/liquefaction (Peterson et al., 2008) and catalytic liquefaction of lignocellulosic materials/biomass, have demonstrated promise for replacing petroleum derived chemicals with more sustainable alternatives (Huber et al., 2006), in accordance to the principles of green chemistry. Production of bio-derived polymers is challenging due to the variability and complexity of the bio-based starting materials; this requires careful control of reaction conditions and the use of catalysts capable of selective bond cleavage (Barta et al., 2014). The biggest challenge comes from the structure and composition of lignocellulosic biomass composed of three biopolymers: cellulose, hemicelluloses and lignin. Cellulose, a linear homopolymer of glucopyranose residues linked by  $\beta$ -1, 4-glycosidic bonds, is the most principal chemical component in different lignocellulosic biomass (accounting for up to more than 50 wt.%), compared to the other two main components (hemicellulose and lignin) (Shen et al., 2011). Currently, cellulose is most widely used component of lignocellulosic biomass for the production of various bioproducts including paper and biofuels (Varanasi et al., 2013). Hemicellulose is easy to undergo hydrolysis/depolymerization under acidic or basic conditions. Lignin represents 30% of all non-fossil organic carbon on Earth. Its availability exceeds 300 billion tons on the earth (Smolarski, 2012), increasing annually by around 20 billion tons by the natural photosynthesis process. Large quantities of lignin (in the range of millions tons) are yearly available from numerous pulping mills and biorefinery industries (such as cellulosic ethanol plants). Lignin is a by-product of pulping process and typically burned in recovery boilers to produce heat and/or electricity within paper mills and biorefineries. However, the utilization of excessive lignin is usually the bottlenecks in recovery boilers. Thus some lignin can be precipitated and removed out from the pulping processes without affecting the pulp production, and the precipitated lignin can be a cheap renewable raw material for various applications in producing bio-based phenolic resins, PU/epoxy resins, etc. Lignin is a naturally occurring aromatic biopolymer consisting of phenylpropanoid units, and provides mechanical support and water transport to the plant and inhibits the action of various biological agents (e.g., insects) on the plants. The presence of phenolic and aliphatic hydroxyl reactive groups and large availability of lignin render a significant opportunity for production of a wide range of

renewable chemicals and materials using lignin after de-polymerization/liquefaction (Varanasi et al., 2013).

Enzymatic hydrolysis of wood/lignocellulosic biomass is already an established approach for the degradation of wood fibers. The major reactions during enzymatic hydrolysis are on the polysaccharides i.e., cellulose/hemicellulose in the woody biomass (Dahlman et al., 2000) for producing sugars for bio-ethanol. The solid residues left after the enzymatic hydrolysis of wood are termed as hydrolysis lignin (HL). With woody biomass, delignification (thermo-chemically or biologically) or acid pre-hydrolysis is beneficial as it provides accessibility to degradable cellulosic part (Santos et al., 2012). The removal of most of lignin and extractives from the fibers, enhances swelling and porosity of the fibers. Consequently, the cellulose and hemicelluloses can be effectively hydrolyzed to their monosaccharides by enzymes. HL is mainly composed of lignin up to 50 to 57% balanced with unreacted cellulose, mono and oligosaccharides. Extensive research was undertaken in the former Soviet Union to find uses for HL. However, unfortunately, the majority of HL was disposed for no valorization, either because the required modifications for HL utilizations were still too expensive or because the HL-derived materials did not function well enough. Advances in the lignin depolymerization/liquefaction and the utilization of depolymerized/liquefied lignin products have shown great promise in the valorization of this type of lignin.

Most of the current depolymerization/liquefaction processes are carried out heterogeneously, requiring rigorous conditions in terms of solvent, temperature and pressure (Long et al., 2012). Wood and lignocellulosic materials can be easily liquefied/depolymerized in the presence of acidic catalysts (sulfuric, hydrochloric, phosphoric and oxalic acids) or basic catalysts (NaOH, NaHCO<sub>3</sub>, FeSO<sub>4</sub> etc.) in the presence of a suitable solvent. Sulfuric acid has been widely used as an effective catalyst for the liquefaction of lignocellulosic biomass (Cheng et al., 2010). More recently, there has been an increasing interest in using hot-compressed and sub-/supercritical fluids for biomass liquefaction/depolymerization. Hot-compressed or subcritical water has been used by many researchers for biomass liquefaction (Karagöz et al., 2005), while the

liquefaction using water alone as a solvent normally produced a relatively lower yield of water-insoluble oily products than that of using sub-/supercritical alcohols or acetone (Xu and Etcheverry, 2008; Yamazaki et al., 2006; Liu and Zhang, 2008). Another advantage of using an alcohol as a solvent or co-solvent for biomass liquefaction is that alcohols are expected to readily dissolve relatively high molecular weight products derived from cellulose, hemicellulose and lignin because of their lower dielectric constants when compared to that of water (Yamazaki et al., 2006). Therefore, biomass solvolysis was found to be greatly affected by the solvent type (Liu and Zhang, 2008). Lignin in woody biomass could be effectively depolymerized using a mixture of water-ethanol (Cheng et al., 2010) to produce low molecular weight products with more reactive aliphatic hydroxyl groups and more accessible phenolic –OH groups for their further utilization either in polyurethane foams (Mahmood et al., 2013) or in phenolic foams (Zhuang et al., 2011).

Inspired from the above research work for the depolymerization/liquefaction of biomasses, this study for the first time, depolymerization of wood-derived HL was comprehensively studied. Both acidic and basic media using sulfuric acid ( $\text{H}_2\text{SO}_4$ ) and NaOH as catalysts, respectively, were tested at 250 °C, 1 h for 20% (w/v) HL concentration. Effects of solvent type (either water alone or water-ethanol mixture) were compared on the DHL and SR products yields and the  $M_w$  of the DHL products.

## 6.2 Methods

### 6.2.1 Materials

Hydrolysis lignin (HL) used in this study was kindly provided by FPInnovations and was initially insoluble in any common organic solvents like ethanol, methanol or acetone etc. Lignocellulosic biomass from any type of plant biomass that is composed of cellulose, hemicellulose and lignin, typically in amounts of 30-55 wt.%, cellulose; 15-35 wt.%, hemicellulose; and 5-31 wt.%, lignin, was used. The novel bio-conversion process used (Yuan et al., 2012) comprises of low- pressure mechanical refining to disintegrate biomass feedstock, hemicellulose extraction, enzymatic hydrolysis, sugar/lignin separation, and fermentation. After hemicellulose extraction and a subsequent hydrolysis,

the remaining substrate (solid) residue contains a high percentage of lignin which was being recovered and further purified to produce high-quality lignin products. Compared to traditional Kraft lignin and steam-explosion lignin, the high-quality sulfur free lignin produced from this invention has little degradation. Therefore, its molecular weight was unpredictable by using GPC-UV, at least >20,000 g/mol. The pH value of the original HL is neutral. The chemical composition of the raw HL (Yuan et al., 2012) is: 56.7 wt.% lignin, 29.8 wt.% carbohydrates, 1.2 wt.% ash and 12.3 wt.% others, with elemental composition (on dry basis) of 62.8 wt.% carbon, 6.1 wt.% hydrogen, 4.0 wt.% nitrogen and 27.1 wt.% others (oxygen plus ash). The other chemicals used in the study included NaOH, H<sub>2</sub>SO<sub>4</sub>, acetone, pyridine, acetic anhydride, dibromomethane and ethanol, all reagent grade chemicals from Sigma-Aldrich etc., and used without further purification or treatment.

### 6.2.2 Depolymerization of hydrolysis lignin

The depolymerization of hydrolysis lignin (HL) was carried out in 100 mL Parr autoclave reactor, equipped with a pressure gauge, thermocouple, stirrer, gas line and sampling line. In a typical run, the reactor was charged with 10 g HL, 0.2-1.0 g of catalyst (NaOH 2-10 wt.% or H<sub>2</sub>SO<sub>4</sub> 2 wt.% of the HL substrate), and ~40 mL of solvent (water or 50/50 (v/v) water-ethanol mixture). The reactor was sealed, purged with nitrogen three times and finally pressurized to 2000 kPa with N<sub>2</sub> to prevent the reactive material from boiling in the course of heating process. The reactor was heated under a fixed stirring rate (290 rpm) and allowed to run over a pre-specified length of time after reaching the required temperature i.e. 250 °C. After the reaction time elapsed (1 h), the reactor was immediately quenched with a water bath to stop further reactions. Once the reactor was cooled down to room temperature, the gaseous products inside the reactor were collected and analyzed by GC-TCD. The total gas yields were negligibly low (<1 wt.%) in all tests because of low reaction temperature and mainly contained (H<sub>2</sub>, CO, CO<sub>2</sub>, CH<sub>4</sub> and C<sub>2</sub>-C<sub>3</sub>). The reaction mixture was then poured into a beaker, and the reactor was thoroughly rinsed with acetone in case of all experiments except where NaOH was used as a catalyst. When NaOH was employed as a catalyst, the reaction products were transferred into a beaker with the help of spatula and 5 mL of water, followed by acidification of sample



using sulfuric acid, sonication and then dissolving in acetone. The combined reaction mixture was filtered through a Buchener funnel. The obtained solid residues (SRs) were dried with filter paper at 105 °C in an oven, and were weighed to obtain the yield of solid residues (SRs). The acetone soluble filtrate was transferred to a pre-weighed Erlenmeyer flask to remove acetone, ethanol and water with a rotary evaporator at 45-60 °C under reduced pressure to obtain the depolymerized HL (DHL) products. The yield of DHL products was calculated based on the dry mass of input HL. Each experiment was repeated 2-3 to ensure that the maximum experimental errors in the DHL yields be within  $\pm 5\%$ .

### 6.2.3 Product characterization

Original HL and the depolymerized HL (DHL) products were analyzed by Fourier Transform Infrared Spectroscopy (FTIR) for functionality changes. The molecular weights of DHLs were measured with a Waters Breeze GPC-UV (gel permeation chromatography-high performance liquid chromatography) instrument (1525 binary pump, UV detector at 270 nm; Waters Styrylgel HR1 column at a column temperature of 40 °C) using THF as the eluent at a flow rate of 1 ml/min with linear polystyrene standards for the molecular weight calibration curve. Proton nuclear magnetic resonance ( $^1\text{H}$  NMR) spectra for DHLs were acquired at 25 °C using a Varian Inova 600 NMR spectrometer equipped with a Varian 5mm triple-resonance indirect-detection HCX probe. A total of 16-32 scans were accumulated using a 2s recycle delay, 3.6s acquisition time, a 45-degree tip angle (pw =4.8 us), and a spectral width from -2 ppm to 14 ppm (sw =9000.9 Hz). Quantitative  $^1\text{H}$  NMR spectra analysis was realized using acetylated samples of the HL or DHL. Briefly, 1 g of dried HL (or DHL) was dissolved in a 1:1 (v/v) mixture of pyridine (5 mL) and acetic anhydride (5 mL) in a vial followed by stirring for 24 to 48 hr. The well-stirred mixture was then transferred into a beaker containing 100 mL of ice-cooled 2 wt.% HCl solution. The resulting precipitates of acetylated samples were washed with distilled water to pH  $\approx 7$ . The samples were then dried at 50 °C under vacuum for 24 hr to remove residual water before further utilization. Dibromomethane ( $\text{CH}_2\text{Br}_2$ ) was used as an internal standard and its characteristic peak is at 4.9 ppm. For determining hydroxyl number through  $^1\text{H}$ -NMR, the samples were

prepared by first weighing 30 mg of the acetylated KL or DL and 15 mg of internal standard in a vial and then the sample was transferred into a 5 mm NMR tube via a transfer pipette using *d*-chloroform ( $\approx 1000$ -1500 mg) for the subsequent NMR analysis. Gas samples were analyzed via GC-TCD. GC-MS analysis was conducted with an Agilent 7890B GC coupled a 5977A MSD using 30 m  $\times$  0.5 mm  $\times$  0.25  $\mu$ m DB-5 columns with temperature programming as follows: a 1 min hold at an initial temperature of 50 °C followed by a 30 °C min<sup>-1</sup> ramp to the final temperature of 280 °C with 1 min hold. The elemental analysis of DHL and SR's was performed using a Thermo Fischer Flash EA 1112 series CHNS-O elemental analyzer. The elemental analysis results were used to check the carbon balance for some typical runs.

## 6.3 Results and discussions

### 6.3.1 Effects of solvent type on non-catalytic HL depolymerization

Depolymerization experiments of HL were conducted employing either single solvent (water) or mixture of water-ethanol at 1:1 (v/v), to investigate their effects on the yield of products (DHL and SR) and  $M_w$  of DHL products. Table 6-1 shows that using water alone depolymerization of HL resulted in  $\sim 68$  wt.% yield of DHL and  $\sim 5$  wt.% yield of SR. The depolymerization of HL leads to DHL product of a low  $M_w$   $\sim 2030$  g/mole. The obtained low  $M_w$  DHL showed good solubility in THF and acetone at room temperature. Hot-compressed water was demonstrated to be an effective solvent for hydrothermal liquefaction of biomass ([Karagöz et al., 2005](#)). The high activity of hot-compressed water for depolymerizing/liquefying lignin in this study could be ascribed to the unique properties of hot-compressed water such as lower dielectric constant, fewer and weaker hydrogen bonds, a higher isothermal compressibility, and an enhanced solubility for organic compounds than ambient liquid water ([Akiya and Savage, 2002](#)). Moreover, hot-compressed water has been found very effective for promoting ionic, polar non-ionic and free-radical reactions, which make it a promising reaction medium for biomass direct liquefaction.

When water-ethanol mixture was employed as a solvent for HL depolymerization the yield of DHL reached up to 70 wt.%, although the SR yield was increased to  $\sim 10$  wt.%

which could be attributed to the presence of organic solvent (ethanol) in the reaction mixture which is less effective for cellulose hydrolysis compared with water alone. The SRs (acetone insoluble phase) are mainly comprised of residual cellulose and the sugar derivatives along with some char, where the char could be resulted from the cross-linking reaction between carbon-carbon double bonds (C=C) which lead to the formation of a highly cross-linked insoluble structure (Mahmood et al., 2013). The presence of residual cellulose in the SRs was confirmed previously by Xu et al. (2012).

Interestingly, the  $M_w$  of DHL was reduced to ~1000 g/mole when employing water-ethanol as a solvent for the HL de-polymerization. The sub/supercritical ethanol-water could acts as a weak acid media therefore, the liquefaction reaction could be considered as an acid-catalyzed process (Chen et al., 2012). Where, water still acts as a nucleophile and reacted with some active centers in the proton-lignin (Li et al., 2009). A mechanism was proposed in earlier literature that (Wang et al., 2012; Yuan et al., 2007) ethanol had hydrogen-donor capability to stabilize the intermediates generated and thus increased the DHL product yield. It was expected that some low-boiling point compounds could be generated in the process, but they might be removed during the rotary evaporation.

Table 6-1 Yields of products (DHL and SRs) and  $M_w$  of DHL (Other reaction conditions: 250 °C, 1h, water-EtOH ratio 50/50 (v/v), substrate (HL) concentration ~ 20% (w/v) and initial reaction system pressure ~ 2000 kPa)

HL	H <sub>2</sub> SO <sub>4</sub>	NaOH	H <sub>2</sub> O	EtOH	DHL yield	SR's yield	$M_w$	$M_n$	PDI
(g)	(g)	(g)	(mL)	(mL)	(wt.%)	(wt.%)	(g/mole)		
10	-	-	40.0	-	68.1±1.0	4.8±0.5	2030	223	9.1
10	-	-	20.0	20.0	70.5±0.5	9.8±0.2	1000	500	2.0
10	0.20	-	40.0	-	32.8±1.0	39.4±0.5	1110	236	4.7
10	0.20	-	20.0	20.0	75.2±0.2	1.8±0.3	1660	259	6.4
10	-	0.50	39.5	-	No depolymerization of HL was observed				

10	-	1.00	39.0	-	55.6±1.0	30.7±1.0	850	300	2.8
10	-	0.50	20.0	20.0	66.5±0.5	20.9±1.0	4710	325	14.5

### 6.3.2 Effects of alkaline catalyst on HL depolymerization

Surprisingly, when NaOH was employed as a catalyst at lower loading (0.5 wt.%, 2 wt.% and 5 wt.%), almost no depolymerization of HL was observed in water solvent. The reason could be on one side the slightly alkaline conditions would suppress the cellulose hydrolysis, and on the other side, the pH level is not high enough for catalyzing lignin hydrolytic degradation. As is well known, depolymerization of cellulose is readily liable to acid and lignin to alkali (Mészáros et al., 2004; Knill and Kennedy, 2003). Base-catalyzed liquefaction/depolymerization usually requires higher liquefaction temperatures (ca. 250 °C) to achieve liquefaction efficiencies comparable to those obtained with acid catalysts. Under weak alkaline conditions, the reaction medium can change gradually from alkaline to neutral or acidic. The carboxylic acids produced by lignin depolymerization reactions could neutralize the input base and the aqueous medium becomes neutral, thus retarding the de-polymerization process (Yin and Tan, 2012). Base catalyzed liquefaction processes although have the advantage of causing less corrosion to metal equipment used in the liquefaction process, when compared to acid catalyzed liquefaction, there are not much work was reported on base-catalyzed liquefaction of biomass (Hu et al., 2014). The composition of the alkali-catalyzed HL degradation products would be influenced by several reaction parameters, e.g. temperature and the nature and concentration of the alkali, etc.

Depolymerization of HL was also carried with increased loading of NaOH (10%, w/w, of the lignin substrate), and interestingly, efficient depolymerization of HL was realized, leading to 55.6 wt.% yield of DHL although accompanied with a high SR yield of ~30.7 wt.%. More interestingly, however, the  $M_w$  of the DHL obtained was very low (850 g/mole). The final pH of the DHL solution was 7.18 which proved that the reaction occurred under an alkaline condition rather than a neutral condition. Similar results were

observed by [Xu et al. \(2012\)](#) in liquefaction of southern pine sawdust, where SR yield was above 80 wt.% at 2.5 wt.% NaOH loading.

Although catalysts are important, the importance of liquefaction solvent cannot be ignored as it plays a paramount role in dissolving the product ([Hu et al., 2014](#)). In general, low molecular weight alcohols provide favorable permeability and fluidity at higher temperatures, which is beneficial for the conversion of lignocellulosic biomass ([Xu et al., 2012](#)). Also, [Cheng et al. \(2010\)](#) showed that water-ethanol mixture was a very effective solvent for the liquefaction of woody biomass. Therefore, depolymerization of HL was also carried out in water-ethanol co-solvent mixture with NaOH as a catalyst (5 wt.% of the HL substrate). The yield of the DHL was ~66.6 wt.% with ~21 wt.% yield of SR (as provided in Table 6-1). However, the  $M_w$  of DHL was very high ~4710 g/mole. The reason could be the unavoidable repolymerization/condensation due to acidic medium (at low NaOH loading) ([Yin et al., 2011](#)). [Bhaskar et al. \(2008\)](#) and [Karagöz et al. \(2006\)](#) studied alkaline hydrothermal conversion of different wood chips to bio-oil and found that bio-oil yield increased with increasing the alkalinity of the aqueous solution. Where, reduced bio-oil yield with decreasing alkalinity was also reported by other researchers ([Minowa et al., 1994](#)). Moreover, the initial alkalinity of the reaction medium may also affect the reaction pathways. The final pH values of less than 7 were reported after alkaline hydrothermal conversion of biomass. This indicates that alkaline hydrothermal conversion may involve not only alkaline pathways, but also acidic pathway under certain conditions. The decrease of pH during alkaline hydrothermal conversion was mainly caused by the formation of carboxylic acids from biomass such as lactic acid, acetic acid and formic acid, neutralizing the alkali compound loaded if weak alkaline solutions were used ([Yin et al., 2011](#)). When the amount of carboxylic acids in the products exceeded that of the input alkalis, the reaction media switched from being alkaline to acidic, promoting the condensation and repolymerization of the DHL products or intermediates, as evidenced by the very large  $M_w$  of DHL (~4710 g/mole).

### 6.3.3 Effects of acidic catalyst on HL depolymerization

The presence of cellulose in biomasses is a big barrier/bottleneck that needs to be tackled for lignin depolymerization (Zhou et al., 2011; Zhang, 2013). Acidic catalysts are well known to be more effective for hydrolysis of cellulose. Sulfuric acid ( $\text{H}_2\text{SO}_4$ ) has been the most frequently used catalyst due to its high catalytic activity combined with lower corrosion rates than other acids. Therefore  $\text{H}_2\text{SO}_4$  was used in the present study as well for hydrolytic depolymerization of HL. In fact, for most lignocellulosic biomass materials,  $\text{H}_2\text{SO}_4$  loadings of around 2-4 wt.% was believed to provide a good balance between high liquefaction efficiency and effective retardation of the detrimental recondensation reactions forming high  $M_w$  liquid products or char (Hu et al., 2014).

Depolymerization of HL was carried employing water alone as a solvent at 250 °C for 1 h under acidic conditions using 2 wt.%  $\text{H}_2\text{SO}_4$  based on the weight of HL substrate. The yield of DHL was ~32.8 wt.%, accompanied by a markedly increased SR yield of 39.36 wt.% (as shown in Table 6-1). The DHL yield is much lower when compared with that of HL depolymerization when employing water alone as a solvent under neutral condition, i.e., 68 wt.%. The  $M_w$  of DHL resulted from acidic depolymerization of HL employing water as a mono-solvent was ~1100 g/mole, much lower than that (2030 g/mole) of DHL obtained in the neutral medium (Table 6-1). The lower molecular weight could be attributed to the acid-catalyzed cleavage of alkyl-aryl ether linkages in lignin, as well as the acid-catalyzed breakage of the 1,4'- $\beta$ -glycosidic bonds in cellulose (Xu et al., 2012).

HL was also depolymerized employing water-ethanol mixture as a solvent with 2 wt.%  $\text{H}_2\text{SO}_4$  as a catalyst. The results, as given in Table 6-1, showed that the yield of DHL was increased to ~75.2 wt.% with the markedly low yield of SR (~1.83 wt.%). This result could be ascribed to the enhanced solubilization of depolymerized products of lignin in ethanol, and the catalyzed degradation of cellulose. This demonstrates that the type of solvent strongly determine the effects of a catalyst on biomass hydrothermal liquefaction (Lin et al., 2009). As expected, the acidic medium resulted in the slightly increased  $M_w$  of DHL to ~1660 g/mole, when compared with that (~ 1000 g/mole) from the un-catalyzed HL depolymerization in ethanol-water mixture.

Hence with respect to both yield and  $M_w$  of the DHL, the best conditions for the depolymerization of HL appeared to be achieved employing water-ethanol co-solvent mixture without any catalyst, leading to ~70.5 wt.% yield of DHL with  $M_w$  of ~1000 g/mole and ~9.83 wt.% yield of SR at 250 °C for 1 h with 20% (w/v) substrate (HL) concentration.

### 6.3.4 Characterization of the depolymerized HL products

#### 6.3.4.1 FTIR

The FTIR spectra of the original HL and DHL (at the best selected operational reaction condition) are shown in Figure 6-1. Both have typical broad hydroxyl group absorption between 3200-3550  $\text{cm}^{-1}$ , attributed to the combination and overlap of aliphatic and phenolic O-H stretching from the phenolic compounds as well as from the moisture inevitably contained in these samples (Cheng et al., 2010). The C-O absorption of aliphatic alcohols at 1000-1100  $\text{cm}^{-1}$  is weaker in the DHL than that in the original HL, suggesting reduced amount of aliphatic alcohols in the DHL. The intensities related to aromatics at 1400-1700  $\text{cm}^{-1}$  remain almost the same in all spectra, suggesting that the liquefaction processes did not vary the aromaticity significantly. The peaks between 1200 and 1300  $\text{cm}^{-1}$  were attributed to the stretching vibrations of C-O connecting to aromatic ring, or C-O of acids and esters stretching. It shall be noted that the DHL is a very complex mixture, and its aromatic structures could originated from both cellulose/hemicellulose through secondary reactions of carbohydrates and the phenolic structure from lignin (Cheng et al. 2010). From Cheng et al. (2010), no big difference in the FTIR spectra is expected for liquefied products produced using the different solvents i.e. water, ethanol (100%) or water-ethanol mixtures.

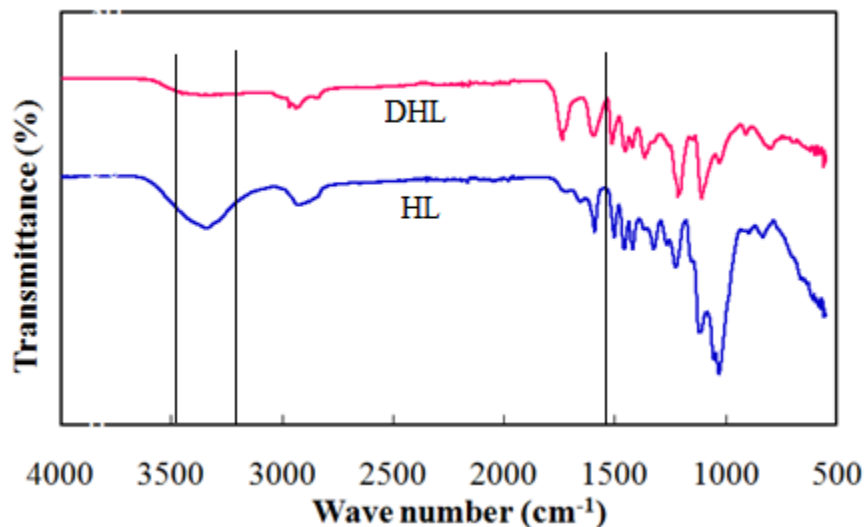


Figure 6-1 FTIR spectra of the original HL and the DHL obtained at the best operating conditions

#### 6.3.4.2 GC-MS

Table 6-2 presents the volatile compounds identified by GC-MS in the obtained DHL from the depolymerization of HL in water-ethanol mixture at 250 °C for 1 h with substrate (HL) concentration of 20% (w/v). The relative area percent of TIC (total ion current) for each compound and the total is shown in Table 6-2. It should be noted that the area percent values that are presented here show only the volatile portion of the DHL. As shown in the Table 6-2, the detectable compounds are mainly phenolic compounds, various types of esters and ethers, and substituted aldehydes such as benzaldehyde.

Table 6-2 GC-MS analysis of DHL obtained from HL depolymerization at the best operating conditions

Peak number	Retention time (min)	Relative composition by percent area	Compound name
1	-	- <sup>a</sup>	-
2	13.0615	17.1308	Phenol, 2,6-dimethoxy-



3	13.6532	5.0582	Undecanoic acid, 10-methyl-, methyl ester
4	14.3212	8.3642	Dodecanoic acid
5	14.5821	11.4956	Dodecanoic acid, ethyl ester
6	15.4091	6.606	Hydroquinone mono-trimethylsilyl ether
7	16.497	8.4224	2,4-Hexadienedioic acid, 3-methyl-4-propyl-, dimethyl ester
8	17.2668	5.0477	Tetradecanoic acid, ethyl ester
9	18.1639	5.6987	Phenol, 2,6-dimethoxy-4-(2-propenyl)-
10	18.3738	14.8142	Benzaldehyde, 4-hydroxy-3,5-dimethoxy-
11	19.748	7.0917	Hexadecanoic acid, ethyl ester
Total area (%)		89.73	

<sup>a</sup>: Not including the small peaks with an area less than 2% of the total area.

### 6.3.4.3 <sup>1</sup>H NMR

As most of the lignin applications are based on phenolic and aliphatic hydroxyl groups, quantitative <sup>1</sup>H NMR analysis was conducted to measure the hydroxyl number of DHL using its acetylated sample (the acetylation was performed to improve their solubility in *d*-chloroform). <sup>1</sup>H NMR spectra of the acetylated DHL produced at the best operating conditions (250 °C for 1 h with substrate concentration of 20% (w/v), employing water-ethanol mixture) is shown in Figure 6-2. <sup>1</sup>H NMR spectra of acetylated DHL showed strong signals at 1.6-2.1 ppm and 2.1-2.6 ppm for aliphatic acetates and phenolic acetates respectively. Aliphatic and phenolic acetate protons in the acetylated samples actually represent aliphatic and phenolic hydroxyls in the original samples prior to acetylation. Quantification of aliphatic and phenolic hydroxyls was made by peak integration in comparison of dibromomethane internal standard. The contents of aliphatic and phenolic hydroxyls in the lignin are presented by hydroxyl numbers as described in [Mahmood et al. \(2013\)](#). The results are given in Table 6-3. The produced DHL has an aliphatic hydroxyl number ~ 227.1 mgKOH/g (total hydroxyl number of ~442.0 mgKOH/g) which makes it suitable for the preparation of rigid PU foams. Also DHL showed phenolic hydroxyl number ~ 215 mgKOH/g, making DHL also a potential candidate for phenolic resins/foams and epoxy resins as well.

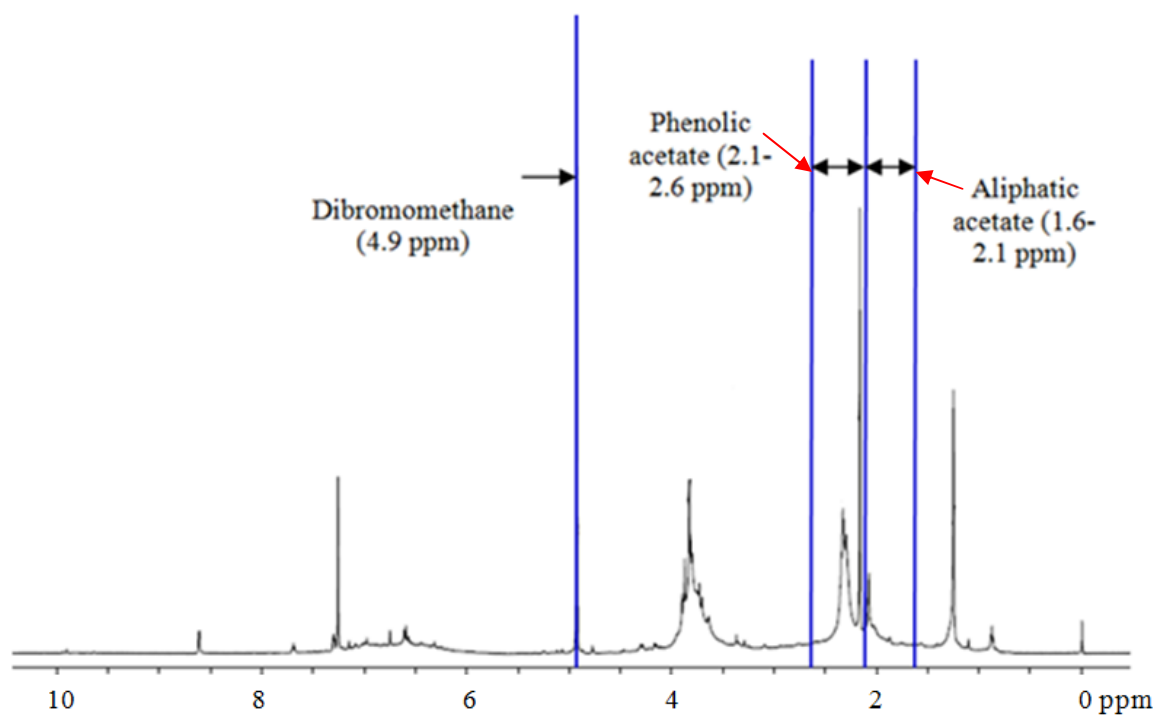


Figure 6-2  $^1\text{H}$  NMR spectra of acetylated DHL

Table 6-3 Relative signals of  $^1\text{H}$  NMR spectra signals of aliphatic/phenolic acetates in acetylated DHL and hydroxyl numbers of DHL

Internal standard (4.9 ppm)	Aliphatic acetate (1.6-2.1 ppm)	Phenolic acetate (2.1-2.5 ppm)	$\text{OH}_{\text{Aliphatic}}$ (mgKOH/g)	$\text{OH}_{\text{Phenolic}}$ (mgKOH/g)	$\text{OH}_{\text{Total}}$ (mgKOH/g)
1.0000	0.9033	0.8539	227.1	215.0	442.0

#### 6.3.4.4 Carbon balance and elemental analysis

Carbon balance was performed based on the elemental composition analysis for the DHL and SR samples obtained from the best operating condition, i.e., 250 °C for 1 h with 20% HL substrate concentration in water-ethanol 50/50 (v/v) mixture. It should be noted that,

in this work, the % carbon recovery in the gas phase was not included because of the negligibly low yield (<1%) of the gas products. The carbon recovery was calculated based on the C contents in the DHL and SR products and their C content. As shown in the Table 6-4, the calculated results showed that the carbon recovery for the test was ~86.5 wt.%, which is reasonable carbon balance considering the unavoidable errors in the experiments and products analysis and carbon loss in the products recovery. For example, the low-boiling point compounds formed from the HL depolymerization process was not recoverable as they would be lost in the rotary evaporation during DHL product recovery.

Table 6-4 Elemental analysis of HL and DHL (at 250 °C for 1h with 20% substrate concentration in water-ethanol mixture)

Sample	Elemental composition (% <sub>w</sub> , d.b) <sup>a</sup>				Carbon recovery (%)
	C	H	N	Others <sup>b</sup>	
HL	62.0	6.0	4.0	28.0	-
DHL	69.4	6.0	0.6	24.0	78.9
SR	47.0	6.1	0.0	46.9	7.6
Total					86.5

<sup>a</sup> Dry basis; <sup>b</sup> Determined by difference

## 6.4 Conclusions

Hydrolytic depolymerization of hydrolysis lignin (HL) was carried out with or without catalyst (H<sub>2</sub>SO<sub>4</sub> or NaOH) in water or water-ethanol mixture solvent at 250 °C for 1 h with 20% (w/v) HL substrate concentration. The results were compared in terms of DHL yield and *M<sub>w</sub>* and SR yield. The comparative results implied that HL depolymerization pathways might be different under different conditions (depending on the solvent and catalyst employed). In view of the utilization of DHL for the preparation of polyurethane foams/resins, depolymerization of HL in water-ethanol mixture without catalyst appeared to be the best route, producing ~70.5 wt.% yield of DHL which has a low *M<sub>w</sub>* (~1000 g/mole) and a suitable aliphatic (227.1 mgKOH/g) and phenolic (215 mgKOH/g)

hydroxyl numbers. The overall % carbon recovery for the test under the best operating conditions was approximately 87%.

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## Chapter 7

### 7 Valorization of hydrolysis lignin for polyols and its direct incorporation in rigid polyurethane foams

#### Abstract

The objectives of this study are to produce polyols through hydrothermal depolymerization of hydrolysis lignin (HL) –a by-product from pre-treatment processes in cellulosic ethanol plants, in 50/50 (v/v) water-ethanol mixture under N<sub>2</sub> atmosphere at 250 °C for 1h, and utilize the polyols in the preparation of rigid polyurethane (PU) foam. Bio-based PU (BPU) foam was prepared with 30% and 50% depolymerized HL (DHL) replacing PPG400 and sucrose polyols. The foam samples were analyzed in terms of their physical, mechanical and thermal characteristics for potential utilization as an insulation material. Foam samples prepared at 0%DHL from sucrose polyol were found to have lower density and thermal conductivity however; mechanical properties were inferior (1030 kPa) to the foam sample prepared from PPG400 & glycerol (compressive modulus ~9199 kPa). The replacement of sucrose polyol with DHL both at 30% and 50% replacement ratio improved foam sample's compressive modulus (~3313±25 kPa) and strengths (~216±31 kPa and 303±79 kPa at 10% and 20% deformations respectively) while maintaining lower thermal conductivities (0.036±0.001 W/mK). Substituting PPG400 with DHL in the foam however resulted in inferior mechanical properties and higher densities.

**Keywords:** Hydrolysis lignin, hydrothermal liquefaction, depolymerization, polyols, polyurethane foam.

## 7.1 Introduction

Polyurethane (PU) is an important polymer, and its annual market in North America is about 2.8 million tons (Yu et al., 2008). In the plastic industry, polyurethanes are one of the most useful polymers due to their versatile characteristics (Gu et al., 2013). Rigid polyurethane foams are mostly closed cell (more or less spherical in shape) foams and have glass transition temperature ( $T_g$ ) well above room utilization temperature (Haboya et al., 2011). Their excellent insulation combined with good adhesion, high strength-to-weight ratio and durability make them indispensable material in the construction industry. The most important commercial polyurethane products are foams commonly classified as either flexible or rigid depending on their mechanical performance and cross-link densities. Rigid polyurethane foams are widely used in building insulation and domestic appliances, due to their low density, superior insulation and mechanical properties.

Polyurethanes are copolymers containing blocks of low molecular weight polyesters or polyethers covalently bonded by a urethane group ( $-\text{NHCOO}-$ ). Depending on the chemical structure of polyols and isocyanates, as well as the isocyanate index and the foam density, the PU can be thermally stable in the range 200-300 °C (Verdolotti et al., 2013). Polyurethane foams (PUFs) account for the largest market among polymer foams, estimated at nearly two billion kilograms in the US alone (Piszczyk et al., 2012).

Currently, polyols such as polyethers and polyesters are mainly synthesized from petroleum resources (Andey et al., 2008). Due to the declining fossil resources and environmental issues, more attention has been paid on producing PUFs from bio-renewable raw materials (Tan et al., 2011). Depending on the formulation, the reaction between isocyanate and polyols can regulate the properties of the material. The foaming is possible due to the in-situ generation of a foaming agent ( $\text{CO}_2$ ) or the vaporization of pre-added low boiling point chemical during the exothermal polymerization reaction, leading to the gas trapped in the crosslinked cellular structures. Depending on the amount, proportions and characteristics of the components, it is possible to obtain foams with different densities and cellular structures, and thus adjustable properties (Antunes et al., 2011).

Lignin is the world's second most abundant plant polymer after cellulose, making up 25-40 % of dry mass of wood and agricultural residuals. About 50 million tons of Kraft lignin (KL) is generated annually as a by-product in the pulp industry (Borges da Silva et al., 2009). There could also be large quantities of hydrolysis lignin (HL) produced as a by-product of hydrolysis of cellulose, if the many proposed projects for cellulosic sugar-based chemicals or ethanol are realized. Different pulping processes produce different types of lignin with different chemical properties. HL is the solid residues from the enzymatic hydrolysis of woody biomass. It is composed mainly of lignin (55-57 wt.%), unreacted cellulose, and mono and oligosaccharides. HL has a very high molecular weight, which makes it insoluble in either water or any organic solvents.

Lignin is an amorphous macromolecule of three phenyl-propanols i.e., p-hydroxyl-phenyl propanol, guaiacyl-propanol and syringyl-propanol. These phenyl-propanols are linked mainly by condensed linkages (e.g., 5-5 and  $\beta$ -1 linkages), and more dominantly by ether linkages (e.g.,  $\beta$ -O-4 and  $\alpha$ -O-4) between the three main lignin building blocks. Therefore, lignin could be potential bio-polyol feedstock to substitute for petroleum-based polyols for the preparation of rigid panel insulation, however, the replacement ratio is generally less than 30% due to its low reactivity and low solubility in the reaction systems caused by its large molecular weight (Pan and Saddler, 2013; Li and Ragauskas, 2012). The macromolecule of lignin can decompose/degrade into oligomeric and monomeric phenolic compounds via thermochemical technologies (such as pyrolysis, hydrothermal liquefaction, and hydrolysis) and some biological processes. Hydrolysis or depolymerization of hydrolysis lignin results in the reduction of molecular weight and steric hindrance and makes the hydroxyl groups, especially aliphatic hydroxyl groups, more accessible for the further urethane synthesis reactions. In addition, these treatments lead to an increase in hydroxyl number (OH number) of the resulting products, which are the most important properties of any polyol.

The main goal of this work is to produce bio-polyols from HL with satisfactory  $M_w$ , yield and hydroxyl number to replace petroleum derived polyol (PPG400) and sucrose polyol (JEFFOL SD-361) for the preparation of rigid PU foam at high replacement ratios of 30% and 50%.

## 7.2 Experimental

### 7.2.1 Materials

The materials used in this study were hydrolysis lignin (HL) containing 55-57 wt.% lignin with the remainder being cellulose, carbohydrates and others. The HL was supplied by FPInnovations researchers (Yuan et al., 2012) who developed a patented fractionation process to produce sugars and HL from woody biomass. The other chemicals used were NaOH, acetone, pyridine, acetic anhydride, dibromomethane (DBM), ethanol, PPG400, glycerol, triethanolamine, triethylene diamine (TEDA), dibutyltin dilaurate, silicon oil, glycerol, etc. were all purchased from Sigma-Aldrich and used as received without further purification. Polymeric MDI and sucrose polyether polyol (JEFFOL SD-361) were kindly provided by Huntsman. Physical properties of chemicals are given in Table 7-1.

Table 7-1 Physical properties of the chemicals

Polyols	Functionality	Hydroxyl value (mgKOH/g)	Equivalent weight (g/mole)	Function
PPG 400	2	280.50	200.00	Petroleum polyol
Glycerol	3	1829.35	30.68	Petroleum polyol
JEFFOL SD-361	-	360.00	-	Sucrose polyol
Water	2	2000.00	-	Chemical blowing agent
Acetone	-	-	-	Physical blowing agent
Poly(siloxane ether)	-	-	-	Surfactant for cell structure stabilization
Triethylene diamine	-	-	-	Blowing catalyst
Dibutyltin dilaurate	-	-	-	Gelation catalyst
Triethanol amine	3	1128.11	-	Co-catalyst
PMDI	2.70	-	135.00	Isocyanate for foaming reaction

### 7.2.2 Hydrothermal depolymerization of HL

The hydrothermal liquefaction of HL was carried out in a 500 mL Parr stirred autoclave reactor. In a typical run, the reactor was charged with 60 g of HL and 300 mL of equi-volume (50/50) denatured ethanol-water co-solvent (i.e., substrate concentration ~ 20% (w/v)). The reactor was sealed, purged and subsequently pressurized to 2-3 MPa with N<sub>2</sub>. The reactor was heated up to 250 °C and then kept constant at this condition for one hour followed by immediate quenching with ice water to impede further reactions. The liquid product was completely rinsed from the reactor using acetone. Vacuum filtration was carried out to separate acetone soluble and insoluble (solid residues) products followed by vacuum rotary evaporation of the acetone soluble phase at 50 °C. The yield of liquefied HL (denoted as DHL) was 70±1wt.% and when free of solvent was in the form of a solid powder denoted as DHL/polyols. The liquefaction process also produced solid residues at a yield of 8 wt.%.

### 7.2.3 Rigid polyurethane foam (RPUF) sample preparation

RPUF samples with different formulations were prepared in 455 mL plastic cups through free rise one-shot foaming method at room temperature. In case of DHL based BPU foams, DHL was pre-dissolved in acetone before utilization in the foam preparation. A typical rigid PU foam formulation used a polyol (reference foam or partially replaced foams) combined with 7.5% (w/w) glycerol (a co-crosslinking agent in case of PPG400 based foams). The reference foams were prepared from PPG400 & glycerol and sucrose polyol at 0% DHL. Additionally the formulation includes a physical blowing agent (acetone at 20% (w/w)), a catalyst combination (mixture with equal amounts of dibutyltin diluarate and triethylene diamine at 2% (w/w)), surfactant at 2% (w/w) and water 2% (w/w). Blowing agents, catalysts and surfactant weight contents were determined with respect to total weight of polyols. PMDI was added at a NCO/OH ratio of 1.2 (fixed for all formulations). The polyols, surfactant agent, cross-linking agent, catalysts and chemical blowing agent were weighed in a cup and thoroughly mixed for 60 s. PMDI were then added to the mixture, and the mixture was stirred vigorously at 650 rpm for 12-15 s and the sample was allowed to rise. The sample was then left for 48 h in the fume hood for curing before being sampled for analysis. All the samples were conditioned at

$23 \pm 2$  °C and  $50 \pm 5\%$  relative humidity for more than 24 h prior to the test for density and mechanical analysis.

## 7.2.4 Analytical methods

### 7.2.4.1 Characterization of depolymerized HL and foams

The depolymerized HL (DHL) was analyzed by Fourier Transform Infrared Spectroscopy (FTIR) and its relative molecular weight was measured with a Waters Breeze GPC–HPLC (gel permeation chromatography–high performance liquid chromatography) instrument (1525 binary pump, UV detector at 270 nm; Waters Styrylgel HR1 column at a column temperature of 40 °C) using THF as the eluent at a flow rate of 1 ml/min with linear polystyrene standards for the molecular weight calibration curve. The hydroxyl number of DHL was determined using quantitative analysis of  $^1\text{H-NMR}$  spectra using dibromomethane as an internal standard.

Foam samples were also analyzed by FTIR. Apparent densities of the foam samples were determined according to ASTM D1622-08. Mechanical properties of PUF samples were measured at ambient conditions with INSTRON Universal Testing Machine (UTM). Compressive modulus and compressive strengths at 10% and 20% deformation were investigated by compressing foam in the foam rise direction according to ASTM D 1621-00. Glass transition temperature was determined using DSC (differential scanning calorimeter) under nitrogen flow (50-60 mL/min), heated at a heating rate of 10 °C/min from 40-250 °C. The water absorption of RPU foam samples was measured according to ASTM D 2842-01. Thermal conductivity of foam samples was measured using KD2 Pro Thermal properties analyzer with SH-1 dual needle.

## 7.3 Results and discussions

### 7.3.1 Depolymerized HL (DHL)

Hydrothermal depolymerization was used to depolymerize HL to low molecular weight products in this study, to reduce molecular weight and steric hindrance of the resulting

DHL for its use as a polyol in the preparation of rigid PU foam. Depolymerization also increases lignin's solubility in acetone which serves as a physical blowing agent. The main related characteristics of DHL as a polyol are given in Table 7-2.

Table 7-2 Characteristics of DHL

DHL's yield (wt.%)	SR yield (wt.%)	$M_w$ (g/mole)	Aliphatic hydroxyl number (mgKOH/g)	Total hydroxyl number (mgKOH/g)
70.5 ( $\pm 1$ )	8 $\pm$ 1.0	~1000	227.1	442

The FTIR spectra of the original HL and DHL are shown in Figure 7-1. They all had the typical broad hydroxyl group's absorption between 3200-3550  $\text{cm}^{-1}$ , attributed to the combination and overlap of aliphatic and aromatic O-H stretching from the phenolic compounds as well as from the moisture inevitably contained in these samples (Cheng et al., 2010). Figure 7-1 shows that the C-O absorption of aliphatic alcohol at 1060  $\text{cm}^{-1}$  is weaker in the DHL than that of the original HL, probably because of the reduced amount of cellulose and hemicelluloses in the DHL. The intensities related to aromatics at 1500-1600  $\text{cm}^{-1}$  remain almost the same in all spectra, suggesting that the liquefaction processes did not change lignin aromaticity. The absorption peaks between 1230  $\text{cm}^{-1}$  and 1260  $\text{cm}^{-1}$  are attributed to the C-O stretching connecting to aromatic ring.

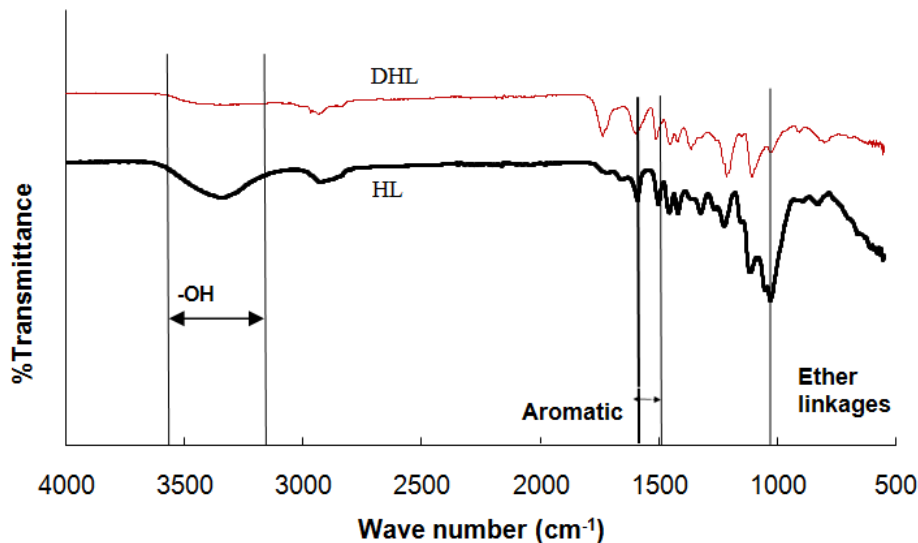


Figure 7-1 FTIR spectra of the HL (original) and depolymerized HL (DHL)

### 7.3.2 Rigid PU and BPU foams

The utilization of bio-based polyols to substitute for commercial polyols at different replacement ratios not only contributes towards overall mixed reactivity but also helps to provide more hard segments, which improves the rigidity of PU foam samples. PPG400, sucrose, and the DHL polyols provide aliphatic hydroxyl groups for urethane formation, where phenolic  $-OH$  groups of the DHL impart rigidity to the foam structure. PPG400 has linear chain structure whereas sucrose polyols have branched structure. Therefore, in this study both polyols were used to prepare PU and Bio-based PU (BPU) foams, and then the properties of the foams were evaluated against the ratios of their replacement with the DHL.

Figure 7-2 shows the FTIR spectra of the BPU foams with 50 wt.% replacement of PPG400 and sucrose polyol, respectively, by the DHL. In the spectra, residual or unreacted isocyanate group (NCO) can be identified at the band of  $2253.6\text{ cm}^{-1}$ . The inter N-H stretching which is in the PU hard segment region is identified at  $3454.53\text{ cm}^{-1}$ .  $1710\text{ cm}^{-1}$  (C=O stretching) and  $1408.84\text{ cm}^{-1}$  and  $1098.30\text{ cm}^{-1}$  (C-N coupled, C-O



stretch) indicates the existence of the urethane linkage (Cinelli et al., 2013; Nurdjannah et al., 2013).

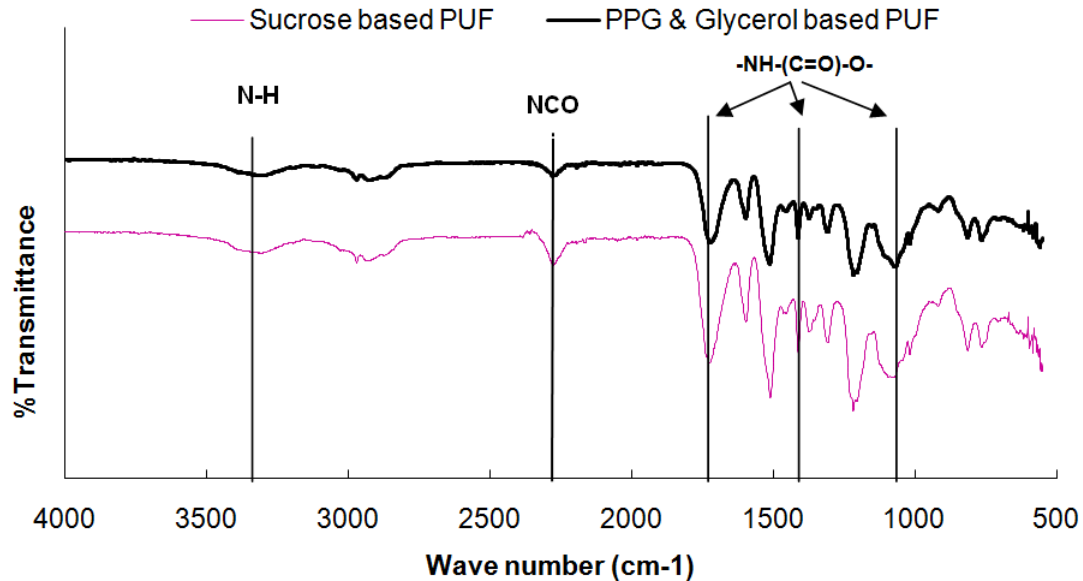


Figure 7-2 FTIR spectra of BPU foams with 50 wt.% replacement of PPG400 and sucrose polyol respectively by DHL

### 7.3.3 Rigid PU foam formulation using PPG400 and glycerol

Rigid PU foams were prepared from the DHL by replacing 30 wt.% and 50 wt.% of PPG400. A reference foam sample was prepared using pure PPG400 & glycerol at 0 wt.% DHL. The surface of foams prepared was very uniform with the DHL when compared with the reference foam. The cells of the foams appeared to be closed and the samples on curing did not shrink. The reference foam sample and foam prepared with 50% replacement of PPG400 are shown in Figure 7-3. The reference foam was found to be more rigid when compared to bio-based foams at different replacement ratios due to the lower hydroxyl number of DHL causing lower cross-link density.



Figure 7-3 PU foams with 100% PPG400 and glycerol (left) and bio-PU foams with 50% replacement of PPG400 with DHL (right)

The obtained foams were cured for at least 24 hours and then the samples were cut according to ASTM standards (ASTM D1622-08 and ASTM 1621-00) and analyzed for their physical and mechanical characteristics. Moreover, sample of the foams were vacuum dried overnight before DSC analysis to determine their glass transition temperatures. The characteristics of the obtained foams of PPG400 with 0-50 wt.% DHL are provided in Table 7-3. All the prepared foams either reference or BPU foams were rigid.

Table 7-3 Physical, mechanical and thermal characteristics of the PPG400 & glycerol-based PU foams

Sample ID	Density (kg/m <sup>3</sup> )	Young's modulus (kPa)	Comp. strength at 10% deformation (kPa)	Comp. strength at 20% deformation (kPa)	Max stress (kPa)	Water absorption (wt.%)	Dimensional stability on curing	Tg (°C)	K (W/mK)
PPG400	58.0	9199.0	521.0	576.0	596.0	0.12	Yes	ND <sup>1</sup>	0.045
DHL (30%)	55.6	181.0	160.3	153.7	158.3	0.15	Yes	138	0.038
DHL (50%)	99.0	110.0	90.2	93.0	97.0	0.20	Yes	146	0.039

<sup>1</sup>ND represents not determined. & K: Thermal conductivity

Table 7-3 shows that the density of reference foam was about  $58 \text{ kg/m}^3$ , and decreased a little to  $55.6 \text{ kg/m}^3$  when 30 wt.% of the PPG400 was replaced with DHL. This was probably because the addition of DHL made the cellular structure of the foam less uniform and formed larger cells (bubbles) which reduced the mass per unit volume of the foam and thereby the density. However, further increasing DHL content to 50% resulted in a higher density, likely because an excess of DHL affected the uniformity of the cells and the part of DHL may be assembled together as granules, which reduced the void volume and increased density. The results are in good agreement with Pan and Saddler's results (Pan and Saddler, 2013). They used Voranol 270 as a reference polyol and replaced it with lignin of  $M_w \sim 2400 \text{ g/mole}$  at ratios of lignin to polyol from 9-28 % (w/w). The density of pure polyurethane foam from Voranol 270 was about  $116 \text{ kg/m}^3$  and reduced to  $100 \text{ kg/m}^3$  and  $70 \text{ kg/m}^3$  with an increasing ratio of lignin in PU foam from 9% (w/w) to 19% (w/w) respectively. However, with further increasing ratio of lignin in PU foam to 28% (w/w) density increased to  $85 \text{ kg/m}^3$  which they suspect was due to non-uniform dispersion of lignin and granule formation.

It was also observed that the reference foam (with PPG400 & glycerol alone) has much higher compressive modulus and compressive strengths till 20% deformation of the foam sample when compared with the BPU foam samples which may be due to higher crosslinking density in the reference foam made from PPG400 & glycerol. The BPU foam sample at 50% replacement ratio has lower compressive strength than both the reference PU foam and the foam with 30% DHL replacement ratio. The reduced compressive strength at 50% replacement ratio could be due to the lesser accessibility of hydroxyl groups when compared to pure polyols which results in lower crosslinking density, or the introduction of DHL reduced the uniformity of the foam cellular structure, and the deficiency in cellular structure weakened the stability and strength of the foam structure (Pan and Saddler, 2013). The glass transition temperature of reference foam from PPG 400 & glycerol was not measured in this study however; it is measurable and is expected to be higher than  $100 \text{ }^\circ\text{C}$  (Cinelli et al., 2013). The flexible/soft segments impart flexibility to foam, responsible for a lower glass transition temperature. Molecular weight of the soft segment also affects glass transition temperature of the foam specimens. As

the soft segment molecular weight increased, it was observed that the glass transition temperature was narrowed and decreased to a lower temperature (Ósickey et al., 2002). As shown in Table 3, the glass transition temperature of 30% BPU foam has a slightly lower  $T_g$  (138 °C) than that of the 50% BPU ( $T_g = 146$  °C), implying that the former has more flexible segments as compared to the latter. Thermal conductivity of the BPU foams is lower (0.038-0.039 W/mK) than that of the reference foam (0.045 W/mK) and lies in the range needed for thermal insulating materials (BING, 2006).

### 7.3.4 RPUF formulation using sucrose polyol

Sucrose polyol, a commercial polyol, was also selected for the preparation of rigid PU foams. Since, sucrose polyols have a higher hydroxyl number than PPG400 with multiple short chain structure it was expected that the sucrose-based foams have sufficient crosslinking densities to provide stable foam structure especially in terms of the foams' mechanical properties. The physical, mechanical and thermal characteristics of the sucrose polyol-based BPU foams with 30 wt.% and 50 wt.% polyol replacement, along with the reference foam sample (using sucrose polyol only), are compared in Table 7-4. Pictures of the PU foams with 100% sucrose polyol and the bio-PU foams with 50 wt.% replacement of sucrose polyol with DHL are illustrated in Figure 7-4. All the prepared foam samples were rigid.

Table 7-4 Physical, mechanical and thermal characteristics of the sucrose polyol-based PU foams

Sample ID	Density (kg/m <sup>3</sup> )	Young's modulus (kPa)	Comp. strength at 10% deformation (kPa)	Comp. strength at 20% deformation (kPa)	Max stress (kPa)	Water absorption (wt.%)	Dimensional stability on curing	Tg (°C)	K (W/mK)
Sucrose polyol	30.1	1030.0	85.0	90.0	101.1	0.99	Yes	ND <sub>1</sub>	0.044
DHL	35.4	3338.0	185.0	224.0	388.0	0.29	Yes	178	0.035

(30%)									
DHL (50%)	65.1	3288.0	247.0	382.0	388	-	Yes	189	0.037

<sup>1</sup>ND represents not determined.

*K: Thermal conductivity*

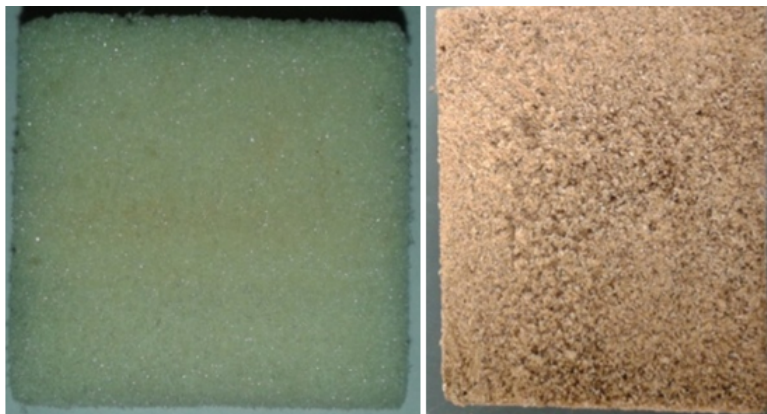


Figure 7-4 Pictures of the PU foams with 100% sucrose polyol (left) and the bio-PU foams with 50 wt.% replacement of sucrose polyol with DHL (right)

Table 7-4, shows that the density of reference foam is about  $30.1 \text{ kg/m}^3$ , and the foam density increases with increasing replacement of sucrose polyol with DHL from 30 wt.% to 50 wt.%. The density of the foam is  $35.4 \text{ kg/m}^3$  and  $65.1 \text{ kg/m}^3$  for the 30% BPU foam and the 50% BPU foam, respectively. The higher density may be due to lesser void volume which leads to higher density of the resulting foams. As shown in Table 7-4, compressive strengths of the BPU foams at both 30% and 50% replacement ratios are higher than that of the reference foam. The reason could be the multiple short chain structure of sucrose polyol, leading to a lower crosslinking density and strength of the resulting foam. However, the introduction of DHL into the foam structure enhanced crosslinking may lead to higher mechanical strengths than the reference foam.

Unlike the PPG400 & glycerol-based PU foams (as shown in Table 7-3), the water absorption capacity of the sucrose polyol-based foam samples containing the DHL in structure was less than that the reference foam, because the DHL containing foams have higher density, therefore less free volume. As is well known, the PU insulating materials are largely characterized by their moisture resistance ability. Insulating materials made of rigid PU foams do not absorb moisture from the air due to their closed cell structure. However, for PU foams, moisture absorption at 2-7wt.% by volume was reported (Bing, 2006). Glass transition temperature of the 30% sucrose polyol replaced BPU foam was as high as 178 °C and increased to 189 °C with the increasing replacement ratio to 50%. Thermal conductivity of the BPU foams prepared by the replacement of sucrose polyols was found to be slightly lower (0.035-0.037 W/mK), nearer to the thermal conductivity values of commercial foams (Bing, 2006), than that of the reference foam (0.044 W/mK) and PPG400 replaced foams, making them a good option for their utilization as potential insulation materials.

Comparing the results presented in Tables 7-3 and 7-4, one can observe that the BPU foams prepared by replacing sucrose polyols with the DHL have superior mechanical characteristics than those prepared by replacing PPG400 with the DHL at the same replacement ratio. This result could be attributed to the presence of multifunctional short chain branched structure in sucrose polyol and the enhanced chemical crosslinking between sucrose polyol and MDI by the low  $M_w$  DHL with suitable aliphatic and phenolic -OH groups. Also the density and thermal conductivity of foams samples prepared by the replacement of sucrose polyol were lower than PPG400 replaced foams.

## 7.4 Conclusions

Hydrolysis lignin (HL) was efficiently depolymerized via hydrothermal depolymerization in 50% ethanol-water medium at 250 °C for 1h. The produced liquefied hydrolysis lignin (DHL) becomes soluble in acetone and tetrahydrofuran (THF) which makes it possible to

be employed as a renewable bio-polyol for the preparation of rigid polyurethane (PU) foams. The DHL has weighted-average molecular weight ( $M_w$ ) of  $\sim 1000$  g/mole and a hydroxyl number of  $\sim 227.1$  mgKOH/g, suitable for application as a polyol for the preparation of PU foams.

In this work DHL was employed to substitute petroleum-based polyol (PPG400 & glycerol) or sucrose polyol for the preparation of rigid polyurethane foams at two different replacement ratios (30 wt.% and 50 wt.%), and the prepared foams were characterized in terms of their physical, mechanical and thermal properties for potential utilization as an insulation material. It was observed on comparing the reference foams that at 0% DHL, sucrose polyol derived foams have lower density and thermal conductivity than PPG400 & glycerol derived foams however, mechanical properties were inferior (compressive modulus  $\sim 1030$  kPa) to foam sample prepared from PPG400 & glycerol (compressive modulus  $\sim 9199$  kPa). The replacement of sucrose polyol with DHL both at 30% and 50% replacement ratio improved foam sample's compressive modulus and strengths while maintaining lower thermal conductivities and density of foam samples. On the other hand, replacement of PPG400 with DHL led to inferior mechanical characteristics of the foam and increased densities.

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## Chapter 8

### 8 Hydrolytic depolymerization of hydrolysis lignin for the preparation of bio-based rigid polyurethane foam: Effects of process parameters

#### Abstract

Hydrolysis lignin (HL) was successfully depolymerized employing 50/50 (v/v) water-ethanol mixture to low weight-average molecular weight ( $M_w$ ) depolymerized HL (DHL) of moderately high hydroxyl number and yield. The DHL was then used in the preparation of rigid polyurethane foam (RPUF) at high bio-content loading (50-70 wt.%). The effects of process parameters including reaction temperature, reaction time and HL concentration on the depolymerization of HL in water-ethanol mixture were investigated. The obtained depolymerized HLs (DHLs) were characterized with GPC-UV, FTIR and  $^1\text{H}$  NMR. The best operating conditions appeared to be at 250 °C, 1 h with 20% (w/v) HL concentration, leading to ~70 wt.% yield of DHL ( $M_w \approx 1000$  g/mole and total hydroxyl number  $\approx 442$  mgKOH/g) and solid residues ~8 wt.%. The DHL, although in solid form, had a suitable hydroxyl number, and was further derivatized into a liquid polyol via oxypropylation to produce a polyol feedstock for the preparation of bio-based rigid polyurethane (BRPU) foams with 50-70 wt.% bio-contents. All BRPU foams were characterized and compared in terms of their physical, mechanical and thermal properties. All BRPU foams exhibit good compression strengths, compared with the reference foam and at a fixed formulation recipe showed the following sequence for increasing compression modulus: sucrose polyol reference foam (2695.0 kPa) <DHL50PO50 (9202.0 kPa) <DHL60PO40 (19847.0 kPa) <DHL70PO30 (21288.0 kPa). For all BRPU foams, the thermal conductivity was low ( $0.030 \pm 0.001$  W/mK) and did not vary much with increased bio-contents, making them suitable for use as an insulation material. The BRPU foams were thermally stable up to approximately 200 °C.

**Key words:** Hydrolysis lignin, depolymerization, oxypropylation, polyols, rigid polyurethane foam.

## 8.1 Introduction

Polyurethanes (PUs) are a broad class of polymers having urethane (-NH-(C=O)-O-) moieties as a main linkage. They are known for their versatility, but one of the problems related to the production of PU nowadays is their dependence on petroleum-derived products (Cinelli et al., 2013). Since petroleum reserves are depleting and their prices are increasing, there had been increasing interest in exploring alternative renewable resources for the preparation of polyols (polymers having multiple hydroxyl groups in their structure) and PUs. Foam materials represent the most important commercial products made of PUs and are commonly classified as flexible, semi-rigid and rigid, depending on cell morphology (closed or open), mechanical characteristics and densities. Among foamed polymers used commercially, rigid polyurethane (RPU) foams have the lowest thermal conductivity (Kacperski and Spychaj, 1999). RPU foams have been widely utilized in appliances and the construction industry because of their excellent and unique combination of thermal insulation and mechanical properties. PU foams are available in a wide range of densities from approximately 30-200 kg/m<sup>3</sup> (Demharter, 1998). However, for use as thermal insulation in buildings the required density of RPU foam lies in the range of 30 kg/m<sup>3</sup> to 45 kg/m<sup>3</sup> (BASF, 2010).

In recent years effective utilization of biomass resources has gained growing attention (Cheng et al., 2010) as an alternative feedstock for bio-chemicals and bio-materials. The major advantages in utilizing biomass include: (1) biomass is renewable and available essentially for all countries in the world, (2) biomass contains negligible sulfur and other detrimental elements, and (3) biomass can be regarded as a carbon-neutral resource as the utilization of biomass does not result in a net increase in the CO<sub>2</sub> concentration in the atmosphere (Tymchyshyn and Xu, 2010). Therefore, biomass is a promising alternative source for polyols production. Lignocellulosic biomass consists of three major components: cellulose, hemicelluloses and lignin. Cellulose comprises the largest fraction of the biomass ranging from 30-50% of the total (MacLellan, 2010). Polysaccharides, i.e., cellulose and different hemicelluloses, are the primary constituents of wood and wood pulps. Cellulose is a homo-polymer of D-glucose units, joined by  $\beta$ -(1-4) glycosidic linkages, whereas the hemicelluloses are heteroglycans containing several different types

of neutral (pentose and hexose) and acidic (uronic acid) monosaccharides as structural elements. Enzymatic hydrolysis of woods and pulps is an already established approach for the degradation of wood fibers. Delignification or acid pre-hydrolysis may be required in order for the enzymes to access the degradable cellulosic components in wood. During enzymatic hydrolysis the polysaccharides in the woody biomass are broken down by the enzymes and the reaction is not hindered by the presence of lignin or lipophilic extractives as long as the enzymes can come into contact with the polysaccharides. This results in the removal of most of the lignin and extractives from the fibers and enhances the swelling and porosity of the fibers. Consequently, the cellulose and hemicelluloses in chemical pulps can be effectively hydrolyzed to their monosaccharide components by enzymes. If enzymatic hydrolysis is performed without pretreatment, then some lignin remains in the hydrolyzed samples (Dahlman et al., 2000; Santos et al., 2012). The solid residues left after enzymatic hydrolysis of wood are known as hydrolysis lignin (HL) or hydrolyzed wood biomass and are composed of unreacted cellulose, mono and oligosaccharides, and lignin, with lignin comprising 50 to 55% (Yuan et al., 2012) of the mass. Conventionally lignin is utilized for producing heat via direct combustion. However, lignin can be a promising source of phenols, aromatics and polyols. Lignin is a natural, aromatic complex biopolymer of three phenyl-propanols, i.e., *p*-hydroxyl-phenyl propanol, guaiacyl-propanol and syringyl-propanol (Tejado et al., 2007). The phenyl-propanols are linked mainly by two types of linkages: condensed linkages (e.g., 5-5 and  $\beta$ -1 linkages) and ether linkages (e.g.,  $\alpha$ -O-4 and  $\beta$ -O-4) (Chakar and Ragauskas, 2004). The ether linkages are reactive and, under proper reaction conditions, can be more easily cleaved than the more stable C-C bonds.

The present paper focuses on the use of hydrolysis lignin (HL) – a by-product from pretreatment processes in cellulosic ethanol plants, for the preparation of polyols and their utilization in the preparation of RPU foams. In order to overcome the low reactivity of lignin, which comprises the largest fraction of HL, and to further increase the ratio of lignin/biomass substitution, an effective and promising approach may be the direct hydrothermal depolymerization of HL. Typical direct liquefaction processes include fast pyrolysis and solvolytic liquefaction. Solvolytic liquefaction is more advantageous than fast pyrolysis because it can be carried out in an organic solvents such as alcohols at

much lower temperatures (<300 °C) (Xu and Etcheverry 2003). Liquefaction processes dissociate the lignin and carbohydrates and partially cleave the primary and secondary ether bonds in both lignin and high molecular weight carbohydrates (cellulose and hemicellulose) into lower molecular compounds. As a result, the solid lignocellulosic biomass is converted into a liquid OH-rich product which can potentially be used as a substitute for polyester or polyether polyol in the preparation of PU foams (Bhunja et al., 1999). The process and products can be environmentally friendly as well (Breslin, 1993).

In the literature, a number of studies have been reported for the hydrothermal depolymerization/ liquefaction of different biomasses employing water as a solvent (Qian et al., 2007; Sun et al., 2010; Minowa et al., 1998; Xu and Lad, 2008) and their utilization for PU foams preparation (Maldas et al., 1996). However, the yields of desired products were low, between 25-60 %. Higher yields were obtained using organic solvents or water/solvent mixtures. Cheng et al. (2010) reported that ethanol-water mixture (50/50, v/v) proved to be more effective solvent for the liquefaction of biomass as they showed synergistic effects on the direct depolymerization/liquefaction of biomass. They carried out direct liquefaction of white pine saw dust in a 50 wt.% ethanol-water medium and achieved approximately 66 wt.% bio-oil yield after 15 min reaction at 300 °C ( $M_w \approx 1373$  g/mole) and used the resulting bio-oil as a substitute for phenol in the production of PF adhesive resins. Inspired by the above research work, the present work is attempted to depolymerize/liquefy HL using a water-ethanol co-solvent to obtain depolymerized HL (DHL) for the utilization in the preparation of PU foams.

The major objectives of this work are; (1) depolymerization of HL employing a water-ethanol co-solvent and investigating the effects of process parameters (reaction temperature, time and HL concentration) to find the best operating conditions; (2) oxypropylation of the DHL obtained at the best operating conditions; and (3) the preparation and characterization of BRPU foams at high percentages of bio-contents (50 wt.% - 70 wt.%). To the author's best knowledge, no systematic study of the successful depolymerization of HL and its effective utilization for the preparation of RPU foams at high percentage of bio-contents has been reported in the literature.

## 8.2 Materials and methods

### 8.2.1 Materials

The hydrolysis lignin (HL) used in this study was provided by FPIInnovations (Yuan et al., 2012) and was insoluble in conventional organic solvents. Lignocellulosic biomass from any type of plant biomass that is composed of cellulose, hemicellulose and lignin, typically in amounts of 30-55 wt.%, cellulose; 15-35 wt.%, hemicellulose; and 5-31 wt.%, lignin, was used. The novel bio-conversion process outlined by Yuan et al. (2012) comprises of low- pressure mechanical refining to disintegrate biomass feedstock, hemicellulose extraction, enzymatic hydrolysis, sugar/lignin separation, and fermentation. After hemicellulose extraction and a subsequent hydrolysis, the remaining substrate (solid) residue contains a high percentage of lignin which was being recovered and further purified to produce high-quality lignin products. Compared to traditional Kraft lignin and steam-explosion lignin, the high-quality sulfur free lignin produced from this invention has little degradation. The original HL was neutral. The chemical components of the raw hydrolysis lignin as well as its elemental compositions are presented in Table 8-1. The other chemicals used in the study were NaOH, acetone, pyridine, acetic anhydride, HCl, dibromomethane, ethanol, polymeric MDI, sucrose polyol (JEFFOL SD-361), triethanolamine, triethylene diamine (TEDA), stannous octoate, silicon oil, glycerol etc., All were reagent grade, purchased from Sigma-Aldrich, used as supplied.

Table 8-1 Chemical and elemental composition (d.a.f) of hydrolysis lignin (HL) (Yuan et al., 2012)

Component	Mass fraction (%)
Lignin %	56.7
Carbohydrates %	29.8
Ash %	1.2
Others, %	12.3
Carbon, %	62.8
Hydrogen, %	6.1

Nitrogen, %	4.0
Others, %	28.3

### 8.2.2 Depolymerization of hydrolysis lignin

The depolymerization of HL was carried out in a 500 mL stainless-steel autoclave reactor equipped with a stirrer and a water-cooling coil. In a typical run, the reactor was loaded with 60 g of HL and 300 mL of denatured ethanol-water (50/50 v/v) co-solvent. The reactor was sealed, purged and was subsequently pressurized to 2 MPa with nitrogen to prevent the reactive material from boiling over the course of the heating process. The reactor was ramped up to the reaction temperature at 10 °C/min and kept at the desired temperature for 60 min before cooling. Once the reactor had cooled to room temperature, the negligible gaseous products were vented into the fume hood. The liquid products and solid residue (SR) were rinsed from the reactor with acetone, and the resulting suspension was filtered under vacuum through a pre-weighed Whatman No. 5 filter paper. The SR products and filter paper were dried at 105 °C for 24 h before weighing. The organic solvents in the filtrate were then removed by rotary evaporation under vacuum at 40-50 °C. The yields of DHL and SR were calculated as the mass fraction of each product relative to the mass of the HL loaded into the reactor. Since the focus of this research was the DHL and due to the difficulty in analysis of the aqueous soluble products (a complex mixture of carboxylic acids, aldehydes, etc.); the aqueous products were not analyzed. For simplicity, the yield of Gas+Aq including pyrolytic water from the biomass was calculated by mass difference. Each experiment was performed twice or thrice to reduce the experimental error to  $\pm 5\%$ . Error bars have been reported based on the variation of result around their average values.

### 8.2.3 Oxypropylation of DHL

The DHL obtained at the best operating conditions, although in solid form, was used as a bio-polyol in this work after being further transformed into a liquid polyol by oxypropylation. The oxypropylated lignin polyol was then employed as a feedstock for the preparation of PU foam. Oxypropylation of DHL was carried out in a 100 mL Parr



reactor. In a typical run, 18.9 g of DHL, 21.21 g propylene oxide (PO), 2.31 g of anhydrous glycerol & KOH (%KOH in mixture was 11 wt.%) and 16.8 g of acetone. After all the ingredients were loaded, the reactor (under atmospheric pressure) was heated up to 150° C. Initially, pressure in the reactor increased to a maximum of 150 psig and then decreased to the original pressure ~14.7 psig (or 1.0 atm-g) after 2 h reaction, implying complete consumption of PO or completion of the reaction. After cooling the system to room temperature, the reactor contents were completely rinsed into a beaker using acetone followed by neutralization of the reaction mixture using sulfuric acid. The neutralized reaction mixture was then filtered through a Buchner funnel to separate the solid residues from the acetone soluble phase. The acetone soluble filtrate was transferred to a pre-weighed flask and the remove acetone and unreacted PO (if any) were removed by rotary evaporation at 60 °C.

#### 8.2.4 Rigid polyurethane (PU) foam preparation

All of the foam samples were prepared in 455 mL plastic cups using a one pot method. Typically, the rigid PU foam formulation in this study includes a polyol combined with 10% (w/w) glycerol (a co-crosslinking agent). The formulation also includes a physical blowing agent (acetone at 20% (w/w)), catalyst comprised of equal amounts of stannous octoate and triethylene diamine at 2% (w/w), surfactant at 2% (w/w) and water at 2% (w/w). For comparison, a reference foam was prepared using sucrose polyols at 0% DHL. The amounts of the blowing agent, catalyst, surfactant and water were determined with respect to the total weight of polyol used. PMDI was added at a NCO/OH ratio of 1:1. The foam preparation procedure used was comprised of the following steps: (1) the polyols, catalysts and blowing agents were all weighed into a cup and mixed at 550 rpm for 10-12 s to obtain a homogeneous mixture and (2) a predetermined mass of PMDI was then added to the cup and the mixture was stirred vigorously for another 12-15s. The mixture was then placed on a level surface in a fume hood and the foam was allowed to rise at ambient temperature (23±2 °C). All of the foam samples were left in the fume hood for 24-48 h for curing before the sample was collected for analysis. Foam shrinkage, structural uniformity, stability and cell appearance could be observed at this point. However, the foam samples were conditioned for a minimum of 24 h to a

maximum of 1 week prior to further characterization, , depending on requirements. In the synthesis of bio-based RPU (BRPU) foams at different bio-contents, sucrose polyol was not used and glycerol was kept at 10 wt.% based on the total weight of polyols used.

### 8.2.5 Product characterization

The relative molecular weights of the depolymerized HL (DHL) and oxypropylated DHL were measured with a Waters Breeze GPC–HPLC (gel permeation chromatography–high performance liquid chromatography) instrument (1525 binary pump, UV detector at 270 nm; Waters Styrylgel HR1 column at a column temperature of 40 °C) using tetrahydrofuran (THF) as the eluent at a flow rate of 1 mL/min using linear polystyrene standards. The functional groups of the HL, DHL and oxypropylated DHLs were analyzed by Fourier Transform Infrared Spectroscopy (FTIR). Proton nuclear magnetic resonance ( $^1\text{H-NMR}$ ) spectra for the DHL and oxypropylated DHLs were acquired at 25°C using a Varian Inova 600 NMR spectrometer equipped with a Varian 5 mm triple-resonance indirect-detection H<sub>13</sub>CX probe. A total of 16-32 scans were accumulated using a 2 s recycle delay, 3.6 s acquisition time, a 45-degree tip angle (pw = 4.8 us), and a spectral width from -2 ppm to 14 ppm (sw = 9000.9 Hz). Quantitative  $^1\text{H-NMR}$  analysis was realized using acetylated samples of DHL and oxypropylated DHL. Briefly, 1 g of dried sample was dissolved in a 1:1 (v/v) mixture of pyridine (5 mL) and acetic anhydride (5 mL) followed by stirring for 24 to 48 hr. The mixture was then transferred into a beaker containing 100 mL of ice-cooled 1 wt.% HCl solution. The resulting precipitates of the acetylated samples were washed with distilled water to pH  $\approx$ 7. The samples were then dried at 105 °C for 24 hr to remove residual water prior to the quantitative  $^1\text{H-NMR}$  analysis. Dibromomethane ( $\text{CH}_2\text{Br}_2$ ) was used as an internal standard with a characteristic peak is at 4.9 ppm. The hydroxyl number of the DHL and oxypropylated DHL were determined by  $^1\text{H-NMR}$ . The samples were prepared dissolving 30.0 mg of the acetylated DHL or oxypropylated DHL and 15.0 mg of the internal standard in *d*-chloroform ( $\approx$ 1000-1500 mg) then transferring the sample into a 5 mm NMR tube via a transfer pipette for analysis. Hydroxyl numbers of the oxypropylated DHL samples were also measured as per ASTM D4274-99 using a Potentiometric

Titration (Titroline 7000 Titrator). The viscosity of the oxypropylated DHL sample was measured by using BROOKFIELD CAP 2000+VISCOMETER at 80 °C.

The apparent densities of foam samples were measured according to ASTM D1622-03. The mechanical properties of PUF samples were measured at ambient conditions on an ADMET Universal Testing Machine (Model SM-1000-38). Modulus of elasticity (Young's modulus or compressive modulus) (initial linear slope of the stress-strain curve) and compressive strength at 10% deformation, were determined by performing the stress-strain tests according to ASTM D 1621-00. Thermal conductivities of the foam samples were measured using a KD2 PRO thermal properties analyzer with SH-1 dual needle sensor (1.3 mm diameter x 3 cm long, 6 mm spacing) capable of measuring thermal conductivity in the range of 0.02 to 2.00 W/mK. The specimen size used for thermal conductivity analysis was 40 mm x 40 mm x 20 mm. Thermal stability and thermal decomposition of the foams were measured using a *Pyris<sup>TM</sup>* Diamond, Perkin–Elmer Thermogravimetric analyzer (TGA), under a N<sub>2</sub> and air flow (20 mL/min) respectively, from 30 °C to 800 °C at 10 °C/min. The glass transition temperature ( $T_g$ ) of the foam samples was determined using a DSC (differential scanning calorimeter: Mettler Toledo DSC 1) under a N<sub>2</sub> flow (50-60 mL/min) where the sample was heated at a heating rate of 10 °C/min from 50-350 °C. Morphology of the foams was observed by a Hitachi S-4500 field emission cross beam scanning electron microscope (SEM). After examination by SEM, selected locations on the foam surface were subjected to a cross-sectional cut and the sample was coated with osmium, and imaged using a focused ion beam LEO (Zeiss, Thornwood, NY, USA) 1540XB SEM.

## 8.3 Results and discussions

### 8.3.1 Depolymerization of HL: Effects of process parameters

#### 8.3.1.1 Effects of reaction temperature

Temperature is the most critical parameter for the liquefaction/depolymerization of lignocellulosic materials in a water/organic solvent. When biomass was heated in hot compressed water, solvolysis of hemicellulose and lignin begins to occur at temperature >190 °C, and all of the hemicellulose and much of the lignin is dissolved in

the water at 220 °C (Mok and Antal, Jr., 1992; Xu et al., 2008). The effects of reaction temperature (from 150 °C to 300 °C) on the depolymerization of HL employing a 50/50 (v/v) water-ethanol mixture are illustrated in Figure 8-1. As seen in the Figure 8-1, and similar to the results observed by Cheng et al., (2010), increasing the reaction temperature from 150 °C to 250 °C increased yield of DHL from ~56 wt.% to ~70 wt.%, indicating the acceleration of depolymerization/liquefaction. However, contrary to the findings of Cheng et al., (2010), increasing the reaction temperature to 300 °C did not further increase the yield of desired product. Rather, the DHL yield decreases to ~66 wt.%. The difference could be due to the difference in composition of HL as compared to white pine saw dust. The yield of solid residues (SR) was found to decrease steadily from ~28 wt.% to ~3 wt.% with increasing reaction temperature.

Increasing reaction temperature (from 150 °C to 250 °C) resulted in a decrease in the  $M_w$  of the DHL (from  $\approx 1440$  g/mole to  $\approx 1000$  g/mole. respectively). This decrease can be attributed to the increased availability of energy necessary to cleave the ether linkages present. Further increase in temperature to 300 °C, resulted in increased  $M_w$ . This increase may be due to increased repolymerization/condensation reactions at higher temperature. Depolymerization and repolymerization reaction occur concurrently during liquefaction. Initially, at lower temperature, depolymerization reactions predominate and lead to the formation of lower  $M_w$  products (Wang and Chen, 2007). However, as temperature increases, repolymerization/condensation reactions are gradually enhanced due to the increased concentration of intermediate products in the reaction system which may lead to increases  $M_w$ . The yield of SRs did not increase at 300 °C, indicating the absence of cross-linking reactions. The yield of gas was very low, therefore, for simplicity, Gas+Aq phase were combined as a single entity and their value was reported by difference. Aqueous (Aq) phase may comprise water produced during glycosidic linkage cleavage, glucose, xylose, aldehydes, acids and other monomers resulting from the complete hydrolysis of polysaccharides etc. The formation of gas during depolymerization reaction is due to the cleavage of the aliphatic propane chain and removal of ring substituents (Gosselink et al., 2012). Given these results, the best reaction temperature for the depolymerization of HL in water-ethanol co-solvent mixture with respect to both yield and  $M_w$  of the DHL products, appeared to be 250 °C.

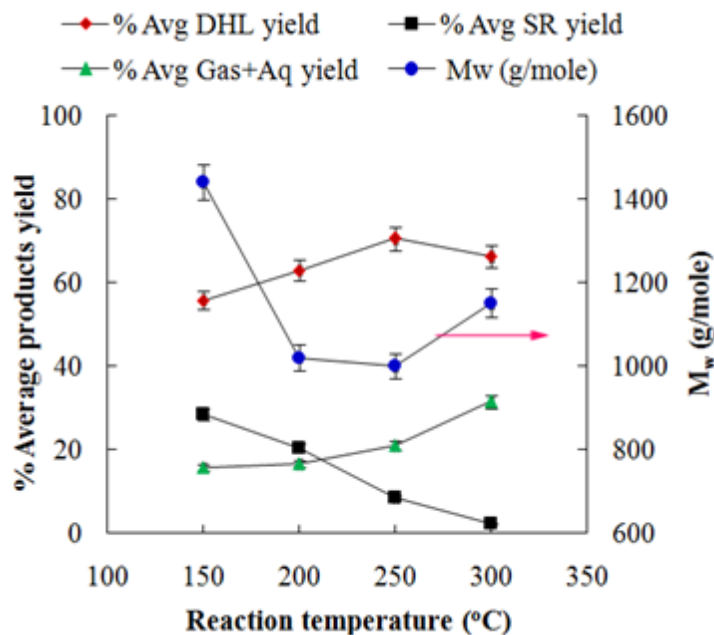


Figure 8-1 Effects of reaction temperature on yield and  $M_w$  of DHL from HL depolymerization (Other reaction conditions: 60 min, 20% (w/v) substrate concentration, EtOH/water ratio of 1.0 and initial-system pressure: 2.0MPa)

### 8.3.1.2 Effects of reaction time

The experiments in this section were carried to examine the effects of reaction time on hydrolytic depolymerization of HL at 250 °C in (50/50, v/v) water-ethanol reaction mixture. The product (DHL and SR) yields and the  $M_w$  of DHL obtained from HL depolymerization after various reaction times (30-120 min) are illustrated in Figure 8-2. At 250 °C, increasing the reaction time from 30 min to 60 min increased the yield of DHL from ~60 wt.% to ~70 wt.% and was accompanied by a decrease in SR (from ~15.5 wt.% to ~8 wt.%). Further increasing the reaction time to 120 min resulted in the lower yield of DHL (~57 wt.%) accompanied by an increase in SR (~16.0 wt.%). The increased SR indicates pronounced cross-linking reactions between the reaction intermediates. There was almost no change in the  $M_w$  of the DHL between 30 min and 60 min. However, prolonged reaction time resulted in a very slight increase in  $M_w$ , from 1000 g/mole to

1100 g/mole, which may be due to repolymerization/condensation reactions at 250°C. Thus, based on the yield and  $M_w$  of the DHL, 60 min appears to be the optimum reaction time.

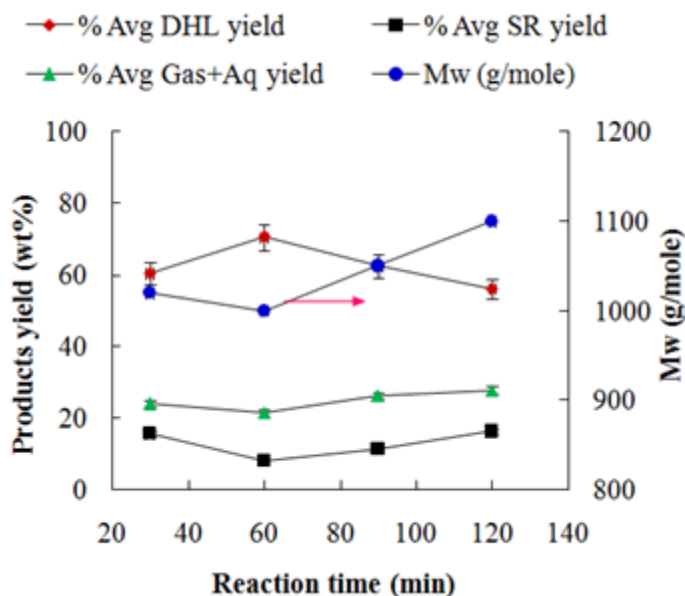


Figure 8-2 Effects of reaction time on yield and  $M_w$  of DHL (Other reaction conditions: 250 °C, substrate concentration ~20% (w/v), and initial system pressure: 2MPa)

### 8.3.1.3 Effects of HL substrate concentration

Feedstock concentration is another important parameter in the hydrothermal liquefaction of biomass, as higher feedstock concentrations improve the economics of overall process (Pye, 1990). The effects of solvent to biomass ratio (HL substrate concentration) were investigated by conducting depolymerization runs for 60 min at 250 °C using water-EtOH mixture. The product (DHL and SR) yields and the  $M_w$  of DHL for different substrate concentrations (5% (w/v) to 30% (w/v)) are illustrated in Figure 8-3. From Figure 8-3, it can be clearly seen that with the increase in HL concentration from 5% (w/v) to 20% (w/v) the yield of DHL increased from ~54 wt.% to ~70 wt.% and then decreased to ~46 wt.% with a further increase in HL concentration to 30% (w/v). The opposite trend was observed for SR yield. The yield of SR decreased as HL concentration was increased to 20% (w/v) but then increased as the HL concentration increased further. This increase

may be due to insufficient solvent to keep the reaction system homogeneous at higher concentrations. This situation would favor the occurrence of pronounced condensation and crosslinking reactions of intermediate products. The  $M_w$  of the DHL was found to increase significantly from 850 g/mole to 2250 g/mole as the HL concentration increased from 5% (w/v) to 30% (w/v). This could also be due to the promotion of repolymerization/condensation reactions. Figure 8-3 suggests that in order to obtain low  $M_w$  DHL products, lower HL concentrations ( $\leq 20\%$  (w/v)) are preferred. However, for process efficiency and economics, it is always better to utilize as high a substrate concentration as possible. Although, lower substrate concentrations result in lower  $M_w$ , the product yields are also lower which would significantly increase the number of runs required to obtain a given amount of DHL product, thus increasing costs. Therefore, keeping both DHL product yield and  $M_w$  in mind, a 20% (w/v) substrate concentration was selected for further runs.

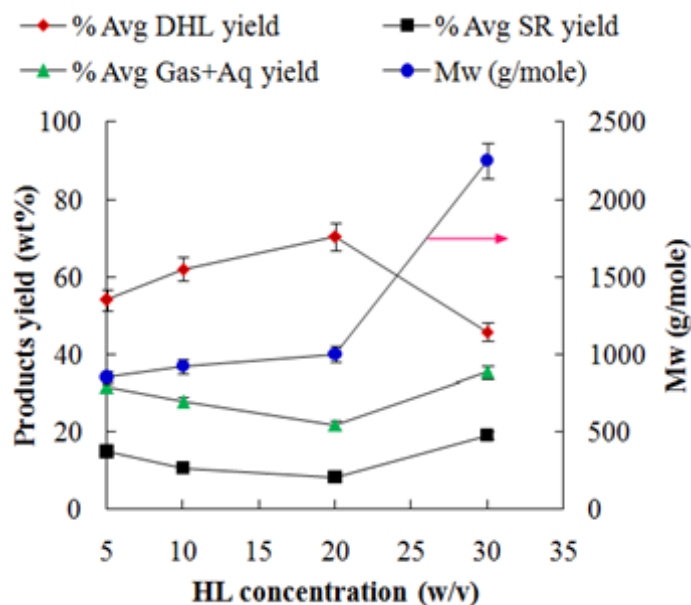


Figure 8-3 Effects of HL concentration (w/v) on yield and  $M_w$  of DHL (Other reaction conditions: 250 °C, 60 min, and initial system pressure: 2MPa)

Hence, with respect to both yield and  $M_w$  of the DHL product, the best operating conditions appear to be liquefaction at 250 °C, for 1 h with a 20% (w/v) HL

concentration, leading to ~70 wt.% yield of DHL ( $M_w \approx 1000$  g/mole and total hydroxyl number ~442 mgKOH/g) with a SR yield ~8 wt.%.

### 8.3.2 Oxypropylation of DHL

DHL obtained at the best operating conditions (250 °C, 1 h, 20% (w/v) HL concentration in water-ethanol mixture (50/50, v/v)) was used for further experimentation. To obtain a large sample of DHL, a 16 L reactor was used and the products were characterized in terms of  $M_w$ , hydroxyl number and yields. The results were found similar to the ones obtained using the 100 mL reactor. Oxypropylation of DHL was carried at three levels of bio-contents i.e., 50 wt.%, 60 wt.% and 70 wt.%. Oxypropylated samples were analyzed in terms of their  $M_w$ , hydroxyl number and viscosity (Table 8-2). These samples were then further used for the preparation of RPU foams.

Table 8-2 Characteristics of DHL and oxypropylated samples

Sample ID	$M_w$ ≈ (g/mole)	Total Hydroxyl number (mgKOH/g)	Viscosity at 80 °C (Pa.s)	State
DHL	1000	442.0	-	Solid powder
DHL50PO50	1730	221.4	0.39	Viscous Liquid
DHL60PO40	1270	235.8	0.48	
DHL70PO30	1220	253.7	0.64	

FTIR spectra of sucrose polyol, original HL and DHL at the best reaction conditions along with oxypropylated DHLs at different bio-contents contents are shown in Figure 8-4. The spectra are normalized to the intensity of the lignin aromatic ring vibration at 1600  $\text{cm}^{-1}$ . In all of the spectra, the O-H stretching vibration at ~3450  $\text{cm}^{-1}$  is easily seen (Li and J. Ragauskas, 2012). The oxypropylation and grafting of PO onto the lignin is evidenced by the following FTIR observations: (a) an increase in the bands at 2971-2870  $\text{cm}^{-1}$  attributed to the stretching of  $\text{CH}_3$ ,  $\text{CH}_2$  and  $\text{CH}$  aliphatic groups; (b) reduction in the intensity of the carbonyl peak at 1714  $\text{cm}^{-1}$ ; (c) a marked increase of the absorption bands in the ether C-O stretching region (1000-1100  $\text{cm}^{-1}$ ); and (d) an increase in the band at 1371  $\text{cm}^{-1}$  confirming the introduction of  $\text{CH}_3$  groups (Cateto et al., 2009).



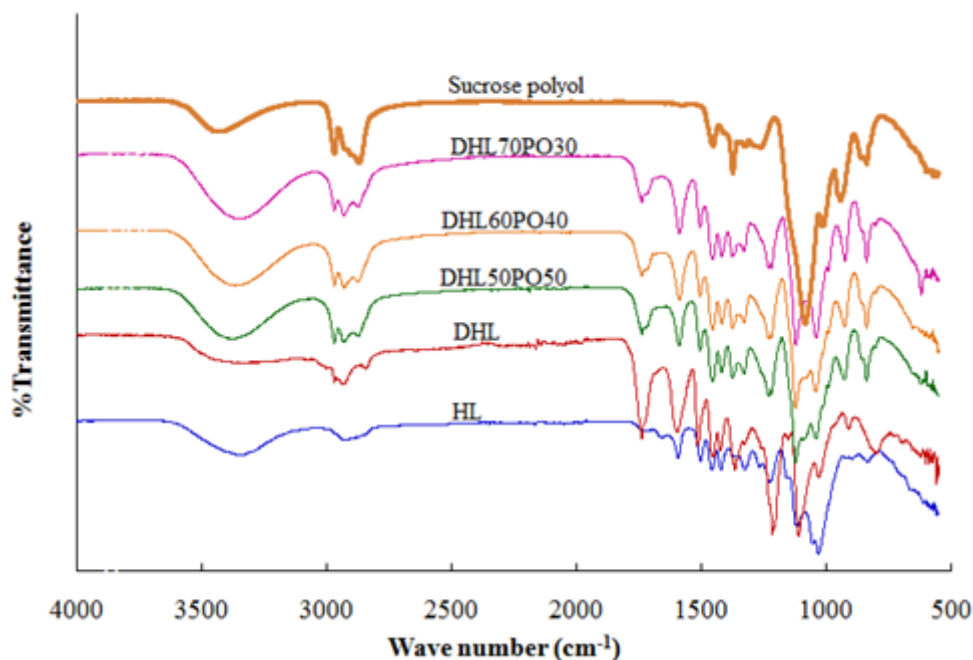
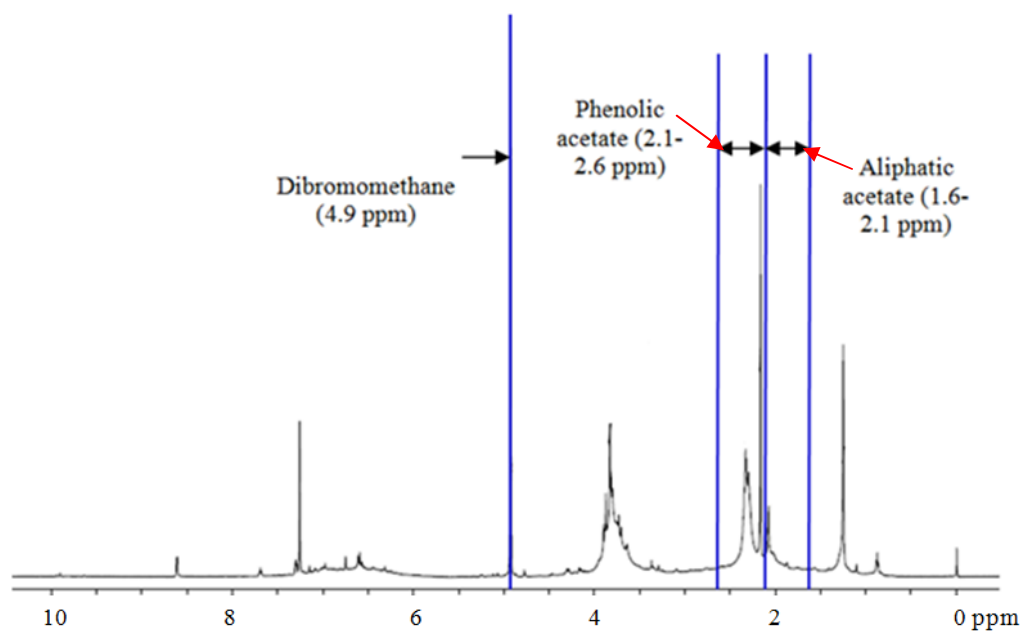
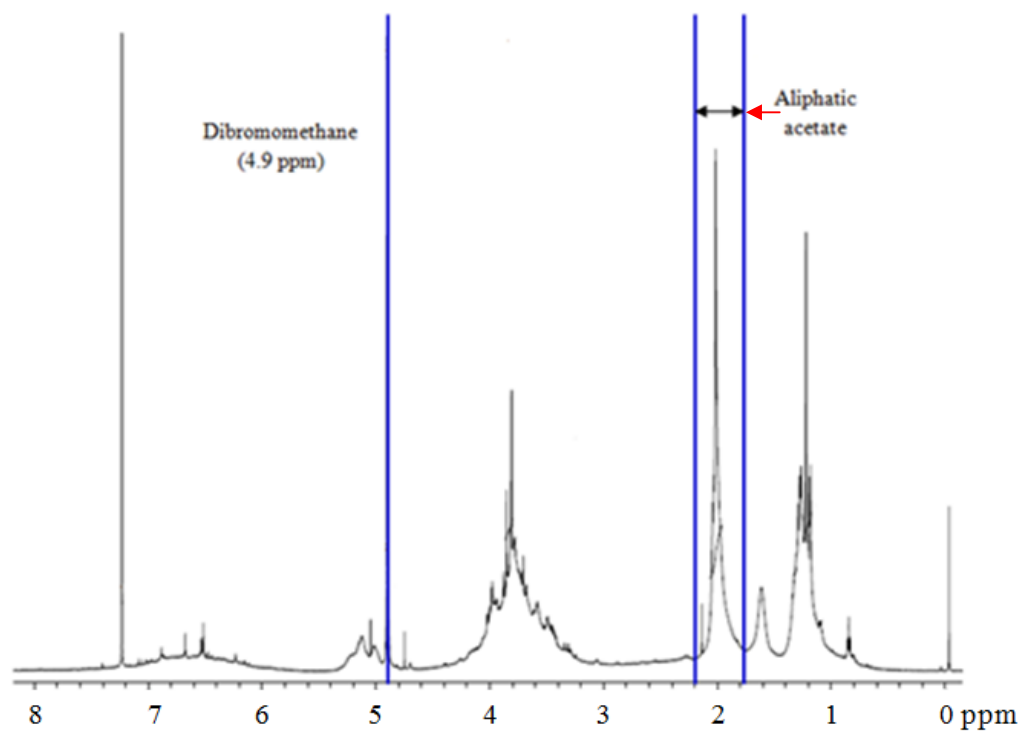


Figure 8-4 FTIR analysis of sucrose polyol, HL, DHL and oxypropylated DHLs

To clearly view the difference in DHL structure before and after oxypropylation, quantitative analysis of  $^1\text{H}$  NMR spectra of acetylated DHL samples was conducted. Acetylation of samples was carried to improve their solubility in *d*- Chloroform. The signals associated with internal standard (Dibromomethane) are shown at 4.9 ppm. The signals associated with aliphatic and phenolic acetates are seen at 1.6-2.05 ppm and 2.1-2.6 ppm, respectively. The aliphatic and phenolic acetate protons actually represent aliphatic and phenolic hydroxyls after acetylation.  $^1\text{H}$  NMR spectrum of acetylated DHL is shown in Figure 8-5, where its oxypropylated samples are shown in Figure 8-6 and 8-7 representing acetylated samples of DHL50PO50 and DHL70PO30, respectively. It can be seen that after oxypropylation there were no phenolic groups left (Figure 8-6 and Figure 8-7) when compared to DHL (Figure 8-5) which has both aliphatic and phenolic groups. The reason is that oxypropylation resulted in the transformation of the phenolic groups into aliphatic groups, a chain extension reaction.

Figure 8-5  $^1\text{H}$  NMR spectra of acetylated DHLFigure 8-6  $^1\text{H}$  NMR spectra of acetylated DHL50PO50

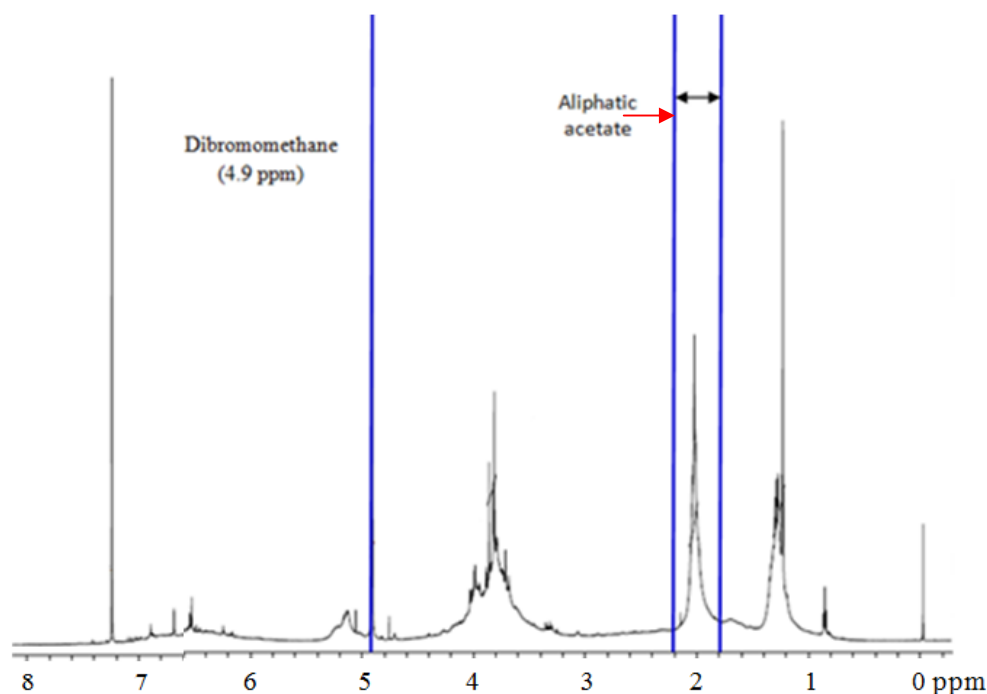


Figure 8-7  $^1\text{H}$  NMR spectra of acetylated DHL70PO30

### 8.3.3 Rigid polyurethane foam (RPUF) from oxypropylated DHL

Polyurethane synthesis is essentially the formation of urethane linkages  $[-\text{NH}-(\text{C}=\text{O})-\text{O}-]$  by the reaction of polyols ( $-\text{OH}$ ) and isocyanates ( $-\text{NCO}$ ). However, linkages other than urethane bonds, such as allophanate bonds, which can arise from the reaction of excess diisocyanates with urethane groups, may also form. Moreover, isocyanate dimerization and trimerization reactions can also occur (Li and Ragauskas, 2012). Density is reported as the main property of RPU foams as it also affects mechanical properties of foam (Thirumal et al., 2008). Therefore, in this study BRPU foams were prepared with polyols containing 50-70 wt.% of oxypropylated DHL via two approaches; (1) under fixed percentage of physical blowing agent (20% (w/w)); and (2) under varying percentages of physical blowing agent (20-26% (w/w)) to keep the final density approximately the same.

The density of BRPU foams prepared with polyols containing 50-70 wt.% oxypropylated DHL with a fixed percentage of physical blowing agent (20% (w/w)) increased with

increasing bio-content (Table 8-3). Consequently, the compressive strength of BRPU foams was also found to increase. The reason for this trend could be that DHL70PO30 has a structure containing multiple short chains when compared to DHL50PO50, which may leads to enhanced chemical cross-linking between the polyol and MDI by low  $M_w$  oxypropylated DHL, and, therefore, more highly cross-linked, denser foam with increased compressive modulus and strength was obtained. When BRPU foams were prepared with polyols containing 50 wt.% - 70 wt.% bio-contents and efforts were made to keep the final density of foam approximately the same to compare mechanical characteristics directly, more physical blowing agents was introduced in the foam's formulations. The results are also shown in Table 8-3. It was a tedious task to control the foam density exactly; however, for the sake of comparison average foam density varied between 38.5-44.7 kg/m<sup>3</sup>. It can be seen from Table 8-3, that the density of the foams slightly decreased with increasing percentage of DHL in oxypropylated sample, which is mostly related to their morphological characteristics (larger and fewer cells) due to the increased amount of physical blowing agent. The SEM images of DHL50PO50, DHL60PO40 and DHL70PO30 at varying percentages of physical blowing agent are shown in Figure 8-8. It can be seen from Figure 8-8 that for BRPU foam prepared at 50 wt.% bio-contents average cell size was ~115  $\mu\text{m}$ . However; increasing bio-content percentage to 60 wt.% to 70 wt.% (and the associated increase in physical blowing agent) resulted in an increase in average cell size to ~418  $\mu\text{m}$  to ~876  $\mu\text{m}$ , respectively. Increased cell size means fewer cells, enclosing larger voids form within a given volume leading to decreased foam density and, consequently, decreased Young's modulus and strength. Thus, foam morphology has a greater direct effect on foam strength than density.

Table 8-3 Physical, mechanical and thermal properties of reference and BRPU foams

Foam ID	Density (kg/m <sup>3</sup> )	Compressive Modulus (kPa)	Compressive strength at 10% deformation (kPa)
Sucrose reference foam	42.5±0.5	2695.0±100.0	182.0±45.0
At fixed percentage of physical blowing agent (20%, w/w)			

DHL50PO50	44.7( $\pm 2$ )	9202.0 $\pm 100.0$	385.0 $\pm 25.0$
DHL60PO40	61.0( $\pm 2$ )	19847.0 $\pm 75.0$	1088.0 $\pm 30.0$
DHL70PO30	64.5( $\pm 1$ )	21288.0 $\pm 50.0$	1151.0 $\pm 20.0$
At varying percentages of physical blowing agent (20% - 26%, w/w)			
DHL50PO50	44.7( $\pm 2$ )	9202.0 $\pm 100.0$	385.0 $\pm 25.0$
DHL60PO40	40.0( $\pm 2$ )	2315.0 $\pm 120.0$	181.0 $\pm 35.0$
DHL70PO30	38.5( $\pm 2$ )	1651.0 $\pm 85.0$	120.0 $\pm 47.0$



Figure 8-8 BRPU foams from DHL50PO50 (left) and DHL60PO40 (right)

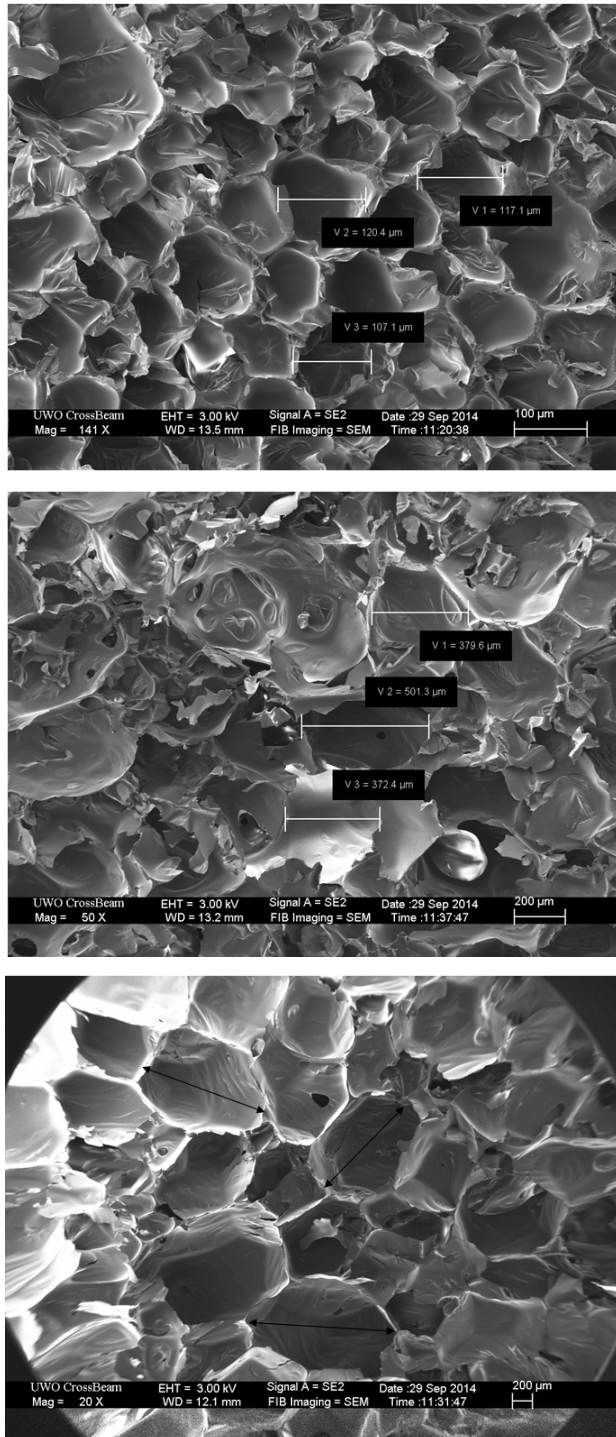


Figure 8-9 SEM images of DHL50PO50 (top), DHL60PO40 (middle) and DHL70PO30 (bottom) at varying percentages of physical blowing agent

Table 8-4 Thermal characteristics of RPUF from oxypropylated samples

Foam ID	Density (kg/m <sup>3</sup> )	Glass transition temperature (°C)	Thermal conductivity (W/m-K)
At fixed percentage of physical blowing agent (20%, w/w)			
DHL50PO50	44.7(±2)	282(±2)	0.029(±0.0010)
DHL60PO40	61.0(±2)	293(±2)	0.030(±0.0010)
DHL70PO30	64.5(±1)	310(±2)	0.030(±0.0010)
At varying percentages of physical blowing agent (20% - 26%, w/w)			
DHL50PO50	44.7(±2)	282(±2)	0.029(±0.0010)
DHL60PO40	40.0(±2)	-	0.032(±0.0010)
DHL70PO30	38.5(±2)	-	0.034(±0.0010)

The glass transition temperature ( $T_g$ ) of the BRPU foams, as shown in Table 8-4, was found to increase with increased bio-contents. This could be attributed to the increased aromatic contents in foam formulation which could lead to a greater number of rigid/hard segments and a consequent increase in  $T_g$  of the associated BRPU foams. Thermal conductivity is the key thermal property that governs insulation applications for RPU foam. Thermal conductivity is closely related to cell morphology. Low thermal conductivity results from small average cell size and high closed cell contents. In this work, as shown in Table 8-4, the thermal conductivity of the BRPU foams was found to vary between 0.029 and 0.034 W/mK at 50-70 wt.% bio-content respectively, which is satisfactory taking into account that the density of the foams is towards the higher limits of common polyurethane construction foams (thermal conductivities between 0.020 and 0.030 W/mK for densities ranging from 30-100 kg/m<sup>3</sup>) (Ribeiro da Silva, 2013). Also some of the specifications available on rigid polyurethane foam report that thermal conductivity of most common insulation materials ranges between 0.02 W/mK and 0.05 W/mK (BING, 2006).

Figure 8-10 shows the FTIR spectra of rigid PU foams prepared from oxypropylated DHL at 50, 60 and 70 wt.% bio-contents. In the spectra, residual or unreacted isocyanate group (NCO) can be identified at the band of  $2253.6\text{ cm}^{-1}$ . The inter N-H stretching which is in the PU hard segment region is identified at  $3454.53\text{ cm}^{-1}$ .  $1710\text{ cm}^{-1}$  (C=O stretching) and  $1408.84\text{ cm}^{-1}$  and  $1098.30\text{ cm}^{-1}$  (C-N coupled, C-O stretch) indicates the existence of the urethane linkage (Cinelli et al., 2013; Nurdjannah et al., 2013; Ribeiro da Silva et al., 2013). Other characteristic bands, the N-H deformation signal at  $1519\text{ cm}^{-1}$  of isocyanurate (resulting from reactions between isocyanate and urethane groups), conjugated and unconjugated C-O stretching at  $1216$  and  $1064\text{ cm}^{-1}$  and CH deformation of aromatic groups in the range of  $800\text{-}600\text{ cm}^{-1}$  are also noted in the spectrums (Ribeiro da Silva et al., 2013).

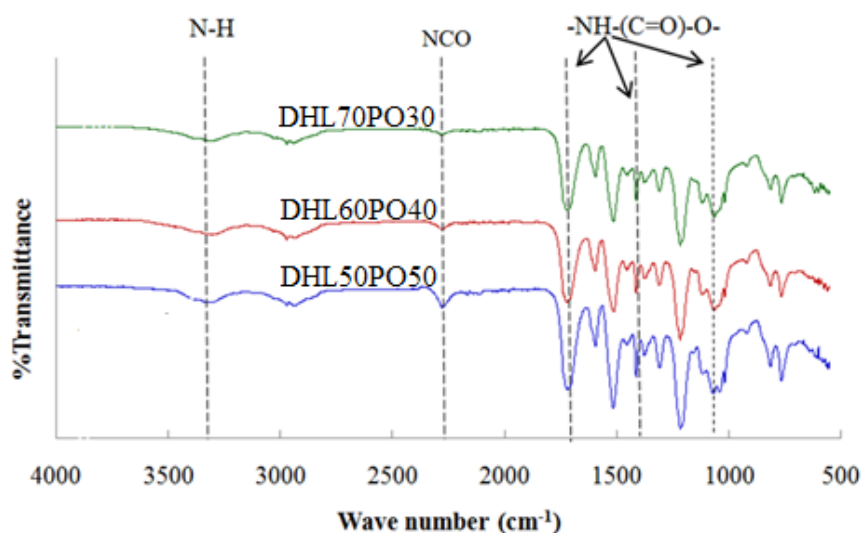


Figure 8-10 FTIR analysis of BRPU foams prepared from oxypropylated samples of DHL at three different percentages of bio-contents

Thermogravimetric analysis was performed to investigate the effect of oxypropylated-DHL incorporation on the thermal behavior of BRPU foam under inert atmosphere. Figure 8-11 shows the thermal stability curve of BRPU foam containing 50 wt.% bio-contents compared to the a reference foam. Thermal degradation of BRPUs is a



complicated process involving the dissociation of the initial polyol and isocyanate components. Thermal decomposition can lead to the formation of amines, small transition components, and carbon dioxide (Zhao et al., 2012). The mass loss up to 150 °C is considered to be due to the evaporation of water. Pyrolysis of PU foam under nitrogen atmosphere starts at ~170 °C and intensified at ~200 °C. Significant decomposition of RPU occurred between 200-450 °C. The decomposition of polyurethane polymer chain, around 350 °C produces compounds including diisocyanates and polyols along with other decomposition products such as amines, olefins and carbon dioxide (Manocha et al., 2010).

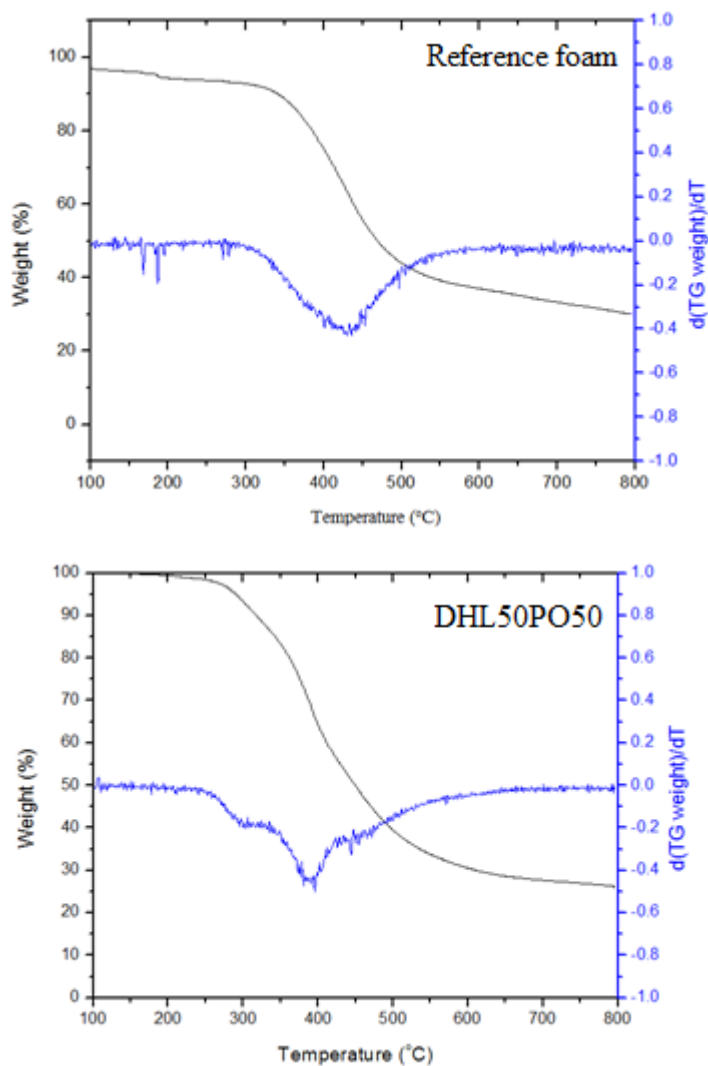


Figure 8-11 Degradation curve and the rate of weight loss of reference foam and BRPU foams containing 50 wt.% bio-contents

## 8.4 Conclusions

Hydrolysis lignin (HL) was successfully depolymerized to low molecular weight depolymerized HL (DHL) in a 50/50 (v/v) water-ethanol reaction mixture. Under the best operating conditions (250 °C, 1h, 20% (w/v)) HL depolymerization produced DHL at a yield of ~70 wt.% with a weight-average molecular weight ( $M_w$ ) as low as ~1000 g/mole and high aliphatic and total hydroxyl numbers (227.1 mgKOH/g and 442.0 mgKOH/g,

respectively). The resulting DHL was solid and derivatized into a liquid polyol via oxypropylation for further utilization in the preparation of bio-based rigid polyurethane (BRPU) foam at high bio-contents (50-70 wt.%). All of the BRPU foams exhibited good compressive strength, compared with the reference foam. At a fixed formulation, i.e. a fixed amount of physical blowing agent, the compressive modulus of the BRPU foams increased in the following order: sucrose polyol reference foam (2695.0 kPa)<DHL50PO50 (9202.0 kPa)<DHL60PO40 (19847.0 kPa)<DHL70PO30 (21288.0 kPa). All of the BRPU foams were thermally stable up to approximately 200 °C. The thermal conductivities of the BRPU foams varied between 0.029 W/mK and 0.034 W/mK, making them suitable for their utilization as an insulation material.

## 8.5 References

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## Chapter 9

### 9 Low pressure depolymerization of hydrolysis lignin for the preparation of bio-based rigid polyurethane foam

#### Abstract

Hydrolysis lignin (HL) was successfully depolymerized to low molecular weight (1400-2000 g/mole) depolymerized HL (DHL) via a highly efficient and cost effective low-pressure (<150 psig) process employing ethylene glycol (EG) as a solvent and H<sub>2</sub>SO<sub>4</sub> as a catalyst. The effects of process parameters including reaction temperature, reaction time, HL loading and acid loading were investigated and the DHLs obtained were characterized by GPC-UV, FTIR and <sup>1</sup>H NMR. The best operating conditions appeared to be at 200 °C, 1 h, HL substrate concentration of 20 wt.%, and H<sub>2</sub>SO<sub>4</sub> ~2 wt.% of input HL, leading to ~70 wt.% yield of DHL (*M<sub>w</sub>* ~1500 g/mole and total-hydroxyl number ~247.1 mgKOH/g) and solid residues ~10 wt.%. The obtained DHL was in solid or powdered form and derivatized into a liquid polyol via oxypropylation at three different bio-contents ratios, i.e. 50, 60 and 70 wt.%. BRPU foams prepared from oxypropylated DHLs were then characterized and compared in terms of their physical, mechanical and thermal properties. All BRPU foams exhibited good compressive strength, compared with to the reference foam. At a fixed formulation, i.e. a fixed percentage of physical blowing agent, the BRPU foams showed the following order of sequence in terms of their compression modulus: sucrose polyol reference foam (2695.0 kPa)<DHL50PO50 (5381.0 kPa)<DHL60PO40 (12360.0 kPa). All BRPU foams were thermally stable up to approximately 200 °C. Thermal conductivity of the BRPU foams varied between 0.030 W/mK and 0.033 W/mK, and did not vary with increasing percentage of bio-polyols, making them suitable for their utilization as an insulation material.

**Keywords:** Hydrolysis lignin, depolymerization, oxypropylation, polyols, rigid polyurethane foam.



## 9.1 Introduction

With an ever-increasing societal focus on environmental and economical sustainability, biorenewable energy and materials from non-food bioresources, especially wood, are drawing increasing attention from consumers, governments, industries, and research institutes (Li and Ragauskas, 2012). Agricultural residues such as cornstalks, wheat straw, corn and nut shells are abundant and renewable bioresources in many agricultural countries, especially in Canada, China, Indian and Brazil. The main components of agricultural residues are cellulose, hemicellulose and lignin (Xu et al., 2012). Where, lignin represents 30% of all non-fossil organic carbon on Earth and its availability exceeds 300 billion tons (Smolarski, 2012), increasing annually by around 20 billion tons. Large quantities of lignin are available from numerous pulping mills and biorefinery industries (such as cellulosic ethanol plants). In pulp/paper mills or bio-refining industry, wood is used as a feedstock and make full use of cellulose, and residues (lignin) are burned in recovery boilers or simply discarded. However, due to its highly functional character (i.e., rich in phenolic and aliphatic hydroxyl groups) lignin can be an excellent renewable feedstock for a variety of bio-based materials through chemical modifications, which has driven numerous research efforts in the past decades. Because of lignin's special phenyl propanol or polymer structure and aryl-alkyl ether bonding, lignin is a potential alternative to petroleum for phenolic chemicals and polymers. Substituting petroleum with renewable feedstock for chemicals and materials production is especially of significance and interests nowadays when petroleum prices are escalating and there are growing concerns on depletion of fossil resources. However, original lignin has a complex structure with much lower reactivity due to the steric hindrance effects (Cheng et al., 2012). In this respect, lignin or for biomasses containing lignin depolymerization can be a very promising approach to increase its functionality and reactivity.

Depolymerization/liquefaction is widely used nowadays by many researchers to make use of abundantly available bioresources in an effective way via employing different types of solvents and catalysts (Hassan and Shukry, 2008; Chen and Lu, 2009; Lee and Lin, 2008). The primary purpose of depolymerization is to convert complex compounds into smaller molecules of oligomers and monomers for further applications (Wang et al.,

2013). In literature, a number of studies have reported the hydrothermal depolymerization/liquefaction of different biomasses employing water as a solvent (Qian et al., 2007; Sun et al., 2010; Minowa et al., 1998; Xu and Lad, 2008). Some researchers (Tymchyshyn and Xu, 2010) have liquefied agricultural and forestry waste biomass using hot-compressed water with and without catalysts. However, the yields of desired products were low, between 25-60 wt.%. Higher yields were obtained using organic solvents or water/solvent mixtures. Cheng et al. (2010) reported that ethanol-water mixture (50/50, v/v) proved to be more effective solvent for the liquefaction of biomasses as they showed synergistic effects on the direct depolymerization/liquefaction of biomass. All the above methods for biomass/lignin depolymerization including the hydrolytic depolymerization are restricted by their high operation costs due to the intense reaction conditions (combination of high temperatures and pressure) under either acidic or basic conditions, with low solvent recovery rates. Rezzoug and Capart (2002) found that ethylene glycol is a very effective solvent for carrying out the depolymerization/liquefaction of woody biomasses under acidic conditions when compared to water alone. Yip et al. (2009) employed different organic solvents (phenol, EG and EC) at 180 °C using HCl as a catalyst for the successful liquefaction of bamboo, and studied the effects of the liquid ratios and treatment time liquefaction yields. Where, Sanghi and Singh (2012) reported that the conversion rate of polysaccharides in biomasses is strongly dependent on the solvent.

Hydrolysis lignin – a byproduct from pretreatment processes in cellulosic ethanol plants, is expected to be produced in large quantity if the many proposed projects for cellulosic sugar-based chemicals or ethanol are realized. HL is a solid residue (Yuan et al., 2012) from the enzymatic hydrolysis of woody biomass and is mainly composed of lignin (56-57 wt.%), unreacted cellulose and mono and oligosaccharides. Compared with sulfur-containing Kraft lignin (KL), the byproduct of most pulping operations, HL is a sulfur-free lignin and an environmentally benign biomass. Extensive research was undertaken in the former Soviet Union to find uses for this material as they had several hydrolysis plants. Several chemical modifications of HL were carried to make an effective use of this abundantly available phenolic rich polymer, however, the majority of the HL was disposed off because the required modifications were either too expensive or the material

did not function well enough in application. These are the same problems that researchers are facing today for an effective use for HL (Monica, 2005). These factors, jointly with a lack of efficient utilization of HL, give emphasis for the need of further research with highlighting aspects such as depolymerization of HL cost effectively and efficiently, utilization of depolymerized products for the production of valuable biomaterials like bio-based PU foams and resins.

Therefore, the production of polyhydroxy compounds (biopolyols) from HL, via its depolymerization, is of interest for the polyurethane (PU) industry. Depolymerization can result in the reduction of structural complexity, molecular weight and steric hindrance (Xu et al., 2012), which can make the hydroxyl groups present, especially aliphatic hydroxyl groups, more accessible for further reactions. The solid depolymerized products can be derivatized into liquid polyols via oxypropylation (Li and Ragauskas, 2012) for their further utilization in the preparation of rigid polyurethane (RPU) foam as a single polyol feedstock. By means of oxypropylation, the hydroxyl groups, especially phenolic hydroxyl groups which are hardly accessible and entrapped inside the molecule, are liberated from steric and/or electronic constraints. Moreover, such chain extension reactions lead to the formation of liquid polyols due to the introduction of multiple ether moieties (Cateto et al., 2014). RPU foams are the materials with a superior combination of low density and thermal conductivity with high dimensional stability and strength, and used for a variety of high end medical, industrial, and technological applications (Cao et al., 2009).

Nevertheless, the current methods for lignin/biomass depolymerization are restricted by their high operation costs due to intense reaction conditions, non-recoverable solvents, lower substrate concentrations and resulting lower yields. There is a growing need for the exploration of efficient and cost-effective routes employing atmospheric to low pressure. The main objectives of the present work were to achieve cost-effective depolymerization of HL at low pressure ( $\leq 150$  psig) employing ethylene glycol (EG) as a solvent and  $H_2SO_4$  as a catalyst, and utilize the produced DHL as bio-polyols after oxypropylation for the preparation of RPU foam at high percentage of bio-contents (50 wt.%-70 wt.%). All bio-based RPU (BRPU) foams were characterized in terms of their physical, mechanical

and thermal properties and compared with reference foam. To the best of the authors' knowledge no systematic study has been reported by far in the public literature for the depolymerization of HL into low  $M_w$  bio-polyols products operating at low pressure, and their effective utilization in the preparation of RPU foams at high bio-contents loading.

## 9.2 Materials and methods

### 9.2.1 Materials

Hydrolysis lignin (HL) used in this study was kindly provided by FPIinnovations (Yuan et al., 2012) and was insoluble in THF or in any organic solvents like ethanol, methanol or acetone etc. Lignocellulosic biomass from any type of plant biomass that is composed of cellulose, hemicellulose and lignin, typically in amounts of 30-55 wt.%, cellulose; 15-35 wt.%, hemicellulose; and 5-31 wt.%, lignin, was used. The novel bio-conversion process used comprises of low- pressure mechanical refining to disintegrate biomass feedstock, hemicellulose extraction, enzymatic hydrolysis, sugar/lignin separation, and fermentation. After hemicellulose extraction and a subsequent hydrolysis, the remaining substrate (solid) residue contains a high percentage of lignin which was being recovered and further purified to produce high-quality lignin products. Compared to traditional Kraft lignin and steam-explosion lignin, the high-quality sulfur free lignin produced from this invention has little degradation (Yuan et al., 2012). The weight average molecular weight ( $M_w$ ) of HL was not possible to determine by using GPC-UV. The pH value of original HL was neutral. The chemical components of raw HL as well as its elemental compositions are presented in Table 9-1. The other chemicals used in the study were NaOH, H<sub>2</sub>SO<sub>4</sub>, acetone, pyridine, acetic anhydride, dibromomethane, ethylene glycol (EG), polymeric MDI, sucrose polyol (JEFFOL SD-361), propylene oxide (PO), triethanolamine (TEA), triethylene diamine (Diaza, TEDA), stannous octoate, silicon oil, glycerol etc. All chemicals were used in experimentation without further purification or any treatment. The physical characteristics of the chemicals used in the foam preparation are given in Table 9-2.

Table 9-1 Chemical (d.b.)<sup>a</sup> and elemental composition (d.a.f.)<sup>b</sup> of hydrolysis lignin (HL)  
(Yuan et al., 2012)

Lignin %	Carbonhydrates %	Ash %	Others, %	Carbon, %	Hydrogen, %	Nitrogen, %	Others, %
56.7	29.8	1.2	12.3	62.8	6.1	4.0	28.3

<sup>a</sup> On dry basis

<sup>b</sup> On dry and ash free basis

Table 9-2 Physical Characteristics of the Chemicals

Ingredients	Functionality	Equivalent weight (g/mol)	-OH # (mgKOH/g)	Comments
PMDI	2.7	135.0	-	NCO contents: 31.2%
Glycerol	3.0	30.7	1829.4	Co-crosslinking agent
Sucrose polyol	8.0	155.8	360.0	JEFFOL SD-361 (commercial polyol)
Water	2.0	9.0	6233.3	Chemical blowing agent
Acetone	-	-	-	Physical blowing agent
Poly(siloxane ether)	-	-	-	Silicon surfactant
Triethylene diamine	-	-	-	Foaming catalyst
Stannous Octoate	-	-	-	Gelation catalyst
Triethanol amine	3.0	49.73	1128.1	Co-catalys

## 9.2.2 Hydrolytic depolymerization of HL

Hydrolysis lignin was depolymerized using EG as a solvent under acidic conditions (H<sub>2</sub>SO<sub>4</sub> as a catalyst) under atmospheric pressure to low pressure (<150 psig). All of the depolymerization reactions were performed in 100 mL Parr Model 4848 reactor, equipped with a pressure gauge, thermocouple, stirrer, gas line and a sampling line. In a typical run, 12 g HL, 0.24 g H<sub>2</sub>SO<sub>4</sub> and 47.8 g EG were loaded into an autoclave reactor. For all runs, the reagents were measured and loaded into the reactor which was then sealed, evacuated and purged with N<sub>2</sub> and finally tested for leaks. The reactor was heated

up to desired temperature, under the stirring (290 rpm). After the desired temperature was attained, the reaction was allowed to proceed until the required duration had elapsed. Reactions were quenched by immersion in a cold water bath. The reaction products were washed from the reactor using acetone and filtered to separate the acetone-insoluble solid residues (SR) and acetone soluble depolymerized HL (DHL). The DHL was isolated via rotary evaporation under vacuum to remove the solvent. EG was then removed from DHL using water as a solvent followed by a subsequent filtration to separate water soluble EG and water insoluble DHL. The DHL cake on filter paper was then dried and the product yields were determined. The SRs were dried at 105 °C in air for 24 hr before weighing and yield was determined relative to the mass of HL. All the data presented is the average of duplicate runs with relative errors.

### 9.2.3 Oxypropylation of DHL

The DHL obtained at the best operating conditions, although in solid form, was used as bio-polyols in this work after being further transferred into a liquid polyol via oxypropylation. DHL sample was initially neutralized to pH ~7.0 before using for oxypropylation reaction. Oxypropylation of DHL was carried out in a 100 mL Parr reactor. In a typical run, for the preparation of oxypropylated feedstock at 50 wt.% bio-replacement, 18.9 g of DHL, 21.21 g propylene oxide (PO), 2.31 g of anhydrous glycerol & KOH (%KOH in mixture was 11wt.%) and 16.8 g of acetone were loaded into the reactor. The reactor was then heated to 150 °C (under atmospheric pressure). Initially, the pressure in the reactor increased to a maximum of 120 psig and then returned to the original pressure ~14.7 psig (or 1 atm-g) after 1.5 h reaction, implying the complete consumption of PO or completion of the reaction. After cooling, the reactor contents were completely rinsed into a beaker using acetone followed by neutralization of the reaction mixture using sulfuric acid. The neutralized reaction mixture was then filtered through a Buchner funnel to separate solid residues (SRs) from the acetone soluble phase. The acetone soluble filtrate was transferred to a pre-weighed Erlenmeyer flask and the acetone and any unreacted PO (if any) were removed by rotary evaporation at 60 °C.

### 9.2.4 Polyurethane foam preparation

All the foam samples were prepared in 455-ml plastic cups using a one pot method. Typically the RPU foam formulation investigated in this study includes a polyol combined with 10% (w/w) glycerol (a co-crosslinking agent). For comparison, reference foam was prepared using sucrose polyols at 0% DHL. Additionally the formulation includes a physical blowing agent (acetone at 20% (w/w)), a catalyst comprising equal amounts of stannous octoate and triethylene diamine at 2% (w/w), surfactant at 2% (w/w) and water at 2% (w/w). The amounts of blowing agent, catalyst, surfactant and water were determined with respect to the total weight of polyol used. PMDI was added at fixed NCO/OH ratio of 1.1. The foam preparation procedure was comprised of the following steps: (1) the desired polyols, catalysts and blowing agents were all weighed in a cup and mixed at 550 rpm for 10-12 s until homogeneous and (2) a predetermined mass of MDI was then added to the cup and the mixture was stirred vigorously for another 12-15s. The mixture was then placed in a fume hood at ambient temperature ( $23\pm 2$  °C) to allow the foam to rise. All of the foam samples were left in the fume hood for 24-48 h for curing before the sample collected for analysis. Foam shrinkage, structural uniformity, stability and cell appearance could be observed at this point. However, prior to further characterization, the foam samples were conditioned for a minimum of 24 h to maximum of 1 week, depending on the requirements. Sucrose polyol was not used in the formulation of BRPU foams at different bio-content percentages.

### 9.2.5 Product characterization

The relative molecular weights of the depolymerized HL (DHL) and oxypropylated DHL were measured with a Waters Breeze GPC–HPLC (gel permeation chromatography–high performance liquid chromatography) instrument (1525 binary pump, UV detector at 270 nm; Waters Styrylgel HR1 column at a column temperature of 40 °C) using tetrahydrofuran (THF) as the eluent at a flow rate of 1 mL/min using linear polystyrene standards. The functional groups of the HL, DHL and oxypropylated DHLs were analyzed by Fourier Transform Infrared Spectroscopy (FTIR). Proton nuclear magnetic resonance ( $^1\text{H}$  NMR) spectra for the DHL and oxypropylated DHLs were acquired at 25°C using a Varian Inova 600 NMR spectrometer equipped with a Varian 5 mm triple-

resonance indirect-detection H<sub>2</sub>CX probe. A total of 16-32 scans were accumulated using a 2 s recycle delay, 3.6 s acquisition time, a 45-degree tip angle (pw = 4.8 us), and a spectral width from -2 ppm to 14 ppm (sw = 9000.9 Hz). Quantitative <sup>1</sup>H-NMR spectra analysis was realized using acetylated samples of DHL and oxypropylated DHL. Briefly, 1 g of dried sample was dissolved in a 1:1 (v/v) mixture of pyridine (5 mL) and acetic anhydride (5 mL) followed by stirring for 24 to 48 hr. The mixture was then transferred into a beaker containing 100 mL of ice-cooled 1 wt.% HCl solution. The resulting precipitates of the acetylated samples were washed with distilled water to pH ≈ 7. The samples were then dried at 105 °C for 24 hr to remove residual water prior to the quantitative <sup>1</sup>H-NMR analysis. Dibromomethane (CH<sub>2</sub>Br<sub>2</sub>) was used as an internal standard with a characteristic peak is at 4.9 ppm. The hydroxyl number of the DHL and oxypropylated DHL were determined by <sup>1</sup>H-NMR spectra analysis. The samples were prepared dissolving 30.0 mg of the acetylated DHL or oxypropylated DHL and 15.0 mg of the internal standard in *d*-chloroform (≈1000-1500 mg) then transferring the sample into a 5 mm NMR tube via a transfer pipette for analysis. Hydroxyl numbers of the oxypropylated DHL samples were also measured as per ASTM D4274-99 using a Potentiometric Titrator (Titroline 7000 Titrator). The viscosity of the oxypropylated DHL sample was measured by using BROOKFIELD CAP 2000+VISCOMETER at 80 °C.

The apparent densities of foam samples were measured according to ASTM D1622-03. The mechanical properties of PUF samples were measured at ambient conditions on an ADMET Universal Testing Machine (Model SM-1000-38). Modulus of elasticity (Young's modulus or compressive modulus) (initial linear slope of the stress-strain curve) and compressive strength at 10% deformation, were determined by performing the stress-strain tests according to ASTM D 1621-00. Thermal conductivities of the foam samples were measured using a KD2 PRO thermal properties analyzer with SH-1 dual needle sensor (1.3 mm diameter x 3 cm long, 6 mm spacing) capable of measuring thermal conductivity in the range of 0.02 to 2.00 W/mK. The specimen size used for thermal conductivity analysis was 40 mm x 40 mm x 20 mm. Thermal stability of the foams were measured using a *Pyris*<sup>TM</sup> Diamond, Perkin-Elmer Thermogravimetric analyzer (TGA), under a N<sub>2</sub> and air flow (20 mL/min) respectively, from 30 °C to 800 °C



at 10 °C/min. Morphology of the foams was observed by a Hitachi S-4500 field emission cross beam scanning electron microscope (SEM). After examination by SEM, selected locations on the foam surface were subjected to a cross-sectional cut and the sample was coated with osmium, and imaged using a focused ion beam LEO (Zeiss, Thornwood, NY, USA) 1540XB SEM.

## 9.3 Results and discussions

### 9.3.1 Depolymerization of HL

Since HL is composed of 50-60 wt.% lignin, therefore initially experiments for the depolymerization of HL were carried under both alkaline and acidic medium at 2 wt.% catalyst loading using NaOH and H<sub>2</sub>SO<sub>4</sub> as catalysts. No depolymerization of the HL was observed under alkaline conditions employing EG as a solvent and, on opening the reactor, the resulting HL product was found to be a charred mass. The reason could be on one side the slightly alkaline conditions would suppress the cellulose hydrolysis, and on the other hand, the pH level is not high enough for catalyzing lignin hydrolytic depolymerization (Xu et al., 2012). Since, under weak alkaline conditions, the reaction medium can change gradually from alkaline to neutral or acidic due to the carboxylic acids produced during depolymerization reactions. Depolymerization was then conducted under acidic medium using sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) as a catalyst and significant depolymerization of HL was observed. Sulfuric acid was selected as a catalyst because of its an ultra high catalytic activity at low dosage in combination with less corrosion rates. Therefore, acid catalyzed depolymerization of HL was considered as a major route for further experimentation to study the effect of process parameters.

#### 9.3.1.1 Effects of reaction temperature

The depolymerization temperature is an important factor for the residue contents and energy saving. Raising the temperature promotes the depolymerization and recondensation of the intermediates simultaneously (Chen and Lu, 2009). Depolymerization of cellulose in acidic media occurs by breaking glycosidic bonds to form glucose monomers and usually requires elevated temperatures of around 200-220 °C. Depending on the acidic medium and its pH, hemicelluloses also decompose into

monosaccharides at temperature above 120 °C. In the case of lignin, -OH and O groups are converted into benzylium ions which attack ether groups at 160-180 °C in weak acid media in a multiple step reaction. Thermal decomposition of lignin at temperatures higher than 250 °C leads to the formation of phenoxy radicals which form solid residues through repolymerization. Therefore, the temperature range selected for investigation was 180 to 240 °C. Figure 9-1 shows the effects of reaction temperature on the yield of products (DHL and SR), and  $M_w$  of the DHL from the tests carried out at temperatures ranging from 180 to 240 °C at 1h. At 180 °C the yield of DHL was ~56 wt.% with ~18 wt.% . The remaining mass (~26 wt.%) could be attributed to water and aqueous products (monomers, aldehydes, alcohols etc.). While employing EG as a solvent for HL depolymerization, there were no gases produced during the reaction. The increased pressure noted during the reaction was due to the vapor pressure of water generated from the rupture of glycosidic linkages present in cellulose during the depolymerization reactions.

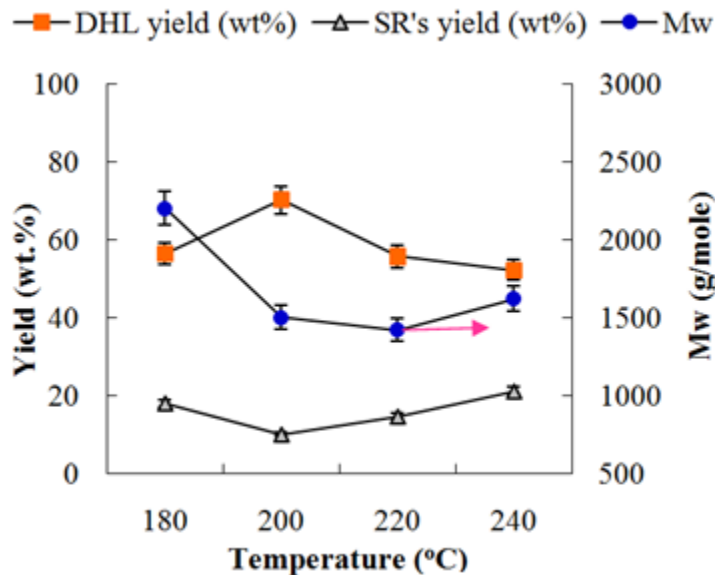


Figure 9-1 Effects of temperature on yields of products and  $M_w$  (Other reaction conditions: 60 min, HL loading of 20% (w/w)), and  $H_2SO_4$ : 2% (w/w))

At 200 °C, the DHL yield increased to 70 wt.%, likely due to the endothermic nature of depolymerization reactions and hence thermodynamically favorable at higher temperatures (Cheng et al., 2012). The SR yield at 200 °C was as low as 10 wt.%. Further increasing the reaction temperature to 220 °C and 240 °C decreased the yields of DHL (55 wt.% at 220°C and 52 wt.% at 240 °C). The yield of SR, on the other hand, increased from 10 wt.% to 21 wt.% as the temperature was increased from 200 °C to 240 °C. The high yield of SR or char may be due to crosslinking reactions between carbon-carbon double bonds (C=C) which leads to the formation of a highly cross-linked structure that is insoluble in water/acetone. Another reason could be acid catalyzed condensation reactions which resulted in the formation of char at higher temperatures.

The  $M_w$  of DHL decreased from 2200 g/mole to ~1500 g/mole when the reaction temperature was increased from 180 °C to 200 °C. The reduced  $M_w$  at 200 °C, suggests that temperature has a drastic effect on the cleavage of alkyl-aryl ether linkages in lignin. When the temperature was increased to 220 °C, there was a slight reduction in  $M_w$  to 1420 g/mole. However, a further increase in temperature to 240 °C, increased  $M_w$  to 1620 g/mole. This can be attributed to repolymerization/condensation reactions between the reaction intermediates which become the dominant reactions at higher temperatures. Although increasing temperature can facilitate the depolymerization/defragmentation of cellulose, hemicellulose and lignin, there is a critical temperature for any depolymerization/liquefaction technique (Rezzoug and Capart, 2002). Hence, with respect to yields of products (DHL and SRs) and DHL and  $M_w$  of DHL products, the best reaction temperature appears to be 200 °C for 1h.

### 9.3.1.2 Effects of reaction time

The experiments in this section were to examine the effects of reaction time on the hydrolytic depolymerization of HL at 200 °C employing EG as a solvent under acidic conditions. The yield of products (DHL and SRs) and  $M_w$  after reaction for various lengths of time (30-180 min) are illustrated in Figure 9-2. Increasing the reaction time from 30 min to 60 min increased the yield of depolymerized HL (DHL) from 62 wt.% to

~70 wt.%. The  $M_w$  of the DHL after 60 min reaction time was 1500 g/mole as compared to 2250 g/mole at 30 min suggesting that the hydrolytic depolymerization reaction proceeded to a greater extent at this longer reaction time. Further increasing the reaction time to 90, 120 and 180 min resulted in decreased DHL yields of ~65 wt.%, 64 wt.% and 60 wt.%, respectively. These decrease DHL yields corresponded with slight increases in SR yield as was similarly observed by (Jin et al., 2011). The  $M_w$  of the DHL at 120 and 180 min were found to have increased to 1550 g/mole and 1780 g/mole, respectively. The decrease in the yield of DHL accompanied by increased SR yield with extended reaction time was likely due to acid catalyzed condensation or char formation, while the increase in  $M_w$  was likely due to repolymerization/condensation reactions which are usually promoted under the acidic conditions. Hence, with respect to both yield and  $M_w$  of the DHL products, the best reaction time appears to be 60 min at 200 °C.

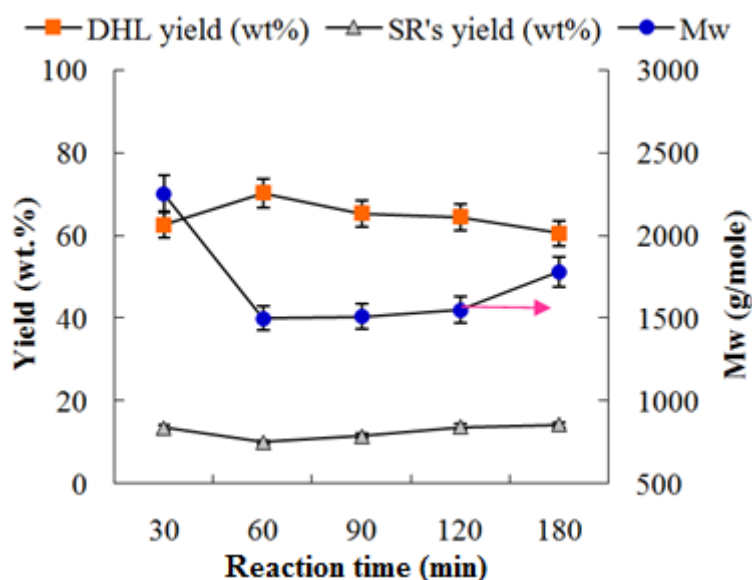


Figure 9-2 Effects of varying reaction time on yields of products and  $M_w$  (Other reaction

conditions: 200 °C, HL loading: 20% (w/w) and  $H_2SO_4$  of 2% (w/w))

### 9.3.1.3 Effects of HL substrate loading

The concentration of feedstock is an important parameter for biomass hydrothermal liquefaction as higher concentrations reduce the required amount of organic solvent in the reactor and hence the cost for solvent recovery, improving the economics of the process (Pye, 1990). Figure 9-3 displays the yield of products (DHL and SRs) and  $M_w$  of DHLs from experiments at 200 °C for 60 min at various loadings of HL. It can be clearly seen that the yield of DHL remained almost the same with an average value of 66.2(±4.0) wt.%, while  $M_w$  and SR yield both increased significantly from ~1300 g/mole (10 wt.%) to ~2200 g/mole (30 wt.%). The increased yield of SRs may be due to the lesser availability of solvent which favors enhanced cross-linking reactions or acid catalyzed condensation or repolymerization reactions. Akhtar et al. (2011) also found that the higher substrate concentrations (or higher biomass-to-solvent mass ratios) resulted in greater yields of solid residue during hydrothermal liquefaction of biomass. Hence, in view of the utilization of produced DHL as polyols for the preparation of bio-based rigid polyurethane foams, 20 wt.% HL loading appears to be the best with high yield and acceptable low  $M_w$ .

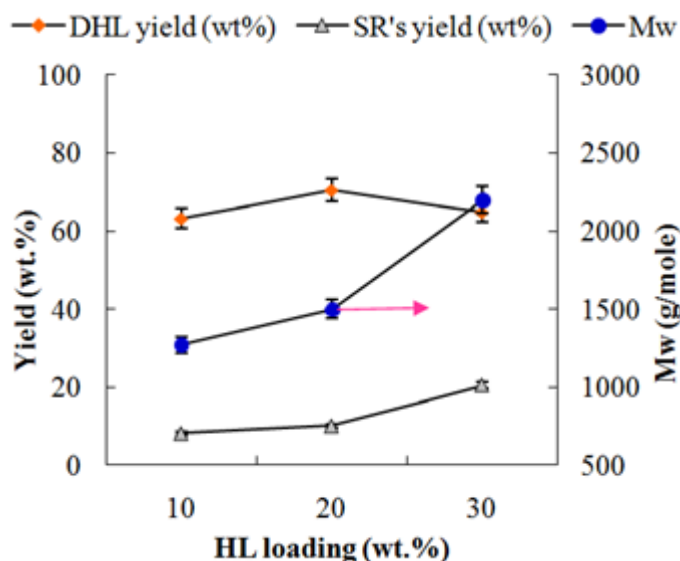


Figure 9-3 Effects of varying HL substrate loading on yields of products and  $M_w$  (Other reaction conditions: 200 °C, 1 h and H<sub>2</sub>SO<sub>4</sub> of 2% (w/w))

#### 9.3.1.4 Effects of acid loading

The presence of an acid catalyst can promote ether bond cleavage during the depolymerization of lignocellulosic biomass and so reduce the liquefaction temperature and time as well as improve the liquefaction yields. However, high acid concentrations can also enhance recondensation reactions for the liquefied fragments resulting in an increase in the amount of insoluble residues after liquefaction (Yao et al., 1993). Figure 9-4 displays the products yields and  $M_w$  of DHL from experiments at 200 °C for 60 min with 20 wt.% HL substrate concentration for various acid loadings. The yield of DHL was found to initially increase from 57 wt.% to 70 wt.% with the increase in acid loading from 1% (w/w) to 2% (w/w) and was accompanied by a decrease in SR yield from 20 wt.% to 10 wt.%. However further increasing the acid loading to 4 % (w/w) resulted in a decreased DHL yield of 50 wt.% and a dramatic increase in SR yield to 35 wt.%. A similar trend was observed for the  $M_w$  values over the studied range of acid loading: the  $M_w$  first decreased then slowly increased with increasing acid loading. The amount of sulfuric acid used in depolymerization also has a direct effect on the amount of alkali needed in the post-processing. Excessive sulfuric acid also exerts a negative effect in polyurethane synthesis (Jin et al., 2011). Hence 2% (w/w) acid loading appears to be the best condition.

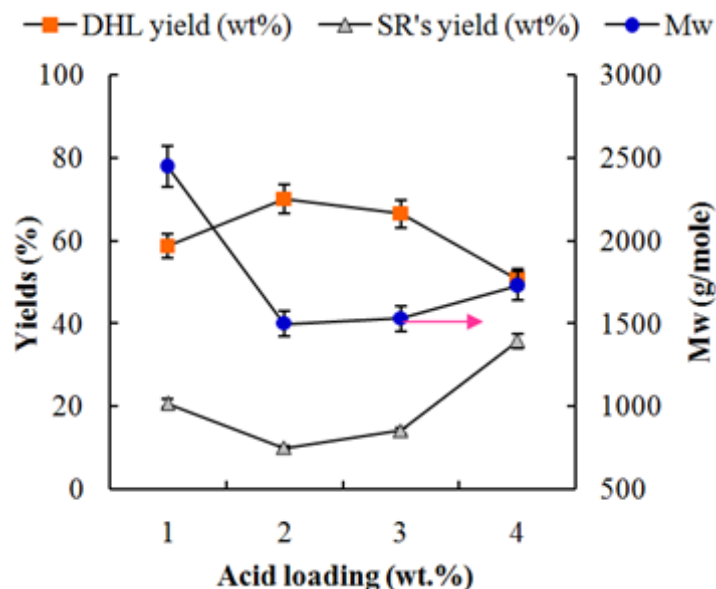


Figure 9-4 Effects of varying acid loading on yields and  $M_w$  (Reaction temperature: 200 °C, reaction time: 60 min, EG/HL ratio: 4.0 (w/w))

Hence, the best operating conditions for obtaining DHL via low pressure acid catalyzed depolymerization appears to be at 200 °C, for 1 h with a HL concentration of 20% (w/w) with 2% (w/w) acid loading, leading to ~70 wt.% yield of DHL, with a SR yield of ~10 wt.% and  $M_w \approx 1500$  g/mole and total hydroxyl number ~247.1 mgKOH/g.

### 9.3.2 Oxypropylation of DHL

DHL obtained at the optimum reaction conditions (200 °C, 1 h, and HL concentration ~20 wt.% with  $H_2SO_4$  ~2 wt.%) was selected for further the experiments. The DHL was a solid and was further oxypropylated at three different percentages of bio-contents (lignin and glycerol) of 50, 60 and 70 wt.%, to produce liquid polyols. Polyols used for the preparation of RPU foams must be in the liquid state and their hydroxyl number and viscosity are the most important physico-chemical properties (Li and Ragauskas, 2012). The oxypropylated DHLs were analyzed in terms of their  $M_w$ , hydroxyl number and viscosity and results are given in Table 9-3. Figures 9-5, 9-6 and 9-7 present  $^1H$  NMR spectra of acetylated DHL, DHL50PO50 and DHL60PO40 respectively. It is clear from Figure 9-5 that DHL has both aliphatic and phenolic -OH groups present in the form of

aliphatic and phenolic acetates, respectively. However, after oxypropylation all of the phenolic –OH have been altered into aliphatic –OH presented as seen by the presence of only aliphatic acetates in Figure 9-6 and Figure 9-7 for DHL50PO50 and DHL60PO40, respectively.

Table 9-3 Characteristics of DHL and oxypropylated DHLs

Sample ID	$M_w$ $\approx$ (g/mole)	Total Hydroxyl number (mgKOH/g)	Viscosity at 80 °C (Pa.s)	State
DHL	1420	247.1	-	Solid powder
DHL50PO50	3160	118.2	0.78	Viscous
DHL60PO40	3130	138.0	0.89	
DHL70PO30	2530	153.0	1.431	Liquid

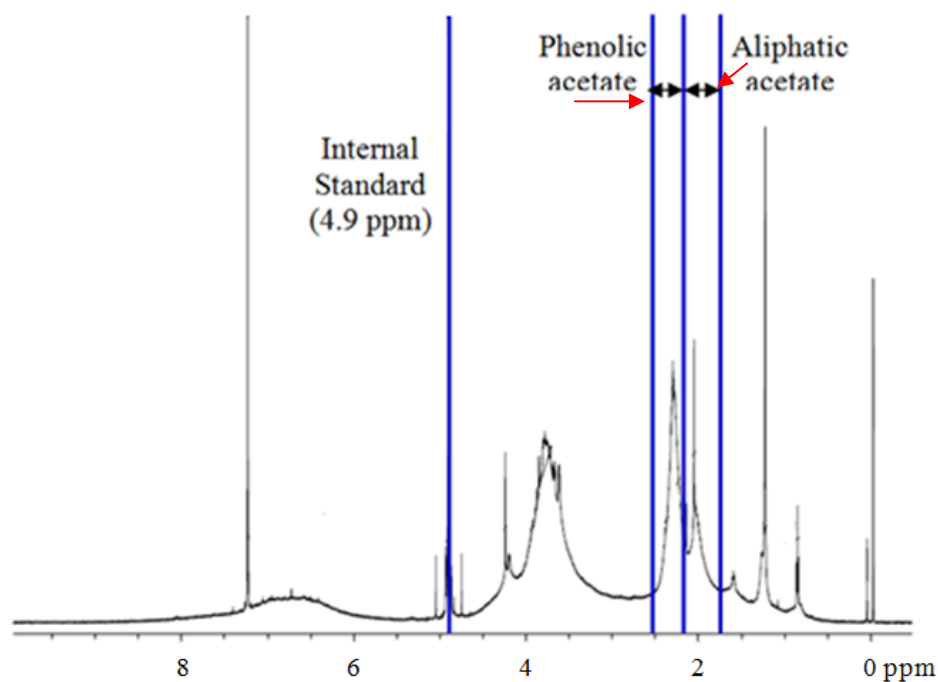


Figure 9-5 <sup>1</sup>H NMR spectra of acetylated DHL



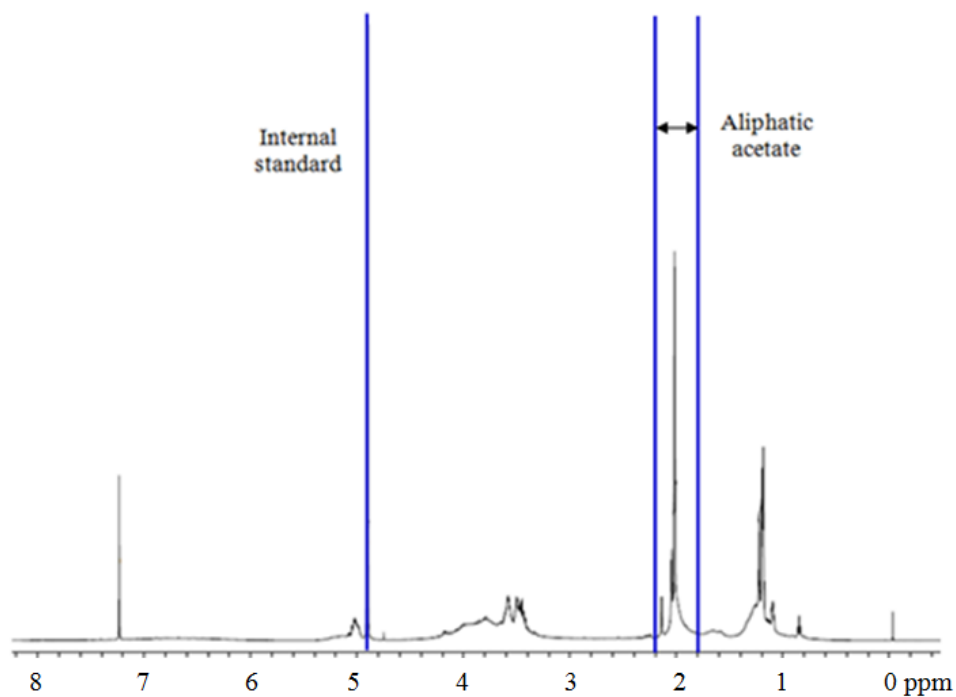


Figure 9-6  $^1\text{H}$  NMR spectra of acetylated DHL50PO50

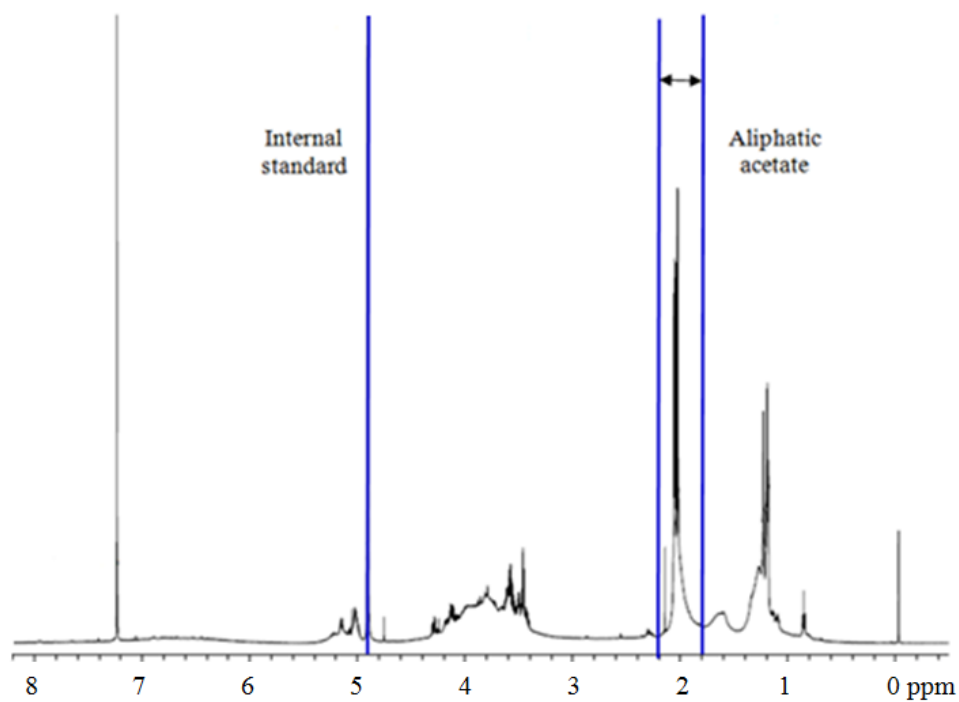


Figure 9-7  $^1\text{H}$  NMR spectra of acetylated DHL60PO40

### 9.3.2.1 FTIR of HL, DHL and oxypropylated samples

FTIR spectra of sucrose polyol, original HL and DHL along with the oxypropylated DHL at different bio-contents are shown in Figure 9-8. The spectra are normalized to the intensity of the lignin aromatic ring vibration at  $1600\text{ cm}^{-1}$ . In all the spectra, the -OH stretching vibration is easily seen at  $\sim 3450\text{ cm}^{-1}$  (Li and J. Ragauskas, 2012). The oxypropylation and occurrence of PO grafting onto the lignin can be evidenced by following FTIR observations: (a) an increase in the bands at  $2971\text{--}2870\text{ cm}^{-1}$  attributed to the stretching of  $\text{CH}_3$ ,  $\text{CH}_2$  and  $\text{CH}$  aliphatic groups; (b) reduction in the intensity of the carbonyl peak at  $1714\text{ cm}^{-1}$ ; (c) a marked increase of the absorption bands in the ether C-O stretching region ( $1000\text{--}1100\text{ cm}^{-1}$ ); and (d) an increase in the band at  $1371\text{ cm}^{-1}$  confirming the introduction of  $\text{CH}_3$  groups (Cateto et al., 2009).

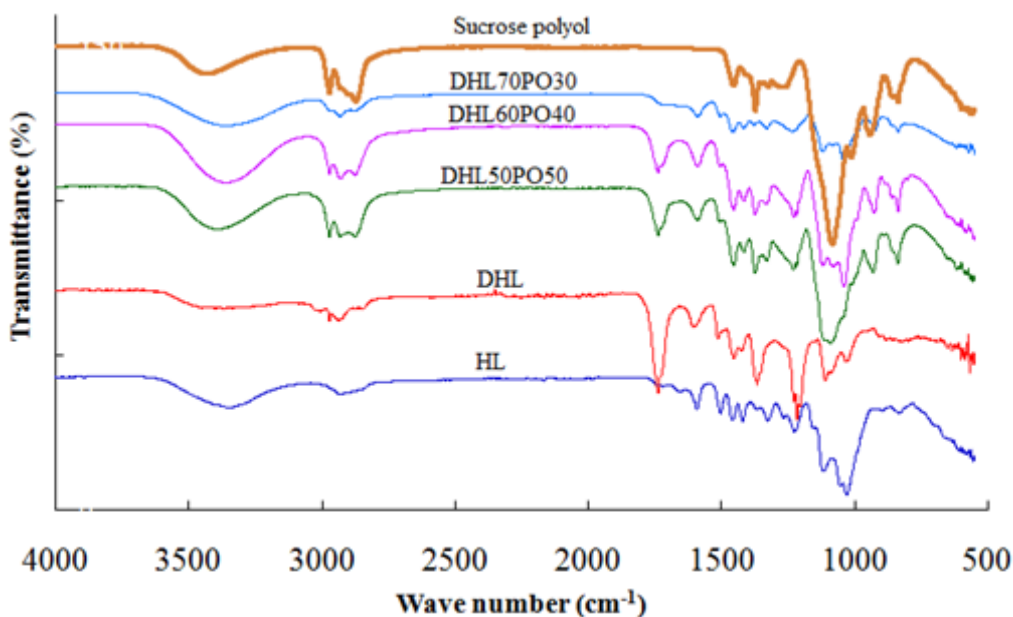


Figure 9-8 FTIR spectra of sucrose polyol, HL, DHL and oxypropylated DHLs

### 9.3.3 Rigid polyurethane (RPU) foam

The density of PU foam is governed by the weight and volume of the foaming ingredients which are responsible for making up the matrix of the foam and the gases trapped within the foam cells. According to the literature, density plays an important role in the

mechanical performance of rigid PU foam (Li and Ragauskas, 2012). The composition of foam matrix includes polyols, additives such as surfactants, catalysts, crosslinking agents and isocyanate. Whereas the gas phase composition includes carbon dioxide generated from the chemical reaction between the chemical blowing agent (water) and the components of the foam formulation (isocyanate), and air, which is either introduced into the reaction vessel during the foaming process or diffuses into the cells during the aging process. In this study a combination of physical and chemical blowing agents was employed to control the density of the resulting foams. The quantity of water was kept at 2 wt.% based on the total weight of polyols and physical blowing agent (acetone) was used to further reduce the density of foam to the desired value, since the consumption of MDI increases with increased water in the reaction mixture. Acetone does not react chemically with isocyanate or any other foaming ingredient. Acetone uses the heat released during exothermic reaction of isocyanate with water (~100-110 kJ/mole of urethane) (Tu, 2008) to produce amine and carbon dioxide. During the foaming reaction temperature increased above 100 °C and can rise to maximum foam temperature of 168 °C (Jimoda, 2011).

### 9.3.3.1 Physical and mechanical characteristics

Density is reported as the main property of RPU foams as it also affects mechanical properties of foam (Thirumal et al., 2008). Therefore, in this study BRPU foams were prepared with polyols containing 50-70 wt.% of oxypropylated DHL via two approaches; (1) under fixed percentage of physical blowing agent (20% (w/w)); and (2) under varying percentages of physical blowing agent (20-26% (w/w)) to maintain approximately constant foam densities. The physical and mechanical properties of the BRPU foams prepared from oxypropylated DHL are provided in Table 9-4.

Table 9-4 Physical and mechanical properties of BRPU foams

Foam ID	Density (kg/m <sup>3</sup> )	Compressive modulus (kPa)	Compression strength at 10% deformation (kPa)
At fixed percentage of physical blowing agent			
Sucrose Ref. Foam	42.5±0.5	2695.0±100.0	182.0±45.0

DHL50PO50	45.0±2.0	5381.0±100.0	235.0±75.0
DHL60PO40	62.1±2.0	12360.0±55.0	513.0±45.0
DHL70PO30	-	Due to high viscosity of DHL70PO30 foam did not form	
At varying percentage of physical blowing agent			
DHL50PO50	45.0±2.0	5381.0±100.0	235.0±75.0
DHL60PO40	39.0±2.0	2825.0±80.0	193.0±42.0
DHL70PO30	-	Due to high viscosity of DHL70PO30 foam did not form	

It is clear from Table 9-4 that both the compressive modulus (5381.0 kPa) and compression strength of BRPU foams at 50 wt.% bio-content were higher than the reference foam (compression modulus: 2695.0 kPa; compression strength at 10% strain: 182.0 kPa). The sucrose polyol used for the preparation of the reference foam has a multiple branched short chain structure. The increased modulus and strengths of BRPU foams may be primarily attributed to the aromatic structure and the high functionality of DHL's hydroxyl groups, which introduces more crosslinking in the PU network and leads to higher crosslinking density as compared to the control foam. When trials were made to keep the final density of BRPU foams approximately the same, more physical blowing agent was introduced in the foaming recipe. Therefore, on increasing the bio-content to 60 wt.%, more acetone was used. The resulting foam showed lower density and compressive strength than the BRPU foam prepared with 50 wt.% bio-content. This can be attributed to its morphological characteristics. Also BRPU foam with 60 wt.% was found to be slightly brittle, possibly due to the introduction of higher percentage of hard lignin block than were present in the BRPU foam with 50 wt.% bio-contents. Therefore, the greater requirement of physical blowing agent leads to changes in the morphological characteristics of the foam, affecting its density and strength. Even so, BRPU foam prepared at 60 wt.% bio-content has a compression modulus (2825.0 kPa) and strength (compression strength at 10% deformation: 193.0 kPa) that are slightly higher than those of the reference foam.

On the other hand, if the percentage of physical blowing agent in the formulation was kept constant, the increasing percentage of bio-contents in the BRPU foam formulations resulted in higher density foams due to extensive cross-linking and, as a result, the compression strength of the foam samples was also improved. Figure 9-9 shows DHL50PO50 based RPU foam and a SEM micrograph of the foam. The foam cells range in size between  $\sim 162.3 \mu\text{m}$  and  $\sim 272.1 \mu\text{m}$ .

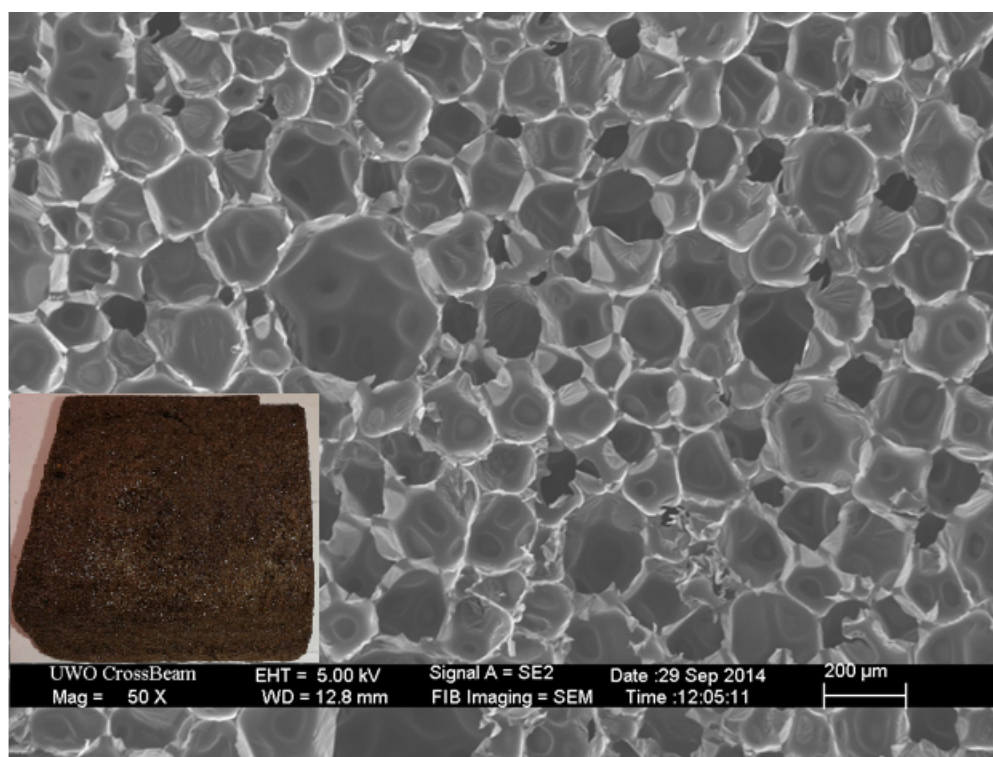


Figure 9-9 SEM image of BRPU foam prepared with DHL50PO50

Figure 9-10 shows the FTIR spectra of BRPU foams prepared from oxypropylated DHL at 50 wt.% and 60 wt.% bio-contents. In the spectra, residual or unreacted isocyanate group (NCO) can be identified at the band of  $2253.6 \text{ cm}^{-1}$ . The inter N-H stretching which is in the PU hard segment region is identified at  $3454.53 \text{ cm}^{-1}$ .  $1710 \text{ cm}^{-1}$  (C=O stretching) and  $1408.84 \text{ cm}^{-1}$  and  $1098.30 \text{ cm}^{-1}$  (C-N coupled, C-O stretch) indicates the existence of the urethane linkage (Cinelli et al., 2013; Nurdjannah et al., 2013; Ribeiro da

Silva et al., 2013). Other characteristic bands, the N-H deformation signal at  $1519\text{ cm}^{-1}$  of isocyanurate (resulting from reactions between isocyanate and urethane groups), conjugated and unconjugated C-O stretching at  $1216$  and  $1064\text{ cm}^{-1}$  and CH deformation of aromatic groups in the range of  $800\text{-}600\text{ cm}^{-1}$  are also noted in the spectrums (Ribeiro da Silva et al., 2013).

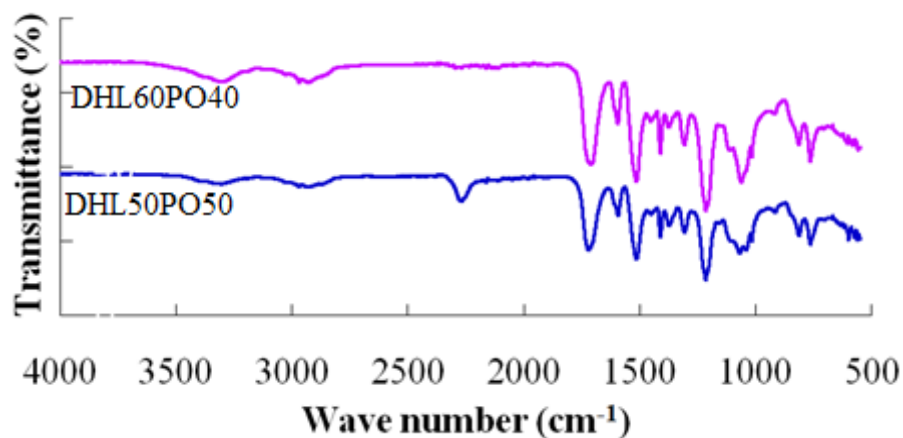


Figure 9-10 FTIR spectra BRPU foams at 50 wt.% and 60 wt.% bio-contents

### 9.3.3.2 Thermal characteristics

RPU foams are remarkable insulation materials due to their low thermal conductivity. RPU foams have been recognized all over the world as the most efficient insulation material commercially available since their introduction (Cunningham and Sparrow, 1986). Thermal conductivity value is closely related to foam cell morphology (Ribeiro da Silva et al., 2013). Table 9-5 shows the thermal conductivity of the reference and BRPU foams. The results showed that the thermal conductivity of the BRPU foams at 50 and 60 wt.% bio-content did not show much variation and was between  $0.030\text{ W/mK}$  and  $0.032\text{ W/mK}$ . There was not much pronounced difference observed for BRPU foams prepared with fixed or varying percentage of physical blowing agent.

Table 9-5 Thermal conductivity of reference and BRPU foams

Foam ID	Thermal conductivity ( $\lambda$ ) (W/m-K)
Sucrose ref. foam	0.033±0.0010
DHL50PO50	0.030±0.0010
DHL60PO40	0.032±0.0010

In this study, the  $\lambda$  values vary between 0.030 W/mK and 0.032 W/mK, which is in good agreement with literature (Cateto et al., 2010) taking into account that the density of the prepared foams is at the higher limit of common polyurethane foams where  $\lambda$  values are between 0.020-0.030 W/mK for densities (Ribeiro da Silva et al., 2013) ranging from 30-100 kg/m<sup>3</sup>. Over time, air diffuses into the cells and can lead to increased thermal conductivity.

Thermogravimetric analysis was performed to investigate the effect of oxypropylated-DHL incorporation on the thermal behavior of BRPU foam under an inert atmosphere. Figure 9-11 shows thermal stability curve of BRPU foam containing 50 wt.% and 60 wt.% bio-contents. Thermal degradation of PUs is usually described as a complicated process involving the dissociation of the initial polyol and isocyanate components. Thermal decomposition can lead to the formation of amines, small transition components, and carbon dioxide (Zhao et al., 2012). Mass loss at temperatures below 150 °C is considered to be due to the evaporation of water. Pyrolysis of PU foam under nitrogen atmosphere starts at ~170 °C and intensifies at ~200 °C. Decomposition of the RPU foams took place mainly between 200-450 °C. Around 350 °C the decomposition of polyurethane produces compounds such as diisocyanates and polyols along with other decomposition products including amines, olefins and carbon dioxide (Manocha et al., 2010). Mass loss for the bio-based foams beyond 600 °C, was negligible.

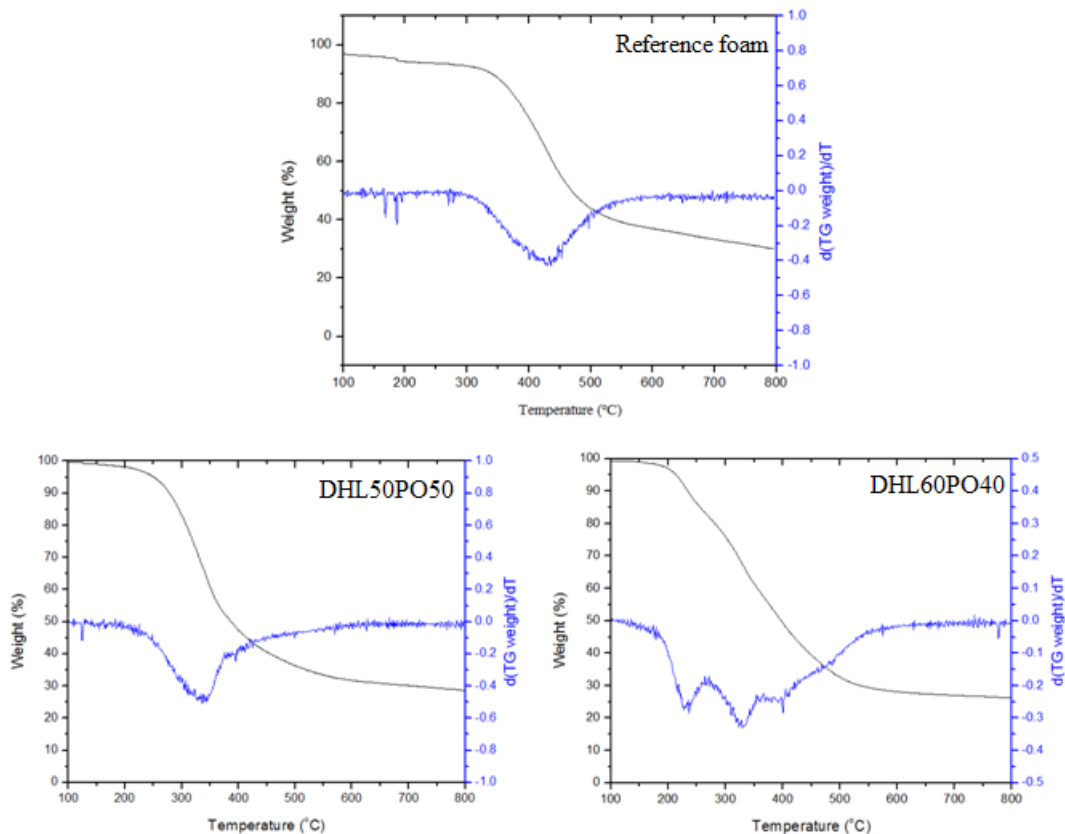


Figure 9-11 Degradation TGA curves and rate of weight loss curves of reference foam and BRPU foams from DHL50PO50 and DHL60PO40

## 9.4 Conclusions

Hydrolysis lignin (HL) was successfully depolymerized to low molecular weight depolymerized HL (DHL) in an acidic medium using sulfuric acid as a catalyst. Under the best operating conditions (200 °C, 1h, 20 wt.% HL substrate loading and 2 wt.% acid loading) depolymerization produced DHL at a yield of ~70 wt.% with a weight-average molecular weight ( $M_w$ ) of ~1500 g/mole and high aliphatic and total hydroxyl numbers (116.0 mgKOH/g and 247.1 mgKOH/g, respectively). The DHL was a solid and was subsequently derivatized into liquid polyols via oxypropylation for their further utilization in the preparation of bio-based rigid polyurethane (BRPU) foam at high percentage of bio-contents (50-70 wt.%). All of the BRPU foams exhibited good compressive strength as compared with the reference foam. At the fixed formulation



recipe, i.e. fixed percentage of physical blowing agent, the compressive modulus of the BRPU foams increased as follows: sucrose polyol reference foam (2695.0 kPa)<DHL50PO50 (5381.0 kPa)<DHL60PO40 (12360.0 kPa). All of the BRPU foams were thermally stable up to approximately 200 °C. The thermal conductivities of the BRPU foams were between 0.030 W/mK and 0.032 W/mK, making them suitable for their utilization as an insulation material.

## 9.5 References

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## Chapter 10

### 10 Low pressure hydrolytic depolymerization of Kraft lignin for the preparation of bio-based rigid polyurethane foam

#### Abstract

A cost-effective and highly efficient low pressure (<150 psig) Kraft lignin (KL) depolymerization proprietary process was developed to produce depolymerized KL (DKL) with a much lower molecular weight (1000-2000 g/mol) from KL ( $M_w \sim 10,000$  g/mole). This process operates in water-polyalcohols (EG, PG or glycerol) mixture media under alkaline conditions employing NaOH as a catalyst. The effects of process parameters including reaction temperature, reaction time, NaOH/KL ratio (w/w) and KL substrate concentration (wt.%) were investigated and the DKLs obtained were characterized with GPC, FTIR,  $^1\text{H}$  NMR and Elemental analysis. The best operating conditions appeared to be 250 °C, 1 h, KL substrate concentration of 20 wt.%, NaOH/KL ratio  $\sim 0.28$  (w/w), leading to  $\leq 0.30\%$  solid residues and  $\sim 90\%$  yield of DKL (with a total hydroxyl number  $\approx 670.1$  mgKOH/g and  $M_w \approx 1050$  g/mole), suitable for the replacement of petroleum polyols in rigid polyurethane (RPU) foam preparation. The effects of type of polyalcohols like ethylene glycol (EG), propylene glycol (PG) and glycerol (G) were also investigate on the yields and  $M_w$ 's of DKLs by performing the reaction at the best operating conditions. The results showed that the depolymerization of KL was effectively achieved in any of the above mentioned polyalcohols; however, it was found that  $M_w$  is slightly higher when employing PG or glycerol as the solvent. The polyalcohols used were recoverable at a recovery rate of  $\sim 95-96$  wt.%, which makes this process more economically viable. The obtained DKL was in solid powder form and further derivatized into liquid polyols via oxypropylation for the preparation of bio-based rigid polyurethane (BRPU) foam at high percentage i.e., 50 wt.% to 70 wt.%, of bio-contents. All BRPU foams were characterized and compared in terms of their physical, mechanical and thermal properties. All BRPU foams exhibit good compressive strength, compared with the reference foam. At the fixed formulation recipe i.e., fixed percentage of physical blowing agent, BRPU foams showed the following order of sequence in terms of their

compressive modulus: Sucrose polyol reference foam (2695.0 kPa)<DKL50PO50 (6936.0 kPa)<DKL60PO40 (8902.0 kPa)<DKL70PO30 (22436.0 kPa). All BRPU foams were thermally stable up to approximately 200 °C and had low thermal conductivities varies between 0.031 W/mK and 0.033 W/mK, and did not show much variation with increasing percentage of bio-polyols, making them suitable for their utilization as an insulation material

**Keywords:** Kraft lignin, depolymerization, catalyst, ethylene glycol, polyols, rigid polyurethane foam.

## 10.1 Introduction

Lignin is considered as the main renewable aromatic resource. It represents a promising alternative feedstock for the production of bio-chemicals, bio-polymers and bio-materials. Lignin (from Latin lignum which means wood) is, after cellulose, the most abundant biopolymer on earth, contributing about 15-30 wt.% of the wood and 12-20 wt.% of the annual plants (Sjöström, 1981). In plants, lignin plays a vital role, ensuring water transportation and providing structural support by cementing cellulose fibers and fibrils (Harkin, 1969). From a chemical point of view, lignin is composed of carbon, hydrogen and oxygen in different proportions and built up of phenylpropane units (C9 or C6-C3) covalently linked by mainly two types of linkages: condensed linkages (e.g., 5-5 and  $\beta$ -1 linkages) and ether linkages (e.g.,  $\alpha$ -O-4,  $\beta$ -O-4 and 4-O-5) (Chakar and Ragauskas, 2004). The type of monomeric units present in lignin structure and their relative abundance depend on its botanic origin, so do the major chemical functional groups presenting in lignin structure such as hydroxyl, methoxyl, carbonyl and carboxyl moieties. Hydroxyl groups and free positions in the aromatic ring are the most characteristic functions in lignin, which determines its reactivity and constitutes the reactive sites being exploited in macromolecular chemistry (Cateto et al., 2011). The percentage of ether linkages in soft- and hardwood lignins was reported to be approximately 56% and 72%, respectively (Pu et al., 2008). Aryl ether linkages can be more easily cleaved than the stable C-C linkages since the latter are stable.

Lignin represents 30% of all non-fossil organic carbon on Earth. Its availability exceeds 300 billion tons (Smolarski, 2012), increasing annually by around 20 billion tons. Large quantities of lignin are yearly available from numerous pulping mills and biorefinery industries (such as cellulosic ethanol plants). It was estimated that 50-55 million metric tons of lignin was extracted in the pulp and paper industry in 2010, but only 2% (1 million tonnes) has been commercialized for the formulation of dispersants, adhesives, and surfactants or as antioxidants in plastics and rubbers. The challenge is then to explore the potential of producing valuable functional molecules from lignin through chemical modifications. One of the major problems still remains is its complex structure and its versatility depending on its origin, separation and fragmentation processes, which limits its utilization.

Currently lignin is often utilized as a filler or additive in plastics, but due to its highly functional character (i.e., rich in phenolic and aliphatic hydroxyl groups) it may be an excellent renewable feedstock for a variety of bio-based materials through chemical modifications, which has driven numerous research efforts in the past decades (Laurichesse and Avérous, 2014). Because of lignin's special phenyl propanol or polymer structure and aryl-alkyl ether bonding, lignin is considered as a potential alternative to petroleum for phenolic chemicals and polymers. Substituting petroleum with renewable feedstock for chemical and material's production is especially of significance and interest nowadays when petroleum prices are escalating and there are growing concerns on depletion of fossil resources. However, original lignin with a very large molecular weight has much lower reactivity due to the steric hindrance effect (Cheng et al., 2012). In this respect, lignin depolymerization can be a very promising approach to increase its functionality and reactivity. The primary purpose of lignin depolymerization is to convert the complex lignin compound into smaller molecules of oligomers and monomers for further applications (Wang et al., 2013). It was found that chemical or thermal chemical depolymerization of lignin via the cleavage of ether linkages in lignin structure (Zakzeski et al., 2010) has advantages for better reaction control and higher yields, which provides great potential in conversion of lignin into renewable chemicals.



Chemical depolymerization of lignin can be divided into five categories according to [Wang et al. \(2013\)](#) based on different chemicals/catalysts applied in the depolymerization process, includes., (1) base-catalyzed, (2) acid-catalyzed, (3) metallic catalyzed, (4) ionic liquids-assisted, and (5) sub- or supercritical fluids-assisted lignin depolymerization. In lignin chemical depolymerization processes, solvents (single solvent or in combination with a co-solvent) and catalysts were found to be critical. Lignin hydrolytic depolymerization in water under acidic conditions has been extensively studied ([Lundquist, 1976](#); [Matsushita and Yasuda, 2005](#)); but its major drawback is the high yield of solid residue due to unavoidable repolymerization/condensation of intermediate products during the process ([Yuan et al., 2010](#)). Metallic catalysts helped to improve the selectivity towards the desired product, while the major issue was their fast deactivation, making their use much more expensive ([Ye et al., 2012](#)). Ionic liquids (ILs) proved to be effective solvents for lignin dissolution ([Kilpeläinen et al., 2007](#)) and depolymerization. However, the high cost of ILs ([Zhu, 2008](#)) and their difficulty in separation from depolymerized products would greatly limit their use ([Zakzeski et al., 2010](#)). Sub- and supercritical organic solvents/fluids alone or in combinations with alkaline catalysts have been reported very efficient in the depolymerization of lignin ([Cheng et al., 2012](#); [Yuan et al., 2010](#)). Similar to ionic liquids, Sub- and supercritical organic solvents/fluids have also been employed for lignin depolymerization owing to their good solubility for lignin ([Hossain and Aldous, 2012](#); [Cox, 2012](#)). Recently, hydrolytic depolymerization using water alone as a solvent under alkaline medium has gained more attention for the depolymerization of KL into low molecular weight products, i.e., depolymerized KL (DKL) in a solid or powder form ([Mahmood et al., 2013](#)).

Polyurethane (PU) is commonly synthesized through a polyaddition reaction between polyfunctional alcohols (polyether or polyester polyols) and polyisocyanate to form urethane linkages (-NH-(C=O)-O-). Currently, both the polyisocyanates and polyols are derived from petroleum resources. PU has rapidly grown to be one of the most widely used synthetic polymers with its continuously increasing global market. It has varied applications in different area, including liquid coatings and paints, adhesives, tough elastomers, rigid foams, flexible foams, and fibers ([Li and Ragauskas, 2012](#)). Rigid PU

foam is a highly crosslinked polymer with a closed cell structure. These materials offer low density, thermal conductivity, moisture permeability and high dimensional stability and strengths leading to wide applications in construction, refrigeration appliances, and technical insulations (Li and Ragauskas, 2012; Abi-Saleh et al., 2002). Rigid PU foam is the most efficient insulating material. Thermal conductivity of RPU foam is normally between 0.020 and 0.030 W/mK depending on the density. The thermal conductivity factor of PU foam is two times lower than that of polystyrene which is an alternative material for insulation purposes. On the other hand the physical and mechanical properties of RPU foam are superior to those of polystyrene (Zatorski et al., 2008).

Until now, polyols are mostly derived from petroleum resources (Li and Ragauskas, 2012). However, due to dwindling petroleum resources there are increasing interests to explore renewable low cost resources as an alternative feedstock for the preparation of polyols and PUs, which are expected to replace petroleum derived polyols either partially or completely and to have a positive impact on the characteristics of resulting foam. The obtained DKLs have multiple hydroxyl groups in their structures, thus they can be used as polyols for the preparation of rigid polyurethanes (RPU) foams (Demharter, 1998). Although with much lower reactivity (Cheng et al., 2012), even crude lignin can be directly incorporated into PU formulations due to the presence of aliphatic and aromatic hydroxyl groups in its structure as the reactive sites (Cateto et al., 2008), however, more than 30 wt.% incorporation negatively affect RPU foam properties (Yoshida et al., 1987). The most critical properties of polyols are their hydroxyl number/functionality and equivalent weight. Original lignins have high molecular weights and lower functionality. Thus, depolymerization of lignin is beneficial by reducing molecular weight of lignin and increasing OH functionality of the depolymerized products, and hence leading to an increase in reactivity. Due to sky-rocketed prices of petroleum-based products, bio-based polyols (Bueno-Ferrer et al., 2012) or ligno-polyols (Borges da Silva et al., 2009) have drawn increasing attention. Hydrolytic depolymerization can produce low molecular weight bio-polyol products with desirable characteristics for their further utilization in the preparation of RPU foams. Also, for the polyols feedstocks which are in solid form oxypropylation can be used for their transformation into liquid polyols. By means of oxypropylation, the hydroxyl groups, in particular the phenolic one which is hardly

accessible because they are entrapped inside the molecule (Cateto et al., 2013) can be liberated from steric hindrance. Moreover, such chain extension reaction leads to the introduction of multiple ether moieties and resulting in liquid polyols from solid lignin.

Nevertheless, the above methods for lignin depolymerization including the hydrolytic depolymerization are restricted by their high operation costs due to the intense reaction conditions (combination of high temperatures and pressure) under either acidic or basic conditions. There is a growing need for exploration of efficient and cost-effective routes employing atmospheric to low pressure. The main objectives of the present work were to achieve cost-effective depolymerization of KL ( $M_w \sim 10,000$  g/mole) at low pressure ( $\leq 150$  psig) employing water-polyalcohol mixture as a novel solvent and NaOH as a catalyst, and utilize the produced DKL as bio-polyols after oxypropylation for the preparation of RPU foam at high percentage of bio-contents (50 wt.%-70 wt.%). All bio-based RPU (BRPU) foams were characterized and compared in terms of their physical, mechanical and thermal properties. To the best of the authors' knowledge no systematic study has been reported by far in the public literature for the depolymerization of KL into low  $M_w$  bio-polyols products operating at low pressure.

## 10.2 Methods

### 10.2.1 Materials

Softwood Kraft lignin (KL) used in this study was provided by FPInnovations produced using the proprietary LignoForce process (Kouisni, 2012) in its pilot plant in Thunder Bay, Ontario. It is a yellow-brown powder with weak odor and specific gravity of 0.80. The relative weight-average molecular weight ( $M_w$ ) of KL is  $\approx 10,000$  g/mol (PDI  $\approx 2.0$ ) based on our GPC-UV analysis. The original KL has an ash content of 0.5 wt.% (by ashing at 700 °C in a muffle furnace for 4 h), and has the following elemental composition (on dry and ash free basis): 63.8 wt.% C, 5.4 wt.% H, 0.02 wt.% N, 5.2 wt.% S and 25.6 wt.% O (by difference). The other chemicals used in the study were NaOH, ethylene glycol (EG), acetone, sulfuric acid ( $H_2SO_4$ ), pyridine, acetic anhydride, *d*-chloroform, tetrahydrofuran (THF, HPLC grade), HCl, dibromomethane ( $CH_2Br_2$ ),

glycerol, KOH, propylene oxide (PO), polymeric MDI, sucrose polyol (JEFFOL SD-361), triethanolamine (TEA), triethylene diamine (TEDA or Diaza), stannous octoate, silicon oil etc, were all reagent grade purchased from Sigma-Aldrich, used without further purification or any treatment. The physical characteristics of the chemicals used in the foam preparation are given in Table 10-1.

Table 10-1 Physical Characteristics of the Chemicals

Ingredients	Functionality	Equivalent weight (g/mol)	-OH # (mgKOH/g)	Comments
PMDI	2.7	135.0	-	NCO contents: 31.2%
Glycerol	3.0	30.7	1829.4	Crosslinking agent
Sucrose polyol	8.0	155.8	360.0	Polyol
Water	2.0	9.0	6233.3	Chemical blowing agent
Acetone	-	-	-	Physical blowing agent
Poly(siloxane ether)	-	-	-	Silicon surfactant
Triethylene diamine	-	-	-	Foaming catalyst
Stannous Octoate	-	-	-	Gelation catalyst
Triethanol amine	3.0	49.73	1128.1	Co-catalys

### 10.2.2 Kraft lignin depolymerization

Kraft lignin (KL) was depolymerized via a proprietary process using water-polyalcohols (EG/PG/GL) mixture as a solvent under acid or alkaline conditions using H<sub>2</sub>SO<sub>4</sub> or NaOH, respectively, as a catalyst under low pressure <150 psig. The KL depolymerization experiments were performed in a 100 mL Parr reactor, equipped with a pressure gauge, thermocouple, stirrer, gas line and a sampling line. In a typical run, 12 g KL with 3.4 g NaOH (NaOH/KL ratio ≈0.28 (w/w)), 2.5 g water and 42.1 g EG were loaded into the reactor. After leak check with compressed nitrogen, the reactor was heated up to the desired temperature (180-280 °C) under the stirring (290 rpm). After reaching the desired temperature, the reactor was soaked to allow reactions for a desired

time, and then the reactions were stopped by quenching the reactor with a cold water bath. The reaction products were washed out from reactor using distilled water followed by acidification to pH ~3-4, in order to facilitate the precipitation of the depolymerized Kraft lignin (DKL) products. The precipitated DKL was then separated by filtration. The aqueous phase was evaporated to recover EG or other polyalcohols. The recovery yield of the solvent polyalcohols was at ~95-96 wt.%. The precipitated solid was dissolved in acetone and filtered to get solid residual (SR) – the acetone insoluble fraction. Finally, the DKL was recovered by rotary evaporation of the acetone under reduced pressure at 50°C, and the DKL products yields were determined. All the data for product yields presented are the average of duplicate-triplicate runs with relative errors. The SRs were dried at 105 °C in air for 24 h in an oven and weighed to obtain SR yield as wt.% of the original KL on a dry basis.

### 10.2.3 Oxypropylation of DKL

The obtained DKL at the best operating conditions, although in solid form, was used as bio-polyols in this work after being further transferred into liquid polyols via oxypropylation. The oxypropylated lignin polyol was then employed as a feedstock for the PU foam preparation. Oxypropylation of DKL was carried out in a 100 mL Parr reactor. In a typical run, 18.9 g of DKL, 21.21 g propylene oxide (PO), 2.31 g of anhydrous mixture of glycerol & KOH (%KOH in mixture was 11wt.%) and 16.8 g of acetone. After all the ingredients were loaded, the reactor (under atmospheric pressure) was heated up to 150 °C. Initially, pressure in the reactor increased to a maximum of 150 psig and then dropped to the original pressure ~14.7 psig (or 1.0 atm-g) after 2 h reaction, implying complete consumption of PO or completion of the reaction. After cooling the system to room temperature, the reactor contents were completely rinsed into a beaker using acetone followed by neutralization of the reaction mixture using sulfuric acid. The neutralized reaction mixture was then filtered through a Buchner funnel to separate solid residues from acetone soluble phase. The acetone soluble filtrate was transferred to a pre-weighed Erlenmeyer flask to remove acetone and any unused PO (if any) with a rotary evaporator at 60 °C.

### 10.2.4 Polyurethane foam preparation

All the foam samples were prepared in 455-ml plastic cups using one pot method. Typically the rigid PU foam formulation in this study includes a polyol combined with 10% (w/w) of glycerol (a co-crosslinking agent). For comparison, reference foam was prepared using sucrose polyols at 0% DKL. Additionally the formulation includes a physical blowing agent (acetone at 20% (w/w)), a catalyst combination (mixture with equal amounts of stannous octoate and Diaza or TEDA at 2% (w/w)), surfactant at 2% (w/w) and water at 2% (w/w). The addition amounts of the blowing agent, catalyst, surfactant and water were determined with respect to the total weight of polyol used. PMDI was added at a NCO/OH ratio of 1.1. The foam preparation procedure used was comprised of the following steps: (1) Desired polyols, catalysts and blowing agents were all weighed in a cup and the premixing of mixture were carried out at 550 rpm for 10-12 s to obtain a well homogeneous mixture and (2) Pre-calculated PMDI was then transferred in to the cup and the mixture was stirred vigorously for another 12-15s. The mixture was then placed on a leveled surface in a fume hood and let the foam rise at the ambient temperature ( $23\pm 2$  °C). All the foam samples were left in the fume hood for 24-48 h for curing before the sample would be further analyzed. The sample shrinkage, structural uniformity, stability and cells appearance could be observed at this point. However, prior to further characterizations, the foam samples were conditioned for a minimum of 24 h to a maximum of 1 week, depending on the requirements. In the synthesis of bio-based RPU (BRPU) foams at different bio-replacements ratios, sucrose polyol was not used and glycerol was kept at 10 wt.% based on the total weight of polyols used.

### 10.2.5 Product characterization

The relative molecular weights of KL, depolymerized KL (DKL) and oxypropylated DKL were measured with a Waters Breeze GPC-HPLC (gel permeation chromatography-high performance liquid chromatography) instrument (1525 binary pump, UV detector at 270 nm; Waters Styrylgel HR1 column at a column temperature of 40 °C) using tetrahydrofuran (THF) as the eluent at a flow rate of 1 ml/min with linear polystyrene standards for building the molecular weight calibration curve. The functional groups of KL, DKLs and oxypropylated DKL were analyzed by Fourier Transform

Infrared Spectroscopy (FTIR). Proton nuclear magnetic resonance ( $^1\text{H-NMR}$ ) spectra for KL and DKL were acquired at  $25^\circ\text{C}$  using a Varian Inova 600 NMR spectrometer equipped with a Varian 5mm triple-resonance indirect-detection HCX probe. A total of 16-32 scans were accumulated using a 2s recycle delay, 3.6s acquisition time, a 45-degree tip angle ( $\text{pw} = 4.8 \text{ us}$ ), and a spectral width from -2 ppm to 14 ppm ( $\text{sw} = 9000.9 \text{ Hz}$ ). Quantitative  $^1\text{H-NMR}$  spectra analysis was realized using acetylated samples of KL and DKLs. Briefly, 1 g of dried sample was dissolved in a 1:1 (v/v) mixture of pyridine (5 mL) and acetic anhydride (5 mL) in a vial followed by stirring for 24 to 48 hr. The mixture was then transferred into a beaker containing 100 mL of ice-cooled 1 wt.% HCl solution. The resulting precipitates of acetylated samples were washed with distilled water to  $\text{pH} \approx 7$ . The samples were then dried at  $105^\circ\text{C}$  for 24 hr to remove residual water prior to the quantitative  $^1\text{H-NMR}$  spectra analysis. Dibromomethane ( $\text{CH}_2\text{Br}_2$ ) was used as an internal standard with a characteristic peak is at 4.9 ppm. To determine hydroxyl number by  $^1\text{H-NMR}$ , the samples were prepared by first weighing 30.0 mg of the acetylated KL or DKL and 15.0 mg of the internal standard in a vial and dissolved in *d*-chloroform ( $\approx 1000\text{-}1500 \text{ mg}$ ) then the sample was transferred into a 5 mm NMR tube via a transfer pipette for the subsequent NMR analysis. Hydroxyl number of the oxypropylated DKL sample was measured as per ASTM D4274-99 using a Potentiometric Titrator (Titroline 7000 Titrator). The viscosity of oxypropylated DKL sample was measured by using BROOKFIELD CAP 2000+VISCOSMETER at  $80^\circ\text{C}$ .

The apparent densities of foam samples were measured according to ASTM D1622-03. The mechanical properties of PUF samples were measured at ambient conditions on an ADMET Universal Testing Machine (Model SM-1000-38). Modulus of elasticity (Young's modulus or compressive modulus) (initial linear slope of the stress-strain curve) and compressive strength at 10% deformation, were determined by performing the stress-strain tests according to ASTM D 1621-00. Thermal conductivities of the foam samples were measured using KD2 PRO thermal properties analyzer with SH-1 dual needle sensor (1.3 mm diameter x 3 cm long, 6 mm spacing) capable of measuring thermal conductivity in the range of 0.02 to 2.00 W/mK. The specimen size used for thermal conductivity analysis was 40 mm x 40 mm x 20 mm. Thermal stability of the

foams were measured by *Pyris 1* TGA Diamond, Perkin–Elmer Thermogravimetric analyzer (TGA), under a N<sub>2</sub> and air flow (20 ml/min) respectively, from 30 °C to 800 °C at 10 °C/min. Morphology of the foams was observed by Hitachi S-4500 field emission cross beam scanning electron microscope (SEM). After examination by SEM, selected locations on the foam surface were subjected to a cross-sectional cut and the sample was coated with osmium, and imaged using a focused ion beam LEO (Zeiss, Thornwood, NY, USA) 1540XB SEM.

## 10.3 Results and discussions

The depolymerized products were soluble in water, but after acidification and subsequent filtration the products were water insoluble but organic soluble (in such as acetone and THF).

### 10.3.1 Depolymerization of KL under acid vs basic medium

KL was depolymerized under both acidic and basic medium using the H<sub>2</sub>SO<sub>4</sub> and NaOH as a catalyst, respectively. Experiments were conducted using same weight percentages of both catalysts based on KL loaded into the reactor i.e. 2 wt.% H<sub>2</sub>SO<sub>4</sub> or 2 wt.% NaOH (corresponding to 10 mol% based on 1:1 mole ratio of NaOH:KL). The results showed that under acidic conditions, the overall yield of DKL was above 100 wt.% implying the prominent occurrence of repolymerization of KL and condensation of KL with the solvent (moreover, the solvent itself such as EG could also self-polymerize under acidic conditions). During acidolysis reaction of KL, repolymerization and condensation reactions also increased the molecular weights of the resulting products (Lundquist, 1976). Under acidic conditions without any added nucleophile, the predominant reactions in lignin could be fragmentation by acidolysis of  $\beta$ -O-4' linkages and repolymerization of the fragments via acid catalyzed condensation between the aromatic C<sub>3</sub> or C<sub>5</sub> and a carbonium ion, normally located at C <sub>$\alpha$</sub>  of the side chain (Lundquist, 1976; Sturgeon et al., 2014). In the former reaction, structures of the Hibbert ketone type would be formed together with a new phenolic end group, whereas the latter would form a new stable carbon-carbon linkage between two lignin units. Both types of reactions have a common intermediate, a carbonium ion, and they occur more or less simultaneously. The



simultaneous repolymerization of lignin during an acid catalyzed treatment is an undesirable reaction since it leads to an increase in heterogeneity of the resulting material. In addition, solubility and reactivity properties of the treated lignin products could be negatively affected (Li et al., 2007). Under acidic conditions, the yield of solid residues (SRs) was as high as ~35 wt.% due to excessive cross-linking reactions. Therefore, depolymerization of KL in acidic media is not desirable for obtaining low molecular weight products.

In contrast, depolymerization of KL under basic medium using NaOH as a catalyst produced DKL products of reduced molecular weights and at very high yields (>95 wt.%). The yields of DKL and SRs achieved from the acid- and base-catalyzed KL depolymerization are given in Table 10-2 and their GPC curves are shown in Figure 10-1. Therefore, more studies on effects of various operating parameters on the KL depolymerization were carried out in a basic medium using NaOH as the catalyst.

Table 10-2 Yields of DKL and SR's for KL depolymerization in acidic and basic medium (Other reaction conditions: 250 °C, 1 h, 20 wt.% substrate concentration, EG/KL ratio of 4.0 (w/w) and 2 wt.% catalyst addition)

Reaction media	Yield of SR's (wt.%)	Yield of DKL (wt.%)	$M_w$ (g/mole)
Original KL	-	-	10,000 (Bimodal)
Acidic	35.37±1.0	124.11±2.1	Bimodal
Alkaline	0.42±1.0	95.32±0.65	9680

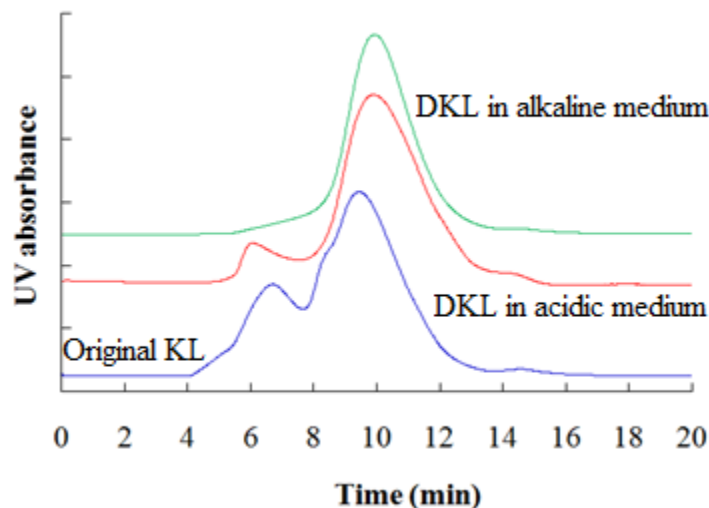


Figure 10-1 GPC curves of the original KL and the obtained DKL product from the KL depolymerization in acidic or alkaline medium (Other reaction conditions: 250 °C, 1 h, 20 wt.% KL substrate concentration, EG/KL ratio of 4.0 (w/w) and 2 wt.% catalyst addition)

### 10.3.2 Effects of addition amount of catalyst

Effects of mole percentage of NaOH on KL depolymerization were studied at 200 °C and 250 °C under two different reaction conditions employing different reaction media, i.e., (a) EG as a sole solvent without the addition of water and (b) water-EG mixture. Initially the experiments were conducted at 200 °C for 1 h at an EG/KL ratio of ~4.0 (w/w) and initial reactor pressure of ~1 atm-g with varying mole % of NaOH from 10% to 50% based on 1:1 mole ratio of NaOH:KL in EG without water. During the whole reaction, the pressure of system remained at ~1 atm-g. The yields of SR and DKLs along with their associated molecular weights are shown in Table 10-3. The results showed that DKL depolymerization at 200 °C employing EG alone as a solvent, no reduction in molecular weight was achieved, and the yields of DKL while increasing the mole % of NaOH remained the same, although the SR yields decreased slightly. Water as a co-solvent was added in reaction system operating at 200 °C, but the results as shown in Table 10-3 were not very satisfactory even the mole % of NaOH was further increased up to 128%.

Table 10-3 Effects of mole % of NaOH on yields of SRs and DKL (Other reaction conditions: 1 h, substrate concentration: 20 wt.% and EG/KL ratio of 4.0 (w/w))

Molar %NaOH	NaOH (wt.%)	Yield of SR's (wt.%)	Yield of DKL (wt.%)	$M_w$ (g/mole)
200 °C in EG without water				
KL	-	-	-	10,000
10	2.2	5.20±1.0	95.11±0.50	Bimodal
20	4.4	4.81±1.0	95.63±0.25	Bimodal
30	6.6	3.52±1.0	96.54±0.50	Bimodal
50	11.1	2.82±1.0	96.61±1.0	Bimodal
200 °C in EG with water as a co-solvent				
50	11.1	2.53±1.0	85.14±1.0	Bimodal
100	22.2	2.85±0.50	83.73±1.0	Bimodal
128	28.4	3.37±0.5	95.52±1.0	Bimodal
250 °C in EG without water				
50	11.1	3.25±1.0	95.81±0.65	Bimodal
100	22.2	2.86±1.0	96.35±0.35	Bimodal
128	28.4	2.37±1.0	96.63±0.50	Bimodal
250 °C in EG with water as a co-solvent				
10	2.2	3.91±1.0	95.34±0.85	9550
20	4.4	3.62±1.0	95.65±0.45	8360
30	6.6	3.55±1.0	95.60±1.1	7360
50	11.1	0.89±1.0	95.10±1.0	5400
100	22.2	0.41±0.65	94.68±1.0	2450
128	28.4	0.30±0.50	90.10±0.50	1050
140	31.1	0.31±0.50	89.95±0.25	960

Temperature is the most critical parameter for hydrolytic depolymerization of lignin in water (Xu et al., 2008). Thus, trials were made at a higher temperature i.e., 250 °C using both solvent systems (EG alone without water and EG with water as a co-solvent). In the EG alone solvent system, the results achieved were not satisfactory as the DKL products

showed very high  $M_w$  values. In contrast, the results were very promising from the experiments at 250 °C when employing water as a co-solvent in EG, as shown in Table 10-3. The presence of a small amount of water in the reaction medium containing KL, EG and NaOH catalyst led to generation of some pressure (up to approx. 150 psig) inside the reaction system, likely due to the water vapor pressure (i.e., ~150 psig at 250 °C).

At 250 °C employing water-EG solvent mixture, the mole percentages of NaOH were varied from 10% to 140% and the corresponding yields of SRs and DKLs and the  $M_w$ 's of DKLs are shown in Table 10-3. It can be clearly seen that at a lower mole% of NaOH between 10% and 50%, the DKL yield remained almost the same. However, the SR yield was significantly reduced at 50% suggesting suppressed extent of repolymerization/condensation reactions at higher NaOH concentration (Mahmood et al., 2013). The yield of SRs dropped further to from approximately 0.89 wt.% to 0.41 wt.% when increasing the mole percentage of NaOH from 50% to 100%, but then it remained almost constant if further increasing the mole % of NaOH from 128% to 140%. The DKL yield remained almost the same at 94.5±0.5 wt.% when increasing molar percentage of NaOH from 50% to 100%. While further increasing the NaOH mole percentage from 128% to 140%, the DKL yield was slightly reduced to 90.5±0.5 wt.%. Although the  $M_w$ 's of DKLs were still high (5000-10000 g/mole) at a lower mole percentage of NaOH (in the range of 10 -50%), the  $M_w$ 's of DKLs dropped significantly to approximately 2450 g/mole and ~1000 g/mole when the mole % of NaOH was increased to 100% and 128 or 140%, respectively. A possible reason could be that a higher mole percentage of NaOH would transform KL to its sodium phenolate form, which helped to dissolve lignin in the solvent, and hence facilitated the depolymerization reactions. The results demonstrated that water-EG mixture is an efficient solvent for depolymerizing high molecular weight KL into low  $M_w$  products under low pressure ( $\leq 150$  psig), which is most likely owing to the positive role of water in hydrolytic de-polymerization of lignin (Mahmood et al., 2013). Therefore, in view of the utilization of produced DKL for preparing polyols for rigid polyurethane foams production (requiring lower  $M_w$  products), 100% and 128 mole percentages of NaOH were selected in further investigations on the other operating

parameters, e.g., reaction temperature, time, substrate concentration, and type of polyalcohol.

### 10.3.3 Effects of reaction temperature

Temperature is one of the most critical parameters for lignin depolymerization in water (Xu et al., 2008). The effects of reaction temperatures were investigated on KL depolymerization were investigated in water-polyalcohols mixture with 100% and 128% mole% of NaOH at a temperature varying from 180 °C to 280 °C. The results are given in Table 10-4. The molecular weight distribution curves of some prominent samples are illustrated in Figure 10-2.

Table 10-4 Effects of reaction temperature on the yields of DKL and SR and  $M_w$ 's of DKL (Other reaction conditions: 1 h, KL substrate concentration of 20 wt.%, EG/KL ratio of 4.0 (w/w))

Reaction temp. (°C)	Molar % NaOH (NaOH; wt.%)	Yield of SR's (wt.%)	Yield of DKL (wt.%)	$M_w$ (g/mole)
KL	-	-	-	Bimodal
180	128 (28.4)	1.46±0.10	98.46±0.25	Bimodal
200	128 (28.4)	3.37±0.15	95.52±0.25	Bimodal
220	128 (28.4)	0.28±0.50	93.28±0.50	7230
250	100 (22.2)	0.41±0.65	94.68±1.0	2560
	128 (28.4)	0.30±0.50	90.10±0.50	1050
280	100 (22.2)	0.67±0.50	86.20±1.0	950
	128 (28.4)	0.53±0.50	87.53±0.5	940

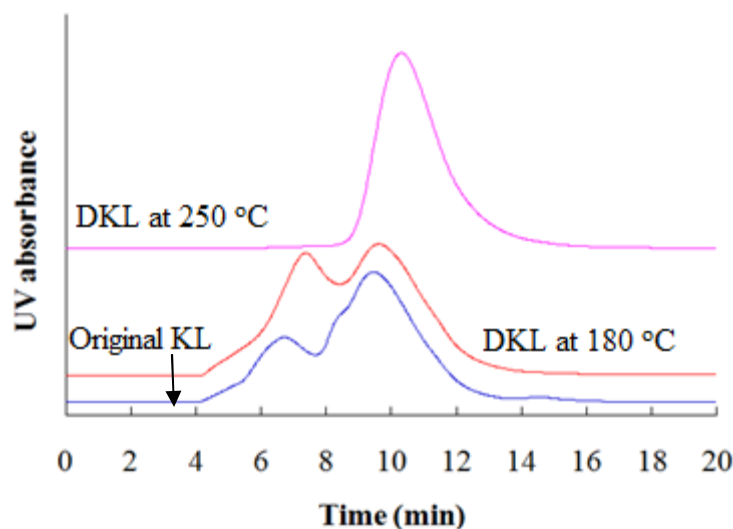


Figure 10-2 GPC curves of DKLs obtained from KL depolymerization at various reaction temperatures (Other reaction conditions: 1 h, 20 wt.% KL substrate concentration, EG/KL ratio of 4.0 (w/w), 128 mole% NaOH or NaOH/KL weight ratio of 0.28)

Experiments were conducted at 128 molar percentages (28.4 wt.%) of NaOH over the temperature range of 180 °C to 280 °C. However, at 250 °C and 280 °C, effect of lower molar % of NaOH i.e. 100% (22.2 wt.%) was also studied to investigate its effect on yield and  $M_w$  values. At the 128 molar % (28.4 wt.%) of NaOH when the temperature was increased from 180 °C to 200 °C there was a relatively very low degree of KL depolymerization. However, at 220 °C for ~128% molar of NaOH (28.4 wt.%),  $M_w$  of DKL reduced to 7230 g/mole. At 250 °C for 100 molar% of NaOH, the yield of DKL was very high (~94.68 wt.%) with a prominent reduction in  $M_w$  ~2560 g/mole was observed. This suggests that the temperature has a drastic effect on the cleavage of alkyl-aryl ether linkages in lignin (Mahmood et al., 2013). At 250 °C varying the molar % of NaOH from 100% to 128% further reduced the  $M_w$  ~1050 g/mole, likely due to the combined effect of increasing lignin solubility as sodium phenolate which instigate the KL hydrolysis reaction and lead to efficient cleavage of alkyl-aryl ether linkages. The hydrolytic depolymerization of KL was mainly due to the breakage of ether linkages being attacked by hydroxyl ions. With further increasing temperature to 280 °C at molar percentage of NaOH of 100%, the yield of DKL (~86.2 wt.%) was reduced slightly, however  $M_w$  (~950

g/mole) decrease significantly with a slight increase of SR's yield (0.41% to 0.67 wt.%). At 280 °C, varying NaOH molar % from 100% to 128% has negligible effects on the yields of DKL and SR's as well as on  $M_w$ . Considering yields of SR and DKL and  $M_w$  of DKL, 250 °C at molar percentage of NaOH ~128% appears to be the best temperature for the hydrolytic depolymerization of KL in water-polyalcohol co-solvent reaction mixture.

### 10.3.4 Effects of reaction time

The experiments in this section were to examine the effects of reaction time on hydrolytic depolymerization of KL at 250 °C with ~128 mole% of NaOH (NaOH/KL =0.28 w/w) in a water-polyalcohol mixture medium. The products yields and the  $M_w$  of DKL obtained from KL depolymerization for various lengths of reaction time (30-240 min) illustrated in Figure 10-3. At 250 °C for 30 min the yield of DKL was the highest (~99 wt.%), but the corresponding  $M_w$  was very high (~4700 g/mole). The yield of DKL dropped to approximately 90 wt.% if increasing the reaction time to 60 min, but  $M_w$  reduced to ~1050 g/mole. However, increasing the reaction time to 120 min and 180 min produced negligible changes in the yield of DKL and  $M_w$ . Further increasing the reaction time to 240 min, yield of DKL remained almost the same, the yield of SR increased to 2.28 wt.% which could be due to the crosslinking reactions, prominent at a longer reaction time (Mahmood et al., 2013). The  $M_w$  of DKLs was increased from 1170 g/mole at 180 min to 1720 g/mole at 240 min, which could be attributed to condensation reactions between the lignin phenolic ortho positions and aliphatic hydroxyl groups forming cross-linking of different lignin molecules. In terms of both yield and  $M_w$  of DKL products, the best reaction conditions appeared to be 60 min at 250 °C.

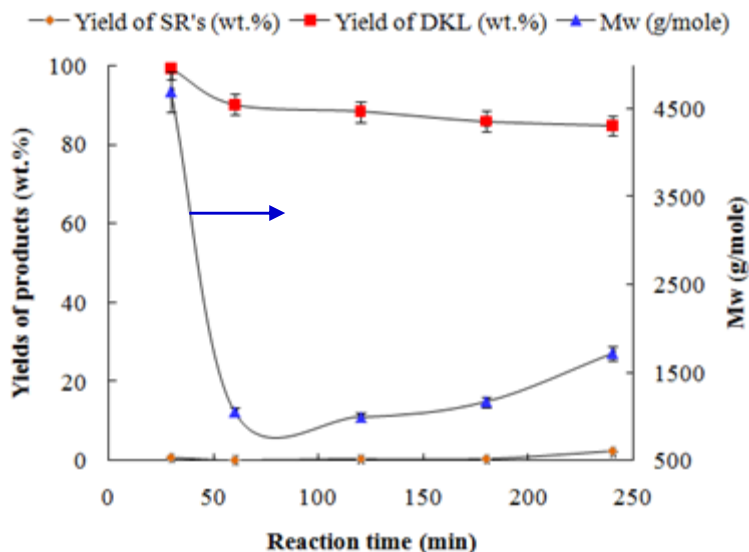


Figure 10-3 Effects of reaction time on yield and molecular weight of DKL (Other reaction conditions: 250 °C, KL substrate concentration of 20 wt.%, EG/KL ratio of 4.0 (w/w) and 128 mole% of NaOH)

### 10.3.5 Effects of KL substrate concentration

KL depolymerization runs with various KL substrate concentration were carried out at 250 °C for 60 min and 128 mole% of NaOH (or NaOH/KL mass ratio of 0.28), and the yields of DKL, SR and the  $M_w$ 's of DKLs are given in Table 10-5. The yield of DKL remained almost the same with increasing KL substrate concentration from 10 wt.% to 30 wt.%, while  $M_w$  increased significantly from 920 g/mole to 3550 g/mole. At a substrate concentration below 20 wt.%, the yield of SR was almost unchanged either. However, the yield of SR was found increased drastically from 0.3 wt.% to ~8.70 wt.% while increasing KL substrate concentration from 20 to 30 wt.%. The sharp increase in SR yield at a very high substrate concentration could be due to the insufficient amount of solvent for the KL hydrolytic depolymerization, which favors condensation/repolymerization reactions, hence increasing the SR yield and  $M_w$  of the DKL. Considering both the efficiency and the yield and  $M_w$  of DKL, 20 wt.% KL substrate concentration was chosen for further studies of this process.



Table 10-5 Effects of varying KL (w/w) substrate concentration on the products yields and  $M_w$  of DKL (Other reaction conditions: 250 °C, 60 min, and 128 mole% of NaOH)

KL concentration (w/w)	Yield of SR's (wt.%)	Yield of DKL (wt.%)	$M_w$ (g/mole)
10.0	0.22±0.50	85.6±1.0	920
20.0	0.30±0.50	90.1±0.50	1020
30.0	8.70±1.0	83.8±1.0	3550

Hence, with respect to both yield and  $M_w$  of the DKL products, the best operating conditions appeared to be at 250 °C, 1 h, 20 wt.% KL concentration, polyalcohol/KL ratio ~4.0 (w/w) and 28.4 wt.% NaOH corresponding to ~128% mole % of NaOH.

### 10.3.6 Effect of type of polyalcohols on KL depolymerization

Three polyalcohols, i.e., ethylene glycol (EG), propylene glycol (PG) and glycerol were tested respectively as a solvent for KL depolymerization, and the yields of DKL & SRs and  $M_w$  of DKL are shown in Figure 10-4. The effects of different polyalcohols were studied at the selected best reaction conditions as described above. Although all these polyalcohols can be used as solvents (with water as a co-solvent) in KL depolymerization, producing low  $M_w$  (~ 1000 g/mole) DKL products at a yield of  $\geq 78$  wt.%. The results as given in Figure 10-4 imply that the type of polyalcohol has a marked influence on the yield and  $M_w$  of DKL. It was reported previously that solvents that are even chemically similar (i.e., with similar functional groups, such as propylene glycol and ethylene glycol) might still differ in their performance when used as a solvent for a reaction (Sanghi and Singh, 2012). It can be seen from Figure 10-4 that for KL depolymerization the EG solvent provides the lowest  $M_w$  and highest DKL yield when compared with PG and glycerol. The superb performance of EG might be attributed to its lower viscosity, superior heat transfer efficiency and moderately low dielectric constant (Rezzoug and Capart, 2002). Thus, in this study, EG was selected as the best solvent. The

KL depolymerization products, i.e., DKLs, are -OH rich polyols which can be very suitable as feedstock for the preparation of polyurethanes (Ye et al., 2014).

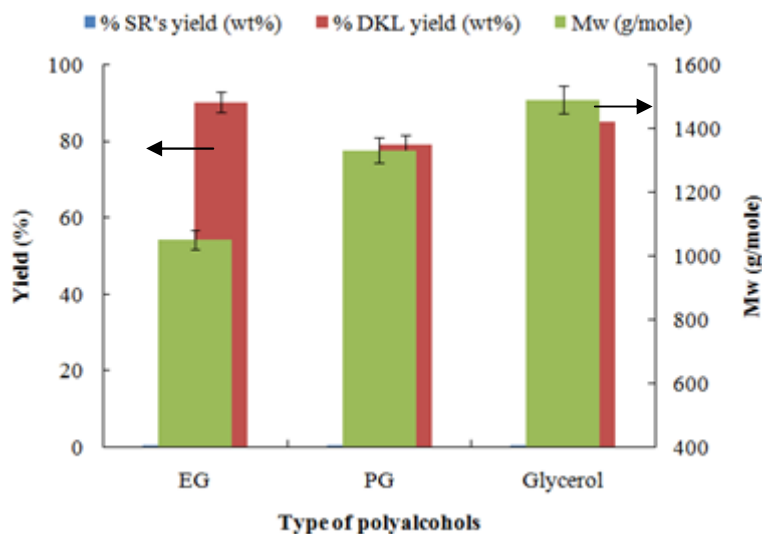


Figure 10-4 Effects of various solvents on yield and  $M_w$  of DKL (Other reaction conditions: 250 °C, 60 min, KL substrate concentration of 20 wt.%, EG/KL ratio of 0.40 (w/w) and 128 mole% of NaOH)

In authors' previous paper (Mahmood et al., 2013) hydrolytic depolymerization of KL was carried using water as the sole solvent in an alkaline medium using NaOH as a catalyst. At the same operating conditions of 250 °C, 60 min, substrate concentration  $\approx$ 20 wt.% and NaOH/KL ratio (w/w)  $\approx$ 0.28 (or 128 mole% of NaOH), the yield of DL was  $\approx$ 92 wt.% with  $M_w \approx$ 3310 g/mole, and SR  $\approx$ 0.5wt.%. To reach  $M_w \approx$ 1000 g/mole, the reaction needed to be carried out at 300 °C. For KL hydrolytic depolymerization reaction in water, depending on the reaction temperature, the pressure of the reactor reached 5 MPa at 250 °C and 8 MPa at 300 °C. However, due to costs associated with the high pressure reactor systems, it is more advantageous to do depolymerize KL under atmospheric to low pressure reaction system.

This present study was conducted to establish a new route for KL depolymerization in water-polyalcohols co-solvent mixture. The best operating conditions for KL

depolymerization using water-EG co-solvent mixture were 250 °C, 60 min, 20 wt.% substrate concentration, NaOH/KL ratio  $\approx 0.28$  (w/w) (or 128 mole% of NaOH). The corresponding yield of DKL was  $\sim 90$  wt.%, and the obtained DKL has a low molecular weight  $M_w \approx 1000$  g/mole and large aliphatic hydroxyl number  $\approx 296$  mgKOH/g. Most importantly, the maximum operating pressure was below 150 psig. With respect to the energy consumption and industrial applications for producing a suitable feedstock for PU foams or resins, KL depolymerization in water-polyalcohols mixtures is certainly more promising.

For industrial applications of the process, it is pivotally important to recover and reuse the solvent. In this study, overall EG recovery was investigated for the tests at the selected best operating reaction conditions. EG used in the KL depolymerization was recovered by post treatment via two routes. One fraction was obtained through distillation from the water soluble phase namely the filtrate, and second fraction was recovered from the acetone soluble phase through rotary evaporation at 120 °C under high vacuum conditions after removal of acetone. As illustrated in Figure 10-5, the EG loss from the process was only 2.5 wt.% based on EG input which is negligibly small. Thus, the process can be very economical since almost full recovery of EG used in the reaction can be attained.

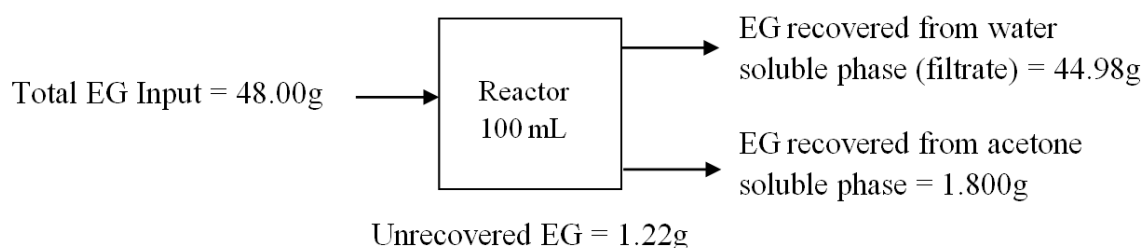


Figure 10-5 Overall EG balance of the system

### 10.3.7 Chemical analyses of DKLs

Elemental composition (the CHNS contents) of the KL and DKL samples were analyzed to provide information on the fate of elements like N and S that are associated with environmental concerns for the industrial applications of lignin. Table 10-6 shows

elemental composition of KL and some typical DKL samples. The C and H contents of DKL from low-temperature experiments were not varied much from those of the original KL, while the high temperature DKL products (250 °C and 260 °C) have a much higher C contents (68.8 wt.% and 69.7 wt.%, respectively, compared to 63.8 wt.% for the original lignin). N contents for all samples are negligible, thus not presented in the Table 10-6. The S contents of all DKLs are 0.6% ( $\pm 0.2$ ) S, significantly lower than that in the original KL (5.2 wt.% S), suggesting that the low pressure hydrolytic depolymerization process is very effective for KL desulfurization. The resulting DKL products have nearly no odor, making them a suitable feedstock for various industrial applications such as manufacture of phenolic adhesives, epoxy resins or polyurethane (PU) foams.

Table 10-6 Elemental composition of the original KL and typical DKL products obtained from KL depolymerization at different temperatures (Other reaction conditions: 1 h, KL substrate concentration of 20 wt.%, EG/KL ratio of 4.0 (w/w) and 128 mole% of NaOH)

Reaction condition	Elements (% , d.a.f) <sup>a</sup>				
T (°C)	N	C	H	S	O <sup>b</sup>
Original KL	0.02	63.8	5.4	5.2	25.6
180	0.10	63.3	5.4	0.8	30.4
200	0.10	64.1	5.4	0.4	30.0
220	0.00	64.7	5.6	0.7	29.0
250	0.04	68.8	5.6	0.5	25.1
260	0.05	69.7	5.6	0.6	24.1

<sup>a</sup> Dry and ash free basis.

<sup>b</sup> Determined by difference

IR spectra of the original KL and the DKL produced in water-EG mixture at 250 °C (other reaction conditions are: 1 h, KL substrate concentration of 20 wt.%, EG/KL ratio of 4.0 (w/w) and 128 mole% of NaOH) are shown in Figure 10-10, along with oxypropylated samples and reference polyols for the sake of comparison. FTIR can be used for qualitatively monitoring the changes of functional groups (particularly, hydroxyl

groups) in the KL after depolymerization. As shown in Figure 10-10, as expected all spectra contain a broad IR absorption at 3200-3550  $\text{cm}^{-1}$  attributed to aromatic and aliphatic O-H stretching. IR absorbance's at 1400-1600  $\text{cm}^{-1}$  are due to the aryl (aromatic) groups. The peaks at 1000-1300  $\text{cm}^{-1}$  correspond to C-O stretching, suggesting the presence of primary, secondary and tertiary alcohols, phenols, ethers and esters (Islam et al., 2005; Kubo and Kadla, 2005). The ether linkage at 1060-1160  $\text{cm}^{-1}$  was clearly observable in the original KL, whereas the ether linkage has much lower IR absorption in the DKL product, suggesting that ether linkages in the KL were cleaved during the hydrolytic de-polymerization reaction. The intensity of the aromatic absorption at 1400-1600  $\text{cm}^{-1}$  in the DKL sample was almost the same as those in the original KL, suggesting that the hydrolytic depolymerization does not change lignin's aromaticity (Mahmood et al., 2013).

### 10.3.8 Rigid polyurethane foam (RPU foam)

Rigid polyurethane (RPU) foams are known for their unique combination dimensional stability, high mechanical strength and lower thermal conductivity. Table 10-7 shows the characteristics of DKL and oxypropylated DKLs. All the polyols produced by oxypropylation of DKL were in viscous liquid form. In this work, the oxypropylated DKL was further used as bio-polyols for the preparation of BRPU foams with high percentage of bio-contents. Figures 10-6, 10-7, 10-8 and 10-9 show the  $^1\text{H}$  NMR spectra of acetylated KL, acetylated DKL, acetylated DKL50PO50 and acetylated DKL70PO30, respectively. It is clear from the Figure 10-6 and Figure 10-7 that original KL and DKL both have aliphatic and phenolic -OH groups presented here in terms of aliphatic and phenolic acetates respectively. However, after oxypropylation all the phenolic -OH transferred into aliphatic -OH presented in terms of aliphatic acetates, can be clearly seen from Figure 10-8 and Figure 10-9.

Table 10-7 Characteristics of DKL and oxypropylated DKL sample

Sample ID	$M_w$ (g/mole)	Aliphatic –OH number (mgKOH/g)	Total –OH number (mgKOH/g)	Viscosity at 80 °C (Pa.s)	State of product
DKL	1050	295.5	670.5	-	Solid powder
DKL50PO50	1550	-	331.0	0.812	Viscous liquid
DKL60PO40	1440	-	340.4	1.101	
DKL70PO30	1420	-	347.5	1.232	

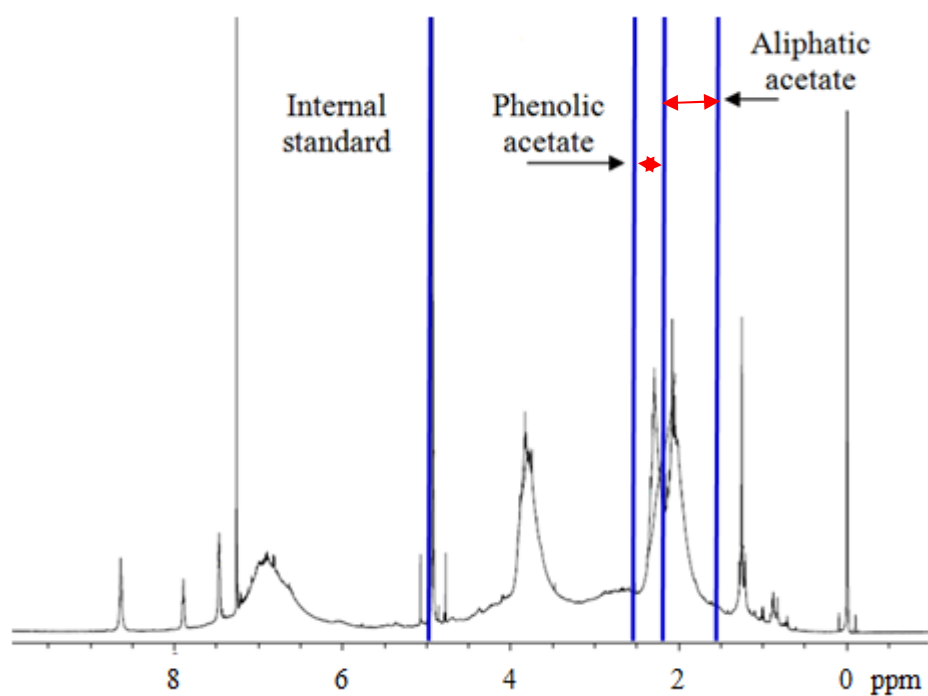
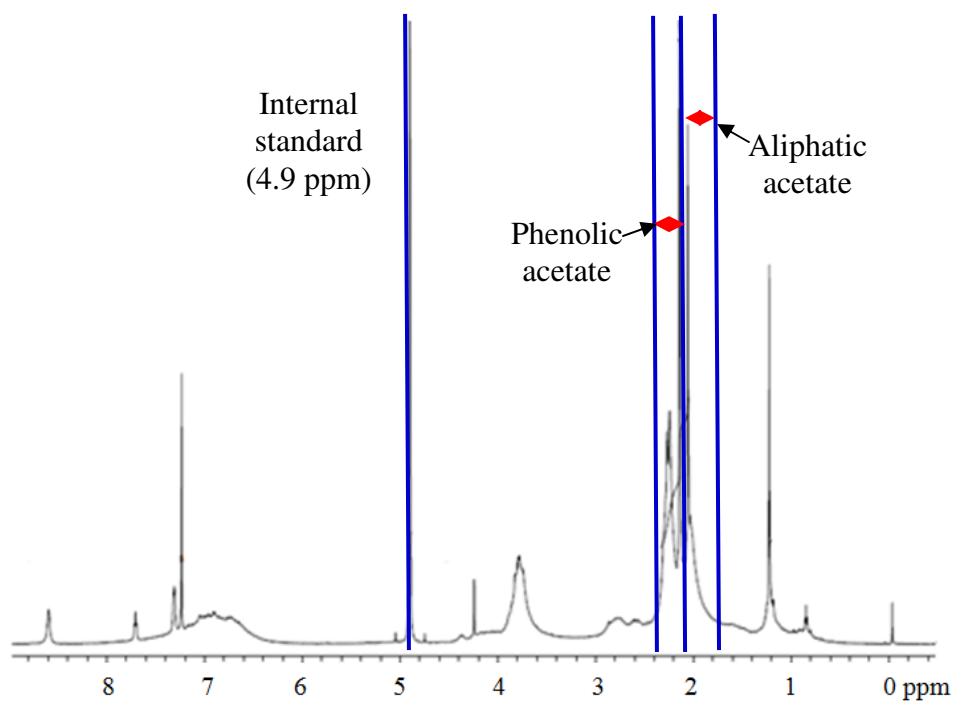
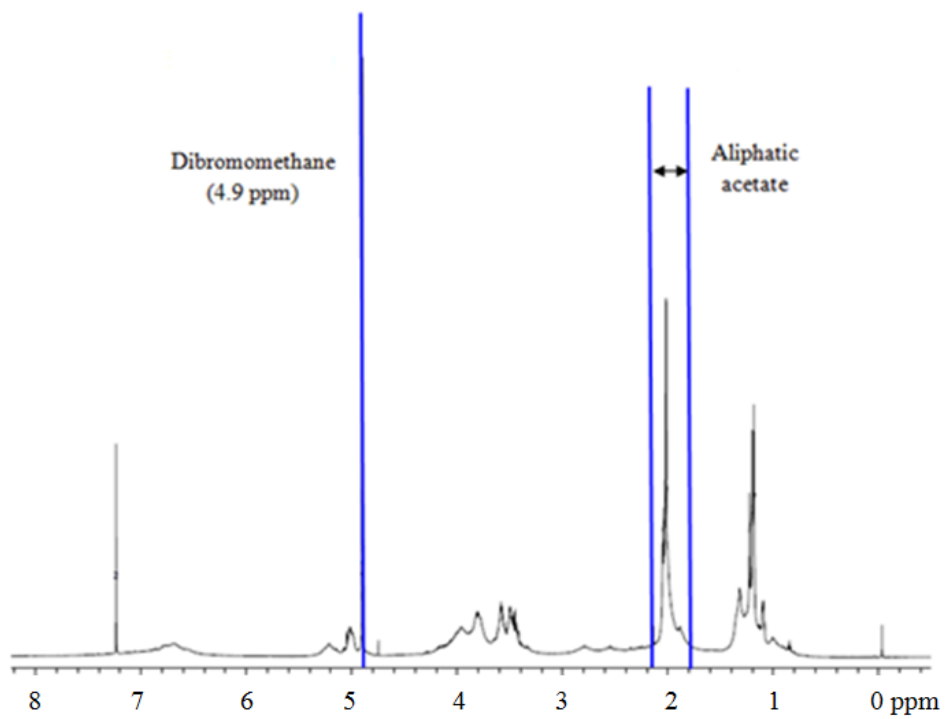


Figure 10-6  $^1\text{H}$  NMR spectra of acetylated KL

Figure 10-7  $^1\text{H}$  NMR spectra of acetylated DKLFigure 10-8  $^1\text{H}$  NMR spectra of acetylated DKL50PO50

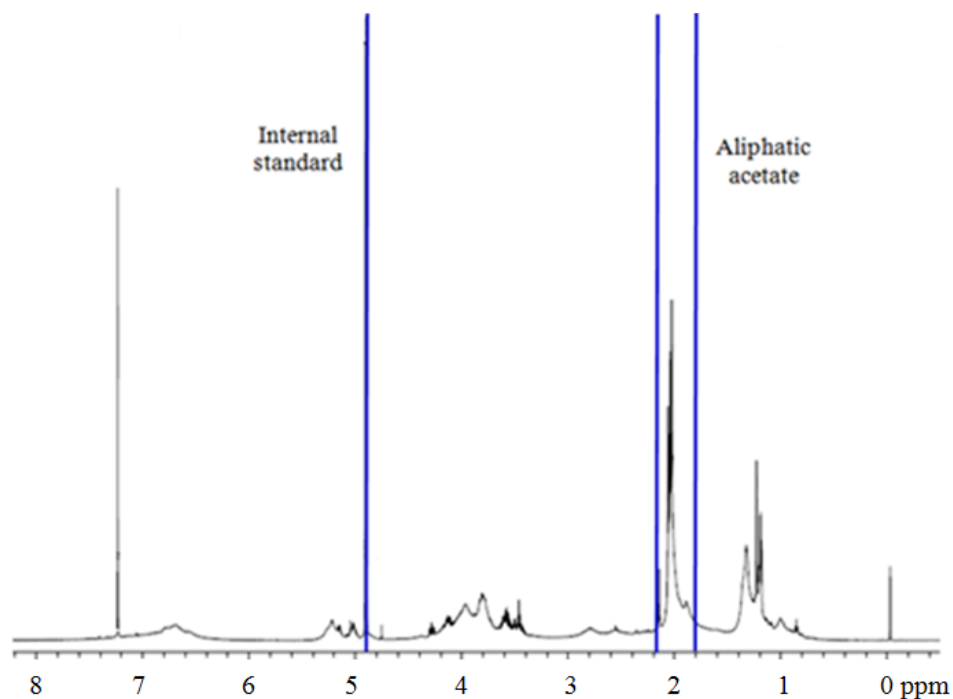


Figure 10-9  $^1\text{H}$  NMR spectra of acetylated DKL70PO30

FT-IR spectra of original KL, DKL and the oxypropylated DKL samples and reference polyol are shown in Figure 10-10. The oxypropylation and occurrence of PO grafting on lignins can be evidenced by following FTIR observations from Figure 10-11:(a) an increase in the bands at  $2971\text{-}2870\text{ cm}^{-1}$  attributed to the stretching of  $\text{CH}_3$ ,  $\text{CH}_2$  and  $\text{CH}$  aliphatic groups; (b) reduction in the intensity of the carbonyl peak at  $1714\text{ cm}^{-1}$ ; (c) a marked increase of the absorption bands in the ether C-O stretching region ( $1000\text{-}1100\text{ cm}^{-1}$ ); and (d) an increase in the band at  $1371\text{ cm}^{-1}$  confirming the introduction of  $\text{CH}_3$  groups (Cateto et al., 2009).



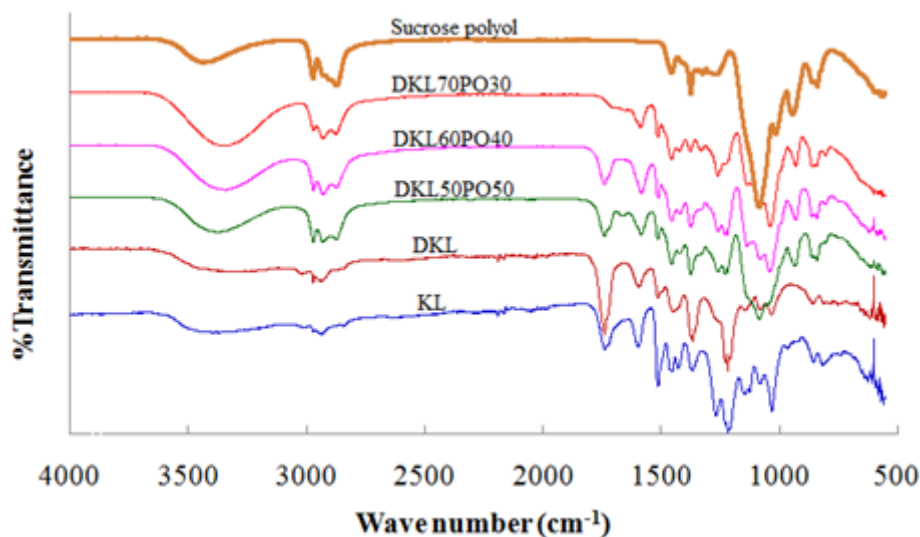


Figure 10-10 FTIR spectra of KL, DKL and oxypropylated DKL samples

### 10.3.8.1 Physical and mechanical properties

According to the literature, density plays an important role in the mechanical performance of rigid PU foam (Li and Ragauskas, 2012) and is one of the most important properties of RPU foams. The density of a foam sample is governed by the weight of the foaming ingredients which are responsible for generating the gases trapped in the foam cells. The foaming gases mainly includes carbon dioxide generated from the chemical reaction between the chemical blowing agent (water) and isocyanate, physical blowing agents, and air which is either introduced into the reaction vessel during the foaming process or diffuses into the cells during the aging process. In this study a combination of physical and chemical blowing agents was employed to control the density of the resulting foams. The quantity of water was kept at 2 wt.% based on the total weight of polyols and physical blowing agent (acetone) was used to further reduce the density of foam to the desired level, since the consumption of MDI will increase with the increase in water %, which will increase the cost and RPU foam fragility. Acetone uses the heat released during exothermic reaction of isocyanate with water and polyol (~100-110 kJ/mole of urethane) (Tu, 2008). During the foaming reaction temperature increased above 100 °C and can rise to maximum foam temperature of 168 °C (Jimoda, 2011). Two routes were investigated in this study: (1) at fixed percentage of physical blowing agent

and, (2) at varying percentage of physical blowing agent to keep the final density approximately at the same level to investigate the effect of increasing bio-contents on foam's mechanical and thermal characteristics. All the prepared foams were dimensionally stable and non-shrinking structure, rigid and of uniform structure. Table 10-9 shows the properties (physical, mechanical and thermal characteristics) of the RPU foam prepared from the oxypropylated DKL and a reference foam prepared using an industrial sucrose polyol (JEFFOL SD-361, HUNTSMAN INTERNATIONAL LLC).

Table 10-8 Physical and mechanical properties of reference and BRPU foams

Sample ID	Density (kg/m <sup>3</sup> )	Compressive modulus (kPa)	Compression strength at 10% deformation (kPa)
Sucrose Ref. Foam	42.5±0.5	2695.0±100.0	182.0±45.0
At varying percentage of physical blowing agent			
DKL50PO50	46.0±1.0	6936.0±55.0	356.0±41.0
DKL60PO40	40.0±0.5	5273.0±70.0	348.1±21.0
DKL70PO30	38.0±1.0	4743.0±120.0	315.0±85.0
At fixed percentage of physical blowing agent			
DKL50PO50	46.0±1.0	6936.0±55.0	356.0±41.0
DKL60PO40	61.8±0.2	8902.0±35.0	381.0±11.0
DKL70PO30	82.7±2.0	22436.0±22.0	566.0±10.0

It is clear from Table 10-8 that the compressive modulus and compressive strength of BRPU foam at 50 wt.% bio-content were higher than the reference foam from sucrose polyol. This could be due to the structural variations between sucrose polyol and DKL. Sucrose polyol has a multi branched short chains ether structure, where, DKL sample also contains aromatic contents. Therefore, the increased strengths of BRPU foams could be primarily attributed to DKL's aromatic structure combined with high functionality of DKL, which lead to higher rigidity and crosslinking density in BRPU foams compared to the reference foam. Further increasing bio-contents to 60 wt.% and 70 wt.% in BRPU

foam formulations, while maintaining approximately the same final density by increasing percentage of acetone, modulus and strength were reduced. This could be either attributed to the morphological characteristics of BRPU foam or to the increased brittleness of foams leading to cell breakage under applied pressure. However, BRPU foam at 70 wt.% bio-contents had higher strength than reference foam. On the other hand, when physical blowing agent percentage was kept constant (20% (w/w)) in formulation recipe, the increasing percentage of bio-contents in BRPU foams, resulted in more crosslinking due to the short chain structure of prepared polyols and lead to dense foams. The final foam's density increased and thus compressive modulus and strength of foam increased as well.

The prepared BRPU rigid PU foams at 50-70 wt.% bio-contents (DKL and glycerol) were analyzed by FTIR for their structural variation. The signal at  $2253.6\text{ cm}^{-1}$  indicates the residual/unreacted isocyanate group (NCO) (Ribeiro da Silva et al. 2013). The signals corresponding to the stretching vibration of N-H were identified at between  $3297\text{ cm}^{-1}$  and  $3454.53\text{ cm}^{-1}$ .  $1710\text{ cm}^{-1}$  (C=O stretching) (Cinelli et al., 2013) and  $1408.84\text{ cm}^{-1}$  and  $1098.30\text{ cm}^{-1}$  (C-N coupled, C-O stretch) indicates the existence of the urethane linkage (Ribeiro da Silva et al. 2013).

### 10.3.8.2 Thermal properties

RPU foams are the most efficient insulation materials due to their low thermal conductivity (Cunningham and Sparrow, 1986). Thermal conductivity value is closely related to foam density and cell morphology (Ribeiro da Silva et al., 2013), and the insulation capacity of foam increases as its thermal conductivity decreases (Lin et al., 1996). Thermal conductivities of reference and BRPU foams are summarized in Table 10-9.

Table 10-9 Thermal conductivity of reference and BRPU foams

Sample ID	Thermal conductivity ( $\lambda$ ) (W/m-K)
Sucrose ref. foam	0.033±0.0010
DKL50PO50	0.033±0.0010
DKL60PO40	0.031±0.0010
DKL70PO30	0.032±0.0010

In this study, foam's  $\lambda$  values vary between 0.032±0.001 W/mK, which is in good agreement with literature (Cateto et al., 2010) taking into account that the density of the prepared foams is towards the higher limit of common PU foams where  $\lambda$  values are between 0.020-0.030 W/mK for densities ranging from 30-100 kg/m<sup>3</sup> (Ribeiro da Silva et al., 2013). Over the passage of time air diffuses into the cells and can lead to the increased thermal conductivity of foams.

Thermogravimetric analysis was also performed to investigate the thermal stability of reference and BRPU foams under inert atmosphere. Figure 10-11 shows thermal stability characteristics of reference foam and BRPU foam with 50 wt.% bio-contents. Thermal stability of the BRPU foam was investigated by TGA in 20 mL/min N<sub>2</sub> flow heated from room temperature to 800 °C at 10 °C/min. As illustrated in Figure 10-11, reference and BRPU foams were thermally stable to 200 °C, and after that degradation started (Zhao et al., 2012). The area below 150 °C is considered to be due to the evaporation of water. Pyrolysis of PU foam under nitrogen atmosphere starts at ~170 °C and intensified at ~200 °C. Main decomposition range of RPU foams took place between 200-450 °C. Where, around 350 °C the decomposition of polyurethane start releasing components like diisocyanates and polyols along with other decomposition products like amines, small transition components, olefins and carbon dioxide because of the destruction of polymer chain (Ribeiro da Silva et al., 2013; Manocha et al., 2010). For all BRPU foams after 600 °C, weight loss was negligible and, there was not much difference between their thermal stability.

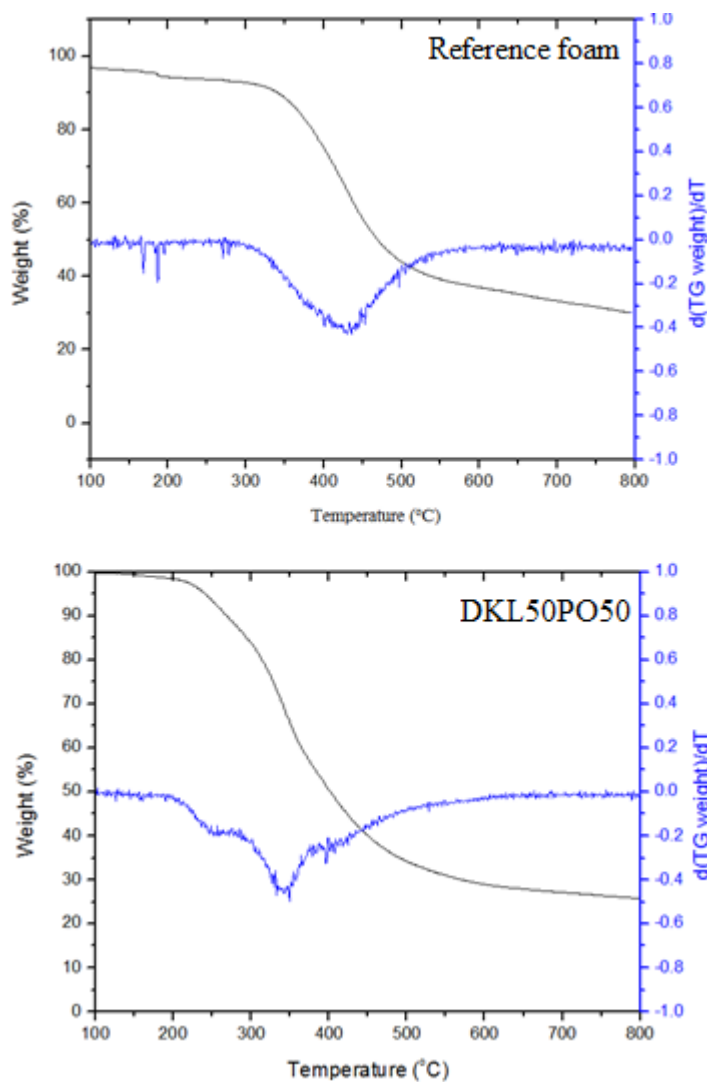


Figure 10-11 Thermal stability and the rate of weight loss of BRPU foams under nitrogen atmosphere

### 10.3.8.3 Morphology

In general, the physical properties of foams are not only dependent on the rigidity of polymer matrix, but also on the morphology of the foam's cell. Thus, it is of interest to observe the cell structure of BRPU foam using SEM. Cellular structure of RPU foam is a balance between the network formation and the expansion of blowing agents, where

surfactants helps to stabilize cell walls through lowering surface tension of foaming mixture and prevent their coalescence. Additionally, both gel and blow catalysts were added in order to accelerate these reactions according to the requirements. The SEM image of BRPU foam prepared with 50 wt.% bio-contents is shown in Figure 10-12. The cell size varies between ~422.1  $\mu\text{m}$  and 572.9  $\mu\text{m}$ .

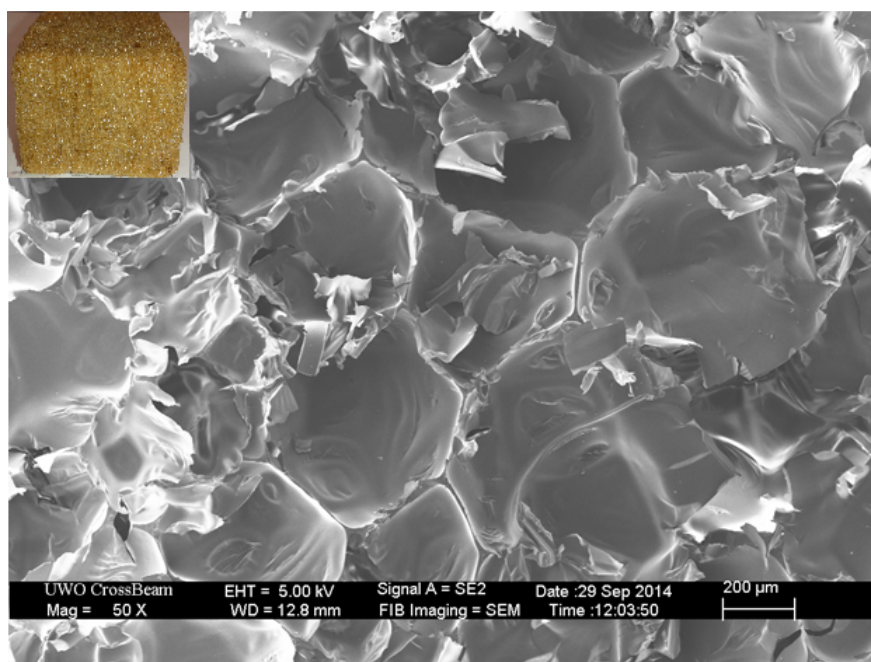


Figure 10-12 BRPU foam from DHL50PO50 and its SEM image

## 10.4 Conclusions

A new low-pressure ( $\leq 150$  psig) proprietary process for hydrolytic depolymerization of very high molecular weight Kraft lignin (KL) was developed in this work, employing water-polyalcohols (EG/PG/glycerol) co-solvent mixture. Under the best operating conditions (250 °C, 1 h, 20 wt.% KL substrate concentration, EG/KL ratio of ~4.0 (w/w) and NaOH/KL ratio of ~0.28 (w/w) or 128 mole% of NaOH) KL depolymerization produced DKL at a yield of ~90 wt.% and with a weight-average molecular weight ( $M_w$ ) as low as ~1050 g/mole and high aliphatic and total hydroxyl numbers (295.5 mgKOH/g and 670.1 mgKOH/g, respectively). In this process, the polyalcohols/solvent

(EG/PG/glycerol) used was recoverable at a recovery rate of ~95-96 wt.%, which further enhance the economic viability of this process. The obtained DKL was in solid form and further derivatized into liquid polyols via oxypropylation for their further utilization in the preparation of bio-based rigid polyurethane (BRPU) foam at high percentage of bio-contents (50-70 wt.%). All BRPU foams exhibit good compressive strength, compared with the reference foam. At the fixed formulation recipe i.e., fixed percentage of physical blowing agent, BRPU foams showed the following order of sequence in terms of their compressive modulus: Sucrose polyol reference foam (2695.0 kPa)<DKL50PO50 (6936.0 kPa)<DKL60PO40 (8902.0 kPa)<DKL70PO30 (22436.0 kPa). Thermal conductivity of all BRPU foams varies between  $0.032\pm 0.001$  W/mK, making them suitable candidate as an insulation material. All BRPU foams were thermally stable up to approximately 200 °C.

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## Chapter 11

### 11 Conclusions

This thesis work successfully demonstrated the effectiveness of hydrolytic depolymerization of Kraft lignin (KL) and hydrolysis lignin (HL) into bio-polyols for their further utilization in the preparation of bio-based rigid polyurethane (BRPU) foams at a high percentage up to 70 wt.% bio-contents. A proprietary process has also been developed for efficient and cost effective depolymerization of KL and HL under low pressure. The two processes (high pressure or low pressure) used for the depolymerization of KL or HL for their further utilization in the preparation of BRPU foams are compared in the following tabulated form before drawing the overall conclusions from the current research work.

Lignin	Solvent	Catalyst/Catalyst loading (wt.%)	T (°C)	Time (h)	KL conc. (wt.%)	P <sub>initial</sub> (psig)	P <sub>max</sub> (psig)	DKL yield (wt.%)	M <sub>w</sub> (g/mole)	OH <sub>Total</sub> (mgKOH/g)
KL	H <sub>2</sub> O	NaOH/ 28.4	250	1.0	10	290	725	77	1700	675.0
	H <sub>2</sub> O-EG	NaOH/ 28.4	250	2.0	20	14.7	120	90	1000	670.5

#### Comments

- KL depolymerization employing water alone as a solvent under alkaline medium is a high pressure process. However, when H<sub>2</sub>O-EG was employed as a solvent overall system pressure was very low making the process highly efficient for effective KL depolymerization.
- Yield of DKL obtained via low pressure KL depolymerization is higher (90 wt.%) than high pressure process (1700 g/mole) at the best operating reaction conditions.
- Polystyrene equivalent molecular weight of DKL in case of low pressure KL depolymerization was lower (1000 g/mole) when compared to high pressure process derived DKL (1700 g/mole).
- The recovery rate of solvent (EG) used in low pressure depolymerization of KL was very high ~ 94-95 wt.%, which makes overall process cost effective.
- The separation of EG from DKL is a single step process which also makes this process highly efficient and easy to employ.

- Although DKL obtained via both routes was in solid powder form, have suitable hydroxyl numbers and can be transferred into liquid polyols via their oxypropylation for their further utilization in the preparation of BRPU foam up to 70 wt.% bio-content loading.
- All BRPU foams exhibit good compression strengths, low densities and thermal conductivities with thermal stability up to approximately 200 °C, making them a suitable material for their applications as an insulation material.
- Therefore, based on overall benefits associated with low pressure depolymerization of KL employing water-EG as a solvent mixture appears to be more economical than high pressure process.

Lignin	Solvent	Catalyst/Catalyst loading (wt.%)	T (°C)	Time (h)	HL conc. (wt.%)	P <sub>initial</sub> (psig)	P <sub>max</sub> (psig)	DHL yield (wt.%)	M <sub>w</sub> (g/mole)	OH <sub>Total</sub> (mgKOH/g)
HL	H <sub>2</sub> O-EtOH	None	250	1.0	20	290	750	70	1000	442.0
	EG	H <sub>2</sub> SO <sub>4</sub> / 2.0	200	1.0	20	14.7	150	70	1400	247.1

#### Comments

- HL depolymerization employing water-EtOH as a solvent mixture is a high pressure process. However, when EG was employed as a solvent overall system pressure was very low making the process highly efficient for effective HL depolymerization.
- Yield of DHL obtained via low or high pressure HL depolymerization process are same i.e., 70 wt.% at the best operating reaction conditions.
- Polystyrene equivalent molecular weight of DHL in case of low pressure HL depolymerization was slightly higher (1400-1500)

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g/mole) when compared to high pressure process derived DHL (1000 g/mole).

- The recovery rate of solvent (EG) used in low pressure depolymerization of KL was very high ~ 90-92 wt.%, which makes overall process cost effective.
  - The separation of desired DHL from solvent (water-ethanol) is a single step process involves filtration followed by evaporation. Where, the separation of EG from DHL is a two step process which makes separation a bit tedious work. The separation of EG solvent from DHL needs to be further improved to make process more convenient to use.
  - Hydroxyl number of DHL obtained via high pressure process is higher (442 mgKOH/g) than the hydroxyl number of DHL obtained as a result of low pressure HL depolymerization employing sulfuric acid as a catalyst.
  - Although DHL, irrespective of their hydroxyl numbers, obtained via both routes was in solid powder form, have suitable hydroxyl numbers and can be transferred into liquid polyols via their oxypropylation for their further utilization in the preparation of BRPU foam.
  - BRPU foams were prepared up to 70 wt.% bio-content from oxypropylated DHL employing DHL obtained via high pressure process. However, when DHL obtained via low pressure process was oxypropylated at 70 wt.% bio-loading the oxypropylated sample viscosity was very high which makes it difficult to mix with other ingredients to synthesize foam. Therefore, when DHL obtained via low pressure was employed the BRPU foams were prepared with the maximum of 60 wt.% bio-contents.
  - All the BRPU showed good compression strengths, low thermal conductivities and thermal stability up to approximately 200 °C.
  - Therefore, based on overall benefits associated with low pressure depolymerization of HL employing EG as a solvent mixture appears to be more economical than high pressure process.
-



The following conclusions could be drawn from this research:

- Kraft lignin (KL) of initial molecular weight ( $M_w$ )  $\approx 10,000$  g/mole was depolymerized to low molecular weight  $M_w \approx 1000-3000$  g/mole depolymerized KL (DKL) via direct hydrolysis of KL employing water alone as a solvent using NaOH as a catalyst, without any organic solvent/capping agent. The effects of process parameters including reaction temperature, reaction time, NaOH/lignin ratio (w/w) and substrate concentration were investigated and DKLs were characterized. The best operating conditions appeared to be at 250 °C, 1 h, and NaOH/lignin ratio  $\approx 0.28$  with 20 wt.% substrate concentration, leading to  $<0.5\%$  solid residues and  $\sim 92\%$  yield of DKL (aliphatic-hydroxyl number  $\approx 352$  mgKOH/mg and  $M_w \approx 3310$  g/mole). The overall % carbon recovery under the above best conditions was  $\sim 90\%$ . A higher temperature favored DKL with lower  $M_w$ s while a longer reaction time promoted dehydration/condensation reactions. NaOH/KL ratio  $\geq 0.28$  (w/w) does not have significant effect on KL depolymerization and lower substrate concentrations ( $\leq 20$  wt.%) are desirable for obtaining low molecular weight DKL.
- Optimum reaction conditions for producing DKL via KL direct hydrolysis in alkaline medium for their utilization in the preparation of bio-based rigid polyurethane (BRPU) foams were determined using response surface methodology (RSM) with a central composite design (CCD). The optimization was constrained by requirements that a polyol should fulfill for use in PU foam synthesis: aliphatic-hydroxyl number  $\geq 300-500$  mgKOH/g,  $M_w < 2000$  g/mole and moderately high yield. The optimum conditions identified were 250 °C, 2h and 10 wt.% substrate concentration. The obtained DKL at optimized reaction conditions had an aliphatic-hydroxyl number  $\approx 365$  mgKOH/g,  $M_w \approx 1700$  g/mole and 77 wt.% yield, suitable for their utilization in the preparation of RPU foam. The predicted and experimental results were in good agreement ( $R^2$  values are 0.90, 0.82 and 0.98 for yield,  $M_w$  and aliphatic-hydroxyl number, respectively). Temperature was the most significant parameter.

- Bio-based rigid polyurethane (BRPU) foams were prepared with depolymerized Kraft lignin (DKL) substituting 50 wt.% of petroleum-based polyols via three routes: directly replacing 50 wt.% of PPG400, directly replacing 50 wt.% of sucrose polyol, and using oxypropylated DKL as a single polyol feedstock. All foams were characterized in terms of physical, mechanical, and thermal properties as well as their morphology, and their properties were found to be strongly dependent on the DKL incorporation routes. The compression modulus of the foams increased in the following order: oxypropylated DKL-based BRPU foam (10986.0 kPa) > BRPU foam with 50 wt.% sucrose polyol and 50 wt.% DKL (5152.0 kPa) > sucrose polyol based reference foam (2086.0 kPa) > BRPU foam with 50 wt.% PPG400 polyol and 50 wt.% DKL (1016.0 kPa) > PPG 400 based reference foam (789.1 kPa). A similar trend was observed for the compression strengths of the foams at 10% and 20% deformations. The lower modulus of PPG400 based RPU foams was believed due to its bi-functional long chain structure which leads to lower crosslinking density when compared to the multifunctional short chain structure sucrose polyol. All the foams showed thermal conductivity between 0.029 W/mK to 0.040 W/mK. Among three routes investigated for the preparation of BRPU foams, the oxypropylated DKL-based BRPU foam showed superior combination of physical, mechanical and thermal properties. All BRPU foams are thermally stable up to approximately 200°C.
- A new low-pressure ( $\leq 150$  psig) proprietary process for hydrolytic depolymerization of KL was also developed in this work, employing a water-polyalcohols (EG/PG/glycerol) co-solvent mixture. Under the best operating conditions (250 °C, 1 h, 20 wt.% KL substrate concentration, EG/KL ratio of  $\sim 4.0$  (w/w) and NaOH/KL ratio of  $\sim 0.28$  (w/w) or 128 mole% of NaOH) KL depolymerization produced DKL at a yield of  $\sim 90$  wt.% and with a  $M_w$  as low as  $\sim 1050$  g/mole and high aliphatic and total hydroxyl numbers (295.5 mgKOH/g and 670.1 mgKOH/g, respectively). In this process, the polyalcohols/solvent (EG/PG/glycerol) used was recoverable at a recovery rate of  $\sim 95$ -96 wt.%, which enhances the economic viability of this process. The obtained DKL was in solid form but it was further transformed into liquid polyols via oxypropylation for their further utilization in the preparation of bio-based rigid polyurethane (BRPU) foams with a high bio-contents (up to 50-70 wt.%). All

BRPU foams exhibited good compressive strength, compared with the reference foam. With the fixed formulation recipe i.e., fixed percentage of physical blowing agent, the mechanical properties (compressive modulus) of the BRPU foams increased in the following order: Sucrose polyol reference foam (2695.0 kPa)<DKL50PO50 foam (6936.0 kPa)<DKL60PO40 foam (8902.0 kPa)<DKL70PO30 foam (22436.0 kPa). Thermal conductivity of all BRPU foams varied between  $0.032\pm 0.001$  W/mK, making them suitable candidates as an insulation material. All BRPU foams were thermally stable up to approximately 200 °C.

- Hydrolytic depolymerization of hydrolysis lignin (HL) was carried out with or without catalyst ( $\text{H}_2\text{SO}_4$  or NaOH) in water or water-ethanol mixture as solvent at 250 °C for 1 h with 20% (w/v) HL substrate concentration. The results were compared in terms of DHL yield,  $M_w$  and SR yield. The comparative results implied that HL depolymerization pathways might be different under different conditions (depending on the solvent and catalyst employed). However, in view of the utilization of DHL for the preparation of polyurethane foams/resins, depolymerization of HL in water-ethanol mixture without catalyst appeared to be the best route, producing ~70.5 wt.% yield of DHL which has a low  $M_w$  (~1000 g/mole) and a suitable aliphatic (227.1 mgKOH/g) and phenolic (215 mgKOH/g) hydroxyl numbers. The overall % carbon recovery for the test under the best operating conditions was approximately 87%.
- The obtained DHL (at the best reaction conditions) was in solid form and was used for the preparation of BRPU foams via three routes: directly replacing 50 wt.% of PPG400, directly replacing 50 wt.% of sucrose polyol, and using oxypropylated DHL as a single polyol feedstock. The DHL-PPG400 foams had lower compressive strengths than the DHL-sucrose polyol foams, which could be attributed to PPG400 bi-functional long chain structure. The oxypropylation treatment transformed the solid DHL into liquid polyols, which enabled their further utilization in the preparation of BRPU foam at a higher percentage of bio-contents (up to 50-70 wt.%). All BRPU foams prepared from oxypropylated DHLs exhibit better compressive strength, compared with the reference foams. With the fixed formulation recipe i.e., fixed percentage of physical blowing agent, the compressive strength of the BRPU

foams increased in the following order: Sucrose polyol reference foam (2695.0 kPa)<DHL50PO50 foam (9202.0 kPa)<DHL60PO40 foam (19847.0 kPa)<DHL70PO30 foam (21288.0 kPa). All DHL-derived BRPU foams were thermally stable up to approximately 200 °C. Thermal conductivities of BRPU foams vary between 0.029 W/mK and 0.034 W/mK, making them suitable for utilization as an insulation material.

- Low pressure ( $\leq 150$  psig) depolymerization of hydrolysis lignin (HL) was successfully realized to obtain low molecular weight depolymerized HL (DHL) in an acidic medium using sulfuric acid as a catalyst. Under the best operating conditions (200 °C, 1h, 20 wt.% HL substrate loading and 2 wt.% acid loading) the low-pressure depolymerization of HL produced DHL at a yield of ~70 wt.% with a weight-average molecular weight ( $M_w$ ) of ~1500 g/mole and reasonably high aliphatic and total hydroxyl numbers (116.0 mgKOH/g and 247.1 mgKOH/g, respectively). The DHL was in solid powder form, but it was subsequently transformed into liquid polyols via oxypropylation for their further utilization for preparation of bio-based rigid polyurethane (BRPU) foam with bio-contents at a high percentage up to 50-70 wt.%. All BRPU foams exhibited good compressive strength as compared with the reference foams. With the fixed formulation recipe, i.e. fixed percentage of physical blowing agent, the compressive strength of the BRPU foams increased in the following order: sucrose polyol reference foam (2695.0 kPa)<DHL50PO50 foam (5381.0 kPa)<DHL60PO40 foam (12360.0 kPa). All of the BRPU foams were thermally stable up to approximately 200 °C. The thermal conductivities of the BRPU foams were between 0.030 W/mK and 0.032 W/mK, making them suitable for utilization as an insulation material.

Therefore, collectively from the above conclusions, several novelties of the current work can be summarized as follows: (1) successful depolymerization of KL and HL and the use of DKL or DHL for the preparation of BRPU foams through direct incorporation of DKL or DHL to substitute 50 wt.% of PPG400 or sucrose polyols, or through oxypropylation treatment to transform DKL or DHL into liquid polyols, enabling production of BRPU foams with 50-70 wt.% bio-contents; (2) Development of a proprietary low-pressure process for depolymerization of KL and HL under basic and

acidic medium respectively, employing water-EG as a solvent at low pressure (<150 psig); (3) Successful utilization of the DKL and DHL prepared via the low pressure depolymerization process for the preparation of BRPU foams with bio-contents at 50-70 wt.%; (4) Effective depolymerization of HL in water alone as a solvent and in water-ethanol mixture, and the preparation of BRPU foams with 50-70 wt.% bio-contents using DHL obtained from the co-solvent mixture. All the prepared BRPU foams in this work exhibit good physical, mechanical and thermal properties with satisfactory thermal stabilities making them suitable for application as an insulation material.

## Chapter 12

### 12 Future work

Although this work has achieved great success in depolymerization of KL/HL and the utilization of de-polymerized lignin products (DKL/DHL) in the preparation of BRPU foam with a high bio-content up to 50-70 wt.%, more research is still needed as follows:

- (1) Conducting pilot scale tests to produce enough amount of depolymerized KL/HL (DKL/DHL) for the preparation of larger BRPU foam samples for industrial testing.
- (2) Overall economical analysis of the low-pressure KL/HL depolymerization process for producing bio-polyols and BRPU foams from KL/HL resources.
- (3) Further study of foaming process for the lignin-based BRPU foams manufacture to tune their physical and mechanical properties for various applications, e.g., insulation, structure, packaging, etc.

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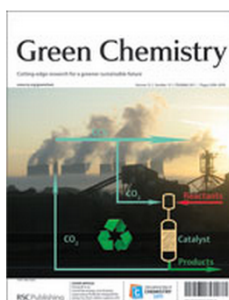


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## Curriculum Vitae

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- University of Engineering and Technology  
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2007-2009 *M.Sc. Chemical Engineering*
- University of Engineering and Technology  
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2003-2007 *B.Sc. Chemical Engineering*

### **Honours and Awards:**

- First place poster award at the Sustainability and Environmental Research Showcase, Western University, London, ON-Canada (March 6, 2014).
- Overall first position with Honours in B.Sc. Chemical Engineering (2003 – 2007)
- Five Gold Medals in B.Sc. Chemical Engineering for the best overall performance and the best performance in unit operations (2003- 2007).
- University of Engineering & Technology merit scholarship (2004 – 2006).
- Board of Intermediated and Secondary Education Merit scholarship (2002- 2006).

### **Related Work Experience**

- Teaching assistant at Western University, London, ON-Canada.  
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- Research assistant at Institute for chemicals and fuels from alternative resources (ICFAR), Western University, London, ON-Canada.  
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- Internship under *Mitacs* Accelerator program in the Country of Lambton Community Development Corp. /CENNATEK- Sarnia Research Park, Sarnia-Canada.  
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- Lecturer at the Department of Chemical Engineering, University of Engineering & Technology, Lahore-Pakistan.  
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### **Publications:**

1. **Mahmood, N.**, Yuan, Z., Schmidt, J., Xu, C., 2013. Production of polyols via direct hydrolysis of Kraft lignin: Effects of process parameters. *Bioresource Technology* 139, 13-20.
2. **Mahmood, N.**, Yuan, Z., Schmidt, J., Xu, C., 2013. Valorization of hydrolysis lignin for polyols and rigid polyurethane foam. *Journal of Science & Technology for Forest Products and Processes (J-FOR)*, special biorefinery issue 3(5), 26-31.
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2. **Mahmood, N.**, Yuan, Z., Schmidt, J., Xu, C., Depolymerization of lignins and their applications for the preparation of polyols and rigid polyurethane foams: Literature review
3. **Mahmood, N.**, Yuan, Z., Schmidt, J., Xu, C., Preparation of bio-based rigid polyurethane foam using hydrolytically depolymerized Kraft lignin (DKL) via direct replacement or oxypropylation.
4. **Mahmood, N.**, Yuan, Z., Schmidt, J., Xu, C., Hydrolytic depolymerization of hydrolysis lignin: Effects of catalysts and solvents.
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6. **Mahmood, N.**, Yuan, Z., Schmidt, J., Xu, C., Low pressure hydrolytic depolymerization of Kraft lignin for the preparation of bio-based rigid polyurethane foam.
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- CBE-Sarnia Research Bridges-Sarnia Research Park, Sarnia-Canada (2012). (*Poster presentation*)
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