Highly Efficient Depolymerization of Kraft Lignin (KL) and Hydrolysis Lignin (HL) via Hydrolysis and Oxidation

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Abstract

Due to dwindling fossil resources, climate change and other environmental concerns as well as the toxicity of certain products derived from petroleum resources, there is a growing interest in exploring and utilizing the abundant biomass resources as alternative feedstocks for the production of bio-based chemicals and materials. Biomass is composed of three main macromolecules, namely: cellulose, hemicellulose and lignin. Even though most of the initial work relating to the valorization of biomass was focused on the carbohydrate components (cellulose and hemicellulose), in the last ten years, lignin, an aromatic biopolymer, has been receiving increasingly more attention. In particular, various routes for lignin valorization such as depolymerization have been extensively investigated. However, current depolymerization/conversion strategies rely on high-temperature, high-pressure hydrogenolysis using a range of various supported metal catalysts and organic/inorganic solvents. These conditions lead to products of reduced functionality and/or difficulties in the recovery of the solid catalyst and the depolymerized lignin products after the reaction. As a result, most depolymerization processes reported in the literature are likely to be associated with high capital and operating costs as well as issues with scalability and industrial applicability. The main objective of this doctoral study was to develop cost-effective and industrially scalable approaches for the production of high-value, bio-based chemicals and materials for use in various applications. In an effort to address this objective, this study led to the development of four approaches for lignin depolymerization. A first approach demonstrated the technical feasibility of depolymerizing kraft lignin in black liquor rather than depolymerizing purified lignin itself. In this case, the presence of several well-known nucleophilic agents in black liquor was exploited to produce low-molecular weight, depolymerized lignin with a high functionality. The desired lignin MW was obtained by adjusting various process parameters such as reaction temperature, catalyst charge (NaOH), capping agent charge (phenol) or co-solvent charge (methanol). A second approach demonstrated the technical feasibility of depolymerizing biorefinery (hydrolysis) lignin using recoverable white liquor (WL) from the kraft recovery cycle at mild temperatures (150-190
°C). In this case, process scalability was demonstrated using a 20-L circulating reactor for the production of low MW, high functionality/reactivity depolymerized hydrolysis lignin (DHL). A third approach demonstrated the technical feasibility of depolymerizing softwood and hardwood kraft lignins (SKL and HKL) under ambient temperature conditions using only hydrogen peroxide (H₂O₂). In this case, the depolymerized kraft lignin exhibited unique properties. A fourth approach demonstrated the technical feasibility of depolymerizing SKL and HKL employing only nitric acid (HNO₃) at ambient temperature. The obtained depolymerized KL products displayed a low molecular weight of about 1300 Da with a high solubility in water at low pH. The nitration of lignin was confirmed by the presence of 5 wt.% N content in the modified lignin after reaction with 35wt.% HNO₃ at room temperature.

In summary, this work contributed new knowledge relating to kraft and hydrolysis lignin depolymerization. In particular, this work led to the development of four novel, simple, cost-effective and industrially scalable approaches for lignin depolymerization. These lignin depolymerization strategies are expected to lead to increased lignin utilization in several lignin applications including as a replacement of phenol in phenolic resins, petroleum-based polyols in polyurethane foams and bisphenol A in epoxy resins. The use of lignin in several applications will lead to reduced reliance on fossil-based resources.

Keywords

Black liquor, kraft lignin, hydrolysis lignin, depolymerization, depolymerized Kraft lignin, depolymerized hydrolysis lignin, nitrolignin, capping agent, co-solvent, nitration.
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Dedication

To the memory of my father and brother

Almighty God to guide me,
your prayers behind me I feel strong. To my mother

Thank you, mom,

TO

MOWTINI - موطنى
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List of Abbreviations and Symbols

ASTM- American Society for Testing and Materials

ATR- Attenuated Total Reflectance

CSTR- continuously stirred tank reactor

Da- Dalton (molecular weight)

d.b. - Dry Basis

DES- Deep eutectic solvents

DHL- Depolymerized Hydrolysis Lignin

DKL- Depolymerized Kraft Lignin

DL- Depolymerized Lignin

DMSO-d6 - Dimethyl Sulfoxide-d6

DSC- Differential Scanning Calorimetry

DTG- Derivative Thermogravimetric Analysis

DW- Deionized water

EA- the effective alkali (NaOH+0.5 Na₂S) (g/L)

EP#- inflection point (titration)

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

GVL- γ-valerolactone

HKL- Hardwood Kraft Lignin

HL- Hydrolysis Lignin

ICP- inductively coupled plasma

IR- Infrared

KBL- Kraft Black Liquor

KL- Kraft Lignin

LCC- lignin carbohydrate complexes

MALLS- Multi-angle laser light scattering

MDI- Methylene diphenyl isocyanate

Mₙ- Number Average Molecular Weight (Da)

MWL- Mill Wood Lignin

Mₗ-UV detector- Weight Average Molecular Weight (Da)

Mₗ-MALLS detector- Weight Average Molecular Weight (Da)

NIST library- national institute of standard and technology (Mass Spectrometry Data Center)

OH number- Hydroxyl Number

OH-Aliphatic- Aliphatic–OH

OH-Phenolic- Phenolic–OH

OSB- oriented strand board
\(^{31}\)P NMR spectra - Phosphorous Nuclear Magnetic Resonance Spectrometry

PDI - Polydispersity Index (\(M_w/M_n\))

PPG - Poly (Propylene Glycol)

pKa - the negative log of the acid dissociation constant

PPG - Polypropylene glycol

PUF - Polyurethane Foam

Py-GC/MS - Pyrolysis Gas Chromatography/ Mass Spectrometry

Qual - Match quality of the chemical structure in GC/MS

SKL - Softwood kraft lignin

SR - Solid Residues

TC - total carbon

TDMP - 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane

Tg - Glass Transition Temperature (°C)

TGA - Thermogravimetric Analysis

THF - Tetrahydrofuran

TRS - Total reduced sulfur

UV - Ultraviolet

V - titration volume (mL)

WL - White liquor

(w: w) - Weight ratio (g/g)
Chapter 1

1 Introduction

The main objective of this PhD project was to develop novel strategies for lignin depolymerisation in an effort to: a) enable its use as a replacement of fossil-based chemicals at higher substitution rates and b) enable its use in applications in which fossil-based chemicals are not presently suitable and/or cost-effective.

1.1 Background

Over the last two-hundred years, human kind experienced tremendous growth in the production and use of fossil-based resources. The discovery and increased use of fossil fuels as the main energy source has played a dominant role in shaping the world that we live in today from an economic, social, political and environmental point of view. In particular, the increasing exploitation of fossil resources over the last two-hundred years, led to irreversible damage to the environment arising from the emission of compounds like carbon dioxide, nitrogen oxides and sulfur dioxide into the atmosphere. These emissions are resulting in potentially devastating long-term contamination of land, air and water resources. To address this problem, extensive research is currently being conducted in an effort to replace fossil resources with renewable forms of energy and/or materials. Biomass is a material of an organic nature that originates from plants and biological wastes. In contrast to fossil resources, biomass is renewable, biodegradable or compostable and non-toxic. Moreover, biomass has the potential of producing low sulfur/nitrogen-containing fuels and chemicals (Connor & Piskorz, 1994).

Lignocellulosic biomass is available in various forms such as wood, grass agricultural and forestry residues, as well as industrial and post-consumer waste. The main challenge in producing biochemicals and biomaterials from biomass is the recalcitrance of lignocellulosic biomass (Brodeur et al., 2011).
Despite the attention that industrial bioproducts (bio-fuels, bio-based chemicals and biomaterials) have received over the last few years, not too many of these products are produced commercially at an industrial scale.

Lignin is one of the three main constituents of biomass. Lignin has received much attention in recent years because it is the only biopolymer of an aromatic nature. Since five out of the twelve main polymers in use today are based on aromatics, lignin has been considered as an ideal source for bio-based aromatics for the replacement of the petroleum-based analogues. Furthermore, it is estimated that the planet currently contains $3 \times 10^{11}$ metric tons of lignin with an annual biosynthetic rate of production of approximately $2 \times 10^{10}$ tons (Calvo-Flores et al., 2015); (Whittaker et al., 1975). However, the complexity of the chemical structure of lignin reduces its reactivity with other chemicals. Hence, even though lignin represents a rich potential source of organic macromolecules that can serve as a precursor for aromatics and their derivatives, it remains an underutilized by-product of biomass conversion processes due to a lack of technically sound and cost-effective routes for its utilization.

Lignin is generated industrially in large quantities especially from the kraft pulping process in the form of “black liquor”. Black liquor is the major residual stream from the kraft pulping process, containing 30-35 wt.% lignin. According to the International Lignin Institute, about 40-50 million tonnes of kraft lignin (KL) are generated worldwide each year in the form of “black liquor”. While combustion of black liquor to regenerate pulping chemicals and to produce steam and power is an integral part of the kraft process, a small portion of the lignin can be removed without compromising mill material and energy balances. 60-70% of North American kraft mills are pulp-production limited due to the thermal capacity of their recovery boilers.

A moderate-capital solution to this problem, is to precipitate a portion of the kraft lignin from black liquor, which would help debottleneck the recovery boiler thereby providing two additional revenue streams to kraft pulp mills namely: incremental pulp and kraft lignin. While, currently, 1-1.5 million tonnes/year of lignin is utilized for a wide range of applications, almost all of this is lignosulfonates from sulfite pulping. Lignosulfonates are water-soluble, highly sulfonated polymers, quite different from kraft lignin. Until
recently, the only commercial source of kraft lignin has been from Mead-Westvaco (now called Ingevity), which produces approximately 20,000 metric tons/year of kraft lignin under the trade name Indulin from a plant in South Carolina. Since 2013, however, three additional kraft lignin plants have been built, namely: Domtar, (Plymouth, Virginia, USA), West Fraser (Hinton, Alberta, Canada) and Stora-Enso (Sunila, Finland). Depolymerization has been considered as one of the most effective strategies for overcoming the recalcitrant nature of lignin, thereby enabling its conversion to smaller, simpler and more reactive fragments. Thus, an enormous research effort has been made in developing technologies for lignin depolymerization and utilization of the depolymerized products in the production of valuable biomaterials such as lignin-based polyurethane (PU) foams, phenolic resins/foams and epoxy resins.

1.2 Lignin importance and applications

Lignin has many potential applications across a variety of industries, including automotive, construction, coatings, plastics and pharmaceuticals. Refined lignin can replace petroleum-based phenols that are used in phenolic resins for plywood, oriented strand board (OSB), laminated veneer lumber (LVL), paper lamination and insulation materials. Other potential uses in the future include carbon fiber and carbon materials for energy storage.

1.2.1 Lignin as a Fuel

Lignin is a material with a high heating value (~26.7 MJ/kg) that can be used directly as a fuel. In the pulp and paper industry, about 7 M³ of black liquor are produced for every cubic meter of pulp. Most kraft pulp mills recover residual black liquor from the pulping process, concentrate it from about 20 to 70% solids using evaporation and then fire it into the recovery boiler for the production of steam, electricity and cooking chemicals for internal mill use. (Jenkins et al., 1998). Lignin recovered from black liquor has also been used as a fuel in the power boiler (e.g. Domtar, Plymouth, US) or as a fuel in the lime kiln (e.g. Stora-Enso, Sunila, Finland).
1.2.2 Lignin as a Binder

Kraft lignin use as a binder in wood pellets has been discussed recently. However, there are many other examples of lignin use in pellets in several industries. Lignosulfonates, for example, have been used for some time as a binder in animal feed pellets as well as elsewhere. A common binding agent for this purpose is a system called LignoBond, based on calcium lignosulfonates. This technology was developed in the late 1980s (Forss et al., 1980).

1.2.3 Lignin in Biosciences and Medicine

Native lignin and some of the extracted lignins and their derivatives have shown promising results in fields such as the biosciences and medicine, as a result of their interactions with living organisms. Antioxidant, antiviral, antitumor, and anticarcinogenic properties have been attributed to lignin. Dizhbite et al. (2004) studied the free radical-scavenging efficiency of a series of lignins isolated from several deciduous and coniferous wood species and 10 lignin fragments as compared to the well-known free radical scavenger 1,1-diphenyl-2-picrylhydrazyl (DPPH) by instrumental methods such as ESR and spectrophotometry. These researchers indicated the importance of the moieties constituted by non-etherified OH phenolic groups, ortho-methoxy groups, hydroxyl groups, and the double bonds between the outermost carbon atoms in the side chain of lignin for increased scavenger activity. Another example reported by researchers at the University of Helsinki is the functionalization of carboxylated lignin nanoparticles for targeted and pH responsive delivery of anticancer drugs. The resulting findings suggest the possible use of lignin in anticancer therapy (Figueiredo et al., 2017).

1.2.4 Lignin in polymer systems

Lignin, in any one of its forms, can be combined with polymers as a macromonomer, or as an additive. For lignin to be used as a macromonomer it must have functional groups similar to the polymer or co-polymer monomers used to make the polymer. Furthermore, lignin must undergo the same type of reactions as the monomers (i.e., esterification, amide formation, condensation), when they are incorporated into polymer chains. For lignin to be used as an additive it must be chemically compatible with the polymer in
question thereby becoming an integral part of the formulation. Lignin can provide added value to polymers by acting as a free-radical scavenger to protect them from oxidation, light, or heat (e.g. in rubbers, polyalkenes, polyesters, and other synthetic polymers (Calvo-Flores et al., 2015). An example of lignin use as a macromonomer is in phenol formaldehyde (PF) resins as a replacement of phenol. PF resins are widely used as adhesives in the manufacture of plywood, chipboard, medium-density fiberboard (MDF), and oriented strand board (OSB). The use of unmodified lignin in the preparation of such adhesives has received much attention since the 1970s (Falkehag, 1975).

Many investigations have been conducted relating to the replacement of phenol with lignin, especially lignosulfonate, in the manufacture of plywood or fiberboards, mostly because of its low cost and availability. The replacement of phenol with lignin makes sense from both an economic and an environmental point of view. (Pizzi, 1994). In addition to lignosulphonates, acetosol, organosolv and hydrolyzed lignins have been used in place of phenol in phenolic resins to produce modified polymers, which exhibit properties with good curing characteristics (Stewart 2008). As much as 50% phenol can be replaced with kraft lignin or lignosulfonates in PF resins, without substantially changing the final product properties. Polyurethane (PU) materials are usually made through the reaction of polyols with isocyanates. Polyols are chemical compounds with multiple hydroxyl groups in their structures.

A wide range of polyols are available as a feedstock in PU production. Polyols can be aromatic or aliphatic. Polyethers and polyesters are two major types of polyols consumed in the global polyl 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. Lignin can be employed as a macromonomer in the synthesis of PU because of its high amounts of hydroxyl groups available in the matrix polymer, capable of forming urethane bonds between lignin units and isocyanate.

Precured PU can be synthesized, for example by the reaction of mixtures of organosolv lignins and polyols such as polyethylene glycol (PEG), polypropylene glycol (PPG), or adipic acid (Ciobanu et al., 2004), and an isocyanate such as methylene diphenyl isocyanate (MDI) together with a plasticizer. Lignin-based acrylamide polymers can be prepared by copolymerization of alkali lignin with acrylamide in basic media by using
K₂S₂O₈ as an initiator. A high Mw polymeric material can thus be made that can act as a flocculant in the dewatering of sludge in combination with aluminum salts (Rong et al., 2013).

1.2.5 Lignin in Lead-Acid Batteries

Lead-acid batteries are the oldest type of rechargeable battery and they are massively used in the automotive industry. To improve the performance of the batteries, chemicals such as inorganic salts and carbon black are added. These additives are called expanders, and without them, the sponge lead in the negative plates of the battery would lose performance rapidly when cycled. Water-soluble lignosulfonates are the main components of battery expanders, and they improve performance of batteries at low temperatures and at high rates of discharge. Different lignosulfonates have been employed as expanders, and these exert widely different effects on the performance of lead-acid batteries (Boden, 1998).

1.2.6 Fertilizers

The modification of lignin can lead to new fertilizers with a higher performance than native lignin. Ammoxidized kraft lignin has been tested as a slow-release fertilizer for the cultivation of such species as sorghum. The experimental plots showed that modified lignin is a satisfactory source of nitrogen, with the advantage that percolated water after application had significantly lower nitrate levels than after conventional fertilization with inorganic salts, with a similar grain and plant development (Ramírez, 1997). The use of lignin as is or after chemical modification has been evaluated in several other applications including: dust control, thin film coatings, as a dispersant for concrete admixtures, pesticides and textile dyes as well as a precursor for making activated carbon, carbon black and carbon fiber. Despite the variety of potential lignin applications, the substitution level of petroleum-based products with lignin is usually limited by the high Mₘ of technical lignins. Hence, lignin depolymerisation could help address this issue thereby contributing to the full utilization of forest resources while addressing most environmental issues associated with the use of fossil resources.
1.3 Research objectives

The main objective of this PhD project was to develop novel strategies for lignin depolymerisation in an effort to: a) enable its use as a replacement of fossil-based chemicals at higher substitution rates and b) enable its use in applications in which fossil-based chemicals are not presently suitable and/or cost-effective. Specifically, this project aimed to develop novel and cost-effective approaches to: (1) depolymerize kraft lignin in black liquor rather than depolymerizing purified lignin itself, (2) depolymerize hydrolysis lignin (DHL) using chemicals recoverable by the kraft recovery cycle (e.g. white liquor (WL)), (3) depolymerize and carboxylate kraft lignin under mild conditions (e.g. ambient temperature and pressure) using only hydrogen peroxide (H$_2$O$_2$) and (4) depolymerize and nitrate kraft lignin under mild conditions (e.g. ambient temperature and pressure) using nitric acid (HNO$_3$) in the absence of a catalyst.

1.4 Research approach and methodology

The chemical structure and reactions of lignin have been studied for more than 100 years. Lignin is characterized by a variety of distinct and chemically different bonding motifs, each demanding different condition for cleavage when selective depolymerisation is targeted (Rinaldi et al., 2016). Biorefinery lignins are characterized by: (a) a high average Mw which leads to low substitution rates in various applications, low solubility/reactivity and high viscosity in various analysis and reaction media. (b) a low number of phenolic groups – this leads to limited reactivity in various applications in which these groups are needed (e.g. PF resins, coagulants, flocculants) and (c) limited solubility in water at any pH. This leads to limited applications in water-based systems. As indicated before, one approach for addressing these issues is lignin depolymerization. This study developed different strategies for improving lignin reactivity, solubility and chemical functionality. Depolymerization reactions were conducted in 100 mL and/or 2-L Parr stirred autoclave reactors. Scale-up of one of the depolymerisation reactions was conducted using a 20-L circulating reactor. Figure 1.4 displays the three reactors used in this research.
Figure 1-1 Pictures of 100-mL, and 2-L autoclave reactor systems and 20-L circulating reactor used for lignin depolymerization

1.5 Contributions and novelty

The main contributions and novelty of this research can be summarized as follows:

1- Development of a new approach for kraft lignin depolymerisation in black liquor instead of re-dissolving purified lignin in a solvent, depolymerizing it and recovering it again in the depolymerized form using a lignin recovery process for a second time.

2- Development of a new approach for hydrolysis lignin depolymerisation using chemicals recoverable by the kraft recovery cycle.

3- Development of a new approach for kraft lignin depolymerisation and carboxylation under ambient conditions in the absence of a catalyst or an organic solvent and with no further purification needed of the final product.

4- Development of a new approach for kraft lignin depolymerisation and nitration under ambient conditions in the absence of a catalyst or an organic solvent with no further purification needed for final product.
1.6 Thesis overview

This PhD thesis is organized into to consist of 7 chapters. Chapter 1 introduces lignin and the importance of valorizing it at this time in the context of climate change and other environment problems caused by the continued use of fossil-based fuels, chemicals and materials. It is a general introduction on the background, motivations and important usage of lignin.

Chapter 2 is presenting a comprehensive literature review on the state-of-the-art of lignin the lignin from black liquor and main depolymerization main exciting strategies.

Chapter 3: discusses is the manuscripts based on kraft lignin depolymerization in the black liquor. In this, in this chapter, the effects of several depolymerization process parameters such as temperature, reaction time, capping agent, co-solvent and lignin substrate concentration were evaluated studied.

Chapter 4: discusses: is the manuscripts based on the depolymerisation of hydrolysis lignin (HL) from the TMP-Bio™ process bioproduct were depolymerized by using chemicals recoverable chemicals recoverable by the kraft recovery cycle (e.g. white liquor, WL). In this study, the effect of various process parameters such as reaction time, (WL: HL) ratio, and reaction temperature on lignin depolymerization were as investigated using a 2-L Parr reactor under a N₂ atmosphere. Furthermore, process scalability-up was has been demonstrated using a 20-L circulating reactor.

Chapter 5: discusses: is the study, a new of lignin depolymerization approach for kraft lignin depolymerisation and carboxylation was demonstrated, an environmentally friendly and cost-effective approach to depolymerization of softwood (SW) and hardwood (HW) lignins under in ambient conditions using hydrogen peroxide (H₂O₂). The ratio of (SW &HW) lignins to H₂O₂ were investigated.

Chapter 6: discusses a new approach for kraft lignin depolymerisation and nitration under ambient conditions using nitric acid: in this chapter, lignin depolymerization with (HNO₃) at room temperature were studied for SW and HW lignins. The effect of HNO₃ concentration and the ratio of lignins to HNO₃ were investigated inspected.
Chapter 7: summarizes the main conclusions from this present work and suggests future research directions.

1.7 References:


Chapter 2

2 Literature Review

Lignin is a promising source of bio-based phenolic compounds that can be used widely in several industrial applications, e.g., as a component or additive in polymer and other systems or as a biogenic fuel substitute (Rößiger et al., 2018). In particular, the material chemistry community is attracted to lignin, which it identified as an optimal aromatic source for the generation of bio-based reconstituted polymers obtained via standard polymer transformations (Graglia et al., 2015). Thus, valorization of lignin is one of the most important challenges for the development of sustainable products in the evolving bio-economy. The alkylphenolic structure of the lignin molecule can be cleaved into lower Mw compounds such as monomeric and oligomeric phenols, alkylphenols and phenol resins that can be replace those obtained from fossil resources. Presently, most industrially produced lignin is produced in the form of residual black liquor from pulping processes and, in particular, the kraft pulping process. In this case, the lignin is combusted in a recovery boiler for the production of chemicals, steam and electricity for internal mill use. Even though these are fine using of lignin, they correspond to a value for the lignin of only $150-200/tonne depending on the incremental fuel being used at any given mill.

2.1 Kraft pulping

In the kraft pulping process, white liquor (a mixture of sodium hydroxide and sodium sulfide) is used to cook the wood chips at high temperatures and pressures. Under these conditions, the lignin matrix which holds the fibers together is broken down thus liberating the wood fibers from each other. The spent cooking liquor coming from the digester is called “black liquor”. The global pulp and paper industry produce about 130 million tonnes per year of kraft pulp which is about two-thirds of the world’s virgin pulp production and over 90% of chemical pulp production (Tran and Vakkilainen, 2007). The advantages of the kraft pulping process over other pulping processes include:
1- High pulp strength;

2- The ability to handle softwood, hardwood and other wood species;

3- Favorable economics due to high chemical recovery efficiency (around 97%) (Sixta, 2006).

\[\text{Figure 2-1} \quad \text{A schematic diagram of the kraft pulping process}\]

Figure 2-1 illustrates the kraft chemical recovery cycle. The regeneration of black liquor to fresh white liquor comprises the following principal steps: concentration of weak black liquor, incineration of concentrated black liquor, causticizing of smelt from the recovery boiler and calcination of the lime needed for causticization (Weizhen, 2013).

For every 1 tonne of kraft pulp that is produced, a mill also produces about 7 tonnes of black liquor at 15% solids containing about 10% organic chemicals and 5% inorganic chemicals with a total heat content of 5500-6500 Btu/lb of solids (Biermann, 1996).

Lignin (a complex polymer of phenylpropane units) in the black liquor is a potential renewable source of biofuels, chemicals, and materials. As much as 40 - 50 million
tonnes per annum of lignin is produced in the form of black liquor at kraft pulp mills worldwide (ILI, 2015).

2.2 Black liquor

Black liquor is a complex aqueous solution containing several components. The black liquor chemical composition depends on the type of the raw wood material processed, i.e. softwoods (such as pine), hardwoods (such as eucalyptus) or fibrous plants (such as bamboo) (Marcelo et al., 2009). Generally, black liquor is composed of water, organic and inorganic compounds. Inorganic compounds mostly originate from the white liquor used in pulping. Organic compounds are mostly derived from both lignin and carbohydrates in wood. Inorganics and degraded carbohydrates are soluble in water. They are present as salts of low molecular weight inorganic and organic compounds. The degraded carbohydrates are present as sodium salts of various saccharinic acids and/or lactones (Horntvedt, 1968). Black liquor properties are affected by the level and composition of these compounds (organic and inorganic constituents). Kraft lignin is not soluble in water, but it is soluble in black liquor because of its high content of residual alkali. It is believed that the lignin polymer exists in black liquor as a spherical, amorphous macromolecule with varying degrees of polyelectrolyte character. The ionizable groups in the lignin macromolecule are responsible for colloidal lignin stabilization at high pH levels. These groups are mainly the phenolic hydroxyl and carboxyl groups. These ionized groups prevent the lignin from agglomerating and precipitating due to the negative electrical charges on the macromolecule. Another important aspect of black liquor is that it contains several chemical species that act as buffers, e.g. H$_2$S (pKa ~ 7), Na$_2$CO$_3$ (pKa ~10.2), lignin phenolic groups (pKa = 9.4–10.8) and carboxyl groups (pKa ~4.4). Black liquor composition has a significant effect on the stability of the lignin colloids (Zhu, 2015). Factors such as the irregular particle structure, intramolecular association through hydrogen bonding, the charge distribution, and ion exchangeability are responsible for the complexity of lignin colloidal suspensions (Goring, 1962) (see Figure 2-2).
2.3 Lignin structure

Lignin is one of the three principal components in plants (i.e., cellulose, hemicellulose, lignin), and its content depends on the type of the plant. For example, lignin comprises about 28 wt.% of softwoods and 20 wt% of hardwoods (Heitner et al., 2010). The cellulose content is approximately 45 wt% in the wood of both types, while the hemicellulose content is roughly 17 wt% in softwoods and 25 wt% in hardwoods.

Lignin is a complex biopolymer, amorphous and cross-linked in three dimensions (as illustrated in Figure 2-3). It is comprised mainly of three lignols as the basic building blocks, as shown in Figure 2-4, i.e., p-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol, which are phenylpropane units (C9 units) differing from each other in the substitutions at the 3 and 5 positions (Figure 2-3). These lignols are linked into lignin aromatic centers in the form of phenyl propanoids, namely p-hydroxyphenyl (H), guaiacyl (G) and syringyl (S) units, respectively. Different types of lignins (i.e., softwood, hardwood, grasses) contain different amounts of methoxyl groups depending on how much of each of the three lignols has been incorporated into the lignin macromolecules (Figure 2-3) (Xu et al., 2014; Heitner et al., 2010).

Figure 2-5 illustrates the main functional groups and numbering system in lignin units. The attachment of the aliphatic side chain to the aromatic ring is at C–1. The phenol oxygen is attached at C–4. If there is only one methoxyl group, it will be on C–3 (not C–5). The side-chain carbons are labelled as (α, β, and γ), with C–α being attached to the aryl ring at its C–1 position.
**Figure 2-3** A model structure of lignin

**Figure 2-4** Three main building blocks of lignin macromolecule (Pu et al., 2008)
The most common linkages between lignin building blocks are aromatic or aliphatic ether units, and a summary of these linkage types and percentages is depicted in Table 2-1. The main linkages in softwood lignin are: β-O-4, 5-5, α-O-4, β-5, 4-O-5, β-1 and β-β, with the β-O-4 linkage being the dominant one, comprising more than 50% of the linkages in softwood lignin.

The dominant weak ether linkages in lignin provide opportunities for hydrolytic depolymerisation of lignin using water (Yuan et al., 2010; Mahmood et al., 2015a; Lancefield et al., 2015) or reductive de-polymerization of lignin using H₂ gas or formic acid (Huang et al., 2014) to produce de-polymerized lignin (DL) products of a reduced molecular weight. Compared to the original KL, a DL with a lower Mₓ (1000-2000 g/mol) has proved to be a more reactive substitute for phenol or polyol in the synthesis of
bio-based phenol formaldehyde (BPF) resins or bio-based polyurethane (BPU) resins /foams, achieving a high bio-substitution ratio (>50 wt.%) (Mahmood et al., 2015b).

### 2.4 LignoForce System™

FPInnovations developed the LignoForce System™ (Figure 2-6b) for the efficient recovery of kraft lignin (KL) from black liquor (BL). In this process, BL is oxidized with oxygen under controlled conditions before the black liquor acidification step of conventional lignin recovery processes. Based on the results obtained, BL oxidation improves the filterability of the acid-precipitated lignin by providing suitable conditions with respect to pH (a lower pH) and temperature (a higher temperature) to allow lignin colloidal particle agglomeration leading to the formation of larger particles, which make filtration and washing easier. In addition, the oxidation minimizes or eliminates total reduced sulphur (TRS) compounds, thereby leading to reduced TRS emissions during all subsequent steps: lignin precipitation, filtration and washing. Furthermore, because the oxidation of TRS compounds and sugars consumes residual effective alkali (sodium hydroxide) in BL, the carbon dioxide and sulphuric acid requirements of the process are significantly reduced. Controlled BL oxidation in the LignoForce™ process results in no major difference in the chemical composition, molecular weight distribution, or main functional groups of the KL produced compared with that produced by conventional acid precipitation methods (Kouisni et al., 2015). Based on the results obtained in laboratory studies, a lignin demonstration plant was designed and built at the Resolute-Thunder Bay mill for the production of 12.5 kg/h of high-quality KL lignin and, subsequently, an industrial size plant was built at the West Fraser Hinton mill for the production of 30 tonne/day of softwood kraft lignin.
Figure 2-6 (a) Conventional acid precipitation process and (b) LignoForce system™ for the recovery of kraft lignin from black liquor.

Since the LignoForce™ process is able to eliminate the downstream generation of TRS compounds from the lignin recovery process while reducing carbon dioxide consumption, it provides the opportunity to depolymerize lignin in black liquor (using added sodium hydroxide or white liquor) before reaching the lignin recovery system. This approach has the potential of significantly reducing the cost of producing depolymerized kraft lignin since it eliminates the need to produce purified lignin from black liquor using any one of the available processes, dissolve it in sodium hydroxide or any other solvent and then recover the lignin once more in a purified form. So far, no research has been reported on depolymerization of kraft lignin directly in black liquor.
2.5 Chemical reactions in kraft pulping

There are two main types of lignin reactions that occur during kraft pulping under alkaline conditions. The first one is lignin degradation reactions, which lead to lignin fragments of low average molecular weight (desirable reactions). The second one is lignin condensation reactions which lead to the formation of alkali-stable linkages (undesirable reactions) (Gierer, 1970). As presented previously in Table 2-1 (Pu et al., 2008), the β-O–4 and α-O–4-ether links together represent the most abundant connections between lignin units (up to 65%) (Zakzeski et al., 2010). The main steps in the degradation/dissolution of phenolic lignin moieties during pulping under alkaline conditions are:

1) Ionization of the phenolic groups

2) Cleavage of α-aryl-ether bonds and β-O-4- ether linkages

3) Liberation of free phenolic groups.

The degradation reactions start with ionization of the phenolic groups under alkaline conditions (Fengel and Wegener, 1983). The ionization triggers the formation of the para-quinone methide intermediate, which is the key intermediate that forms the β-aryl ether structure upon ionization of the phenolic group. The oxygen of the quinone group draws the electron density to the double bond thus making the carbon more positive. This, in turn, shifts the electron densities of the other bonds in this conjugated system as shown in Figure 2.7.
Figure 2-7 Formation of quinone-methide intermediate (3) and subsequent reaction pathways.

Since HS\(^-\) is a powerful nucleophilic agent, it attacks the quinone methide intermediate at the C-\(\alpha\) position in the manner illustrated in Figure 2-8.

Figure 2-8 Addition of hydrosulfide to quinone methide structure.

In particular, after the addition of HS\(^-\) to the quinone methide intermediate, an intramolecular attack at the neighboring \(\beta\)-carbon [structure 5] causes formation of a thiiran intermediate [structure 6]. Finally, elimination of elemental sulfur (formation of polysulfide), associated with re-aromatization, yields coniferyl-type structures [structure 8] (Sixta, 2006). This reaction scheme, ultimately, leads to break up of \(\beta\)-ether bonds thereby depolymerizing lignin.
2.6 Hydrolysis lignin

Hydrolysis lignin (HL) is a by-product from acid or enzymatic biomass pre-treatment processes such as the ones employed in cellulosic sugar and/or ethanol plants. HL could be, for example, the solid residue from the enzymatic hydrolysis of woody biomass which is mainly composed of lignin (50-65 wt.%), unreacted cellulose and mono and oligosaccharides. One such process was recently developed by FPInnovations researchers (Yuan et al., 2012) who patented a biomass fractionation process for producing value-added products from lignocellulosic biomass, such as wood-derived sugar and hydrolysis lignin. Acid hydrolysis of biomass was practiced in the former Soviet Union for the production of ethanol. Extensive research was undertaken at the time to find uses for acid hydrolysis lignins as they had several operating wood hydrolysis plants. Several chemical modifications of HL were investigated at the time in an effort to develop cost-effective uses of this abundantly available polymer rich in phenolic groups; however, the majority of the HL was disposed of because the required modifications were either too expensive or the material did not function well enough in application (Rabinovich, 2010). Similar problems are faced by researchers today in developing effective uses for HL.

2.7 Strategies developed for lignin depolymerization

The goal of most lignin degradation strategies is to reduce the structural complexity of the lignin macromolecule, as it exists in nature, by lowering its molecular weight and by increasing its chemical functionality. The chemical valorization of this biopolymer requires the selective deconstruction of its polymeric structure into a narrow range of molecules. A summary of the most common linkages in lignin was presented previously in Table 2.3, suggesting that cleaving the ether linkages, such as β-O-4 and α-O-4, can be the most effective approach for de-polymerization of the lignin macromolecule to produce aromatic monomers and oligomers for chemical applications (Yuan et al., 2010; Mahmood et al., 2015a).

Depolymerized lignin (DL) with a lower Mw (1000-2000 g/mol) has proved to be a more reactive substitute than crude lignin for phenol or polyol in the synthesis of bio-based phenol formaldehyde (BPF) resins or bio-based polyurethane (BPU) resins /foams,
achieving a high bio-substitution ratio (>50 wt.%) (Mahmood et al., 2015b). In general, two types of interunit linkages (C–C and C–O linkages) are connecting different aliphatic and aromatic units of the lignin structure. The bond energies of C–C linkages are higher than those of C–O linkages. Therefore, a high-temperature lignin depolymerisation approach should be able to break down both types of inter-unit linkages. However, under certain conditions, new C–C inter-unit bonds (condensation) can be produced (Guadix-Montero et al., 2018). Considering the dominant abundancy of β-O-4 linkages in lignin (see Table 2-1), various lignin-de-polymerization strategies have been developed targeting the cleaving of β-O-4 linkages through mainly hydrolytic, reductive and oxidative approaches (Seonah et al., 2011).

### 2.7.1 Alkali-catalyzed hydrolytic de-polymerization of lignin and lignin model compounds

The presence of alkali metal and alkaline earth metal hydroxides in various reaction media facilitates ether and other bond cleavage and, in some cases, increases the formation of formic or acetic acid during the lignin depolymerization process. As already reported earlier, base catalysts are required in water to solubilize the lignin, to avoid condensation and to increase product yield. Condensation reactions are noticeably suppressed during base-catalyst depolymerization processes compared to processes in acid or neutral media (Toledano et al., 2012).

Lignin dissolves in cold alkaline water at high pH. The depolymerization into smaller monomers taking place to any significant extent, depends on temperature, residence time, base concentration, alkali metal ion and/or alkaline earth metal ion concentration. Mainly two types of reactions take place, namely: the base-catalyzed cleavage of aryl-aryl-ether bonds and aryl-alkyl-ether bonds. Alkali metal and alkaline earth metal ions appear to polarize the ether bonds and affect the thermodynamics and kinetics of the process (Schmiedl et al., 2012). Alkali-catalyzed depolymerization of lignin by hydrolysis is one of the main proposed approaches for the production of high-value depolymerized lignin products. Roberts et al. (2011) examined the de-polymerization of lignin as catalyzed by NaOH in aqueous media. The types of aromatic molecules obtained from this reaction are
depicted in Figure 2-9a. The mechanism of the cleavage of the phenyl ether linkage was explained using a model compound incorporating a β-O-4 linkage.

A transition state involving a hydroxide ion and a sodium cation was proposed, leading to several possible monomeric aromatics (see Figure 2-9 b.). However, re-condensation of the monomeric aromatics caused the formation of products of a wide molecular weight range sometimes larger than the original lignin M_w. Using a capping agent such as phenol was recommended to suppress these side reactions, and this was confirmed in other studies (Yuan et al., 2010; Toledano et al., 2014).

![Figure 2-9](image)

**Figure 2-9** (a) Aromatic monomeric products obtained from lignin de-polymerization using 25 wt.% NaOH in water at 300 °C and 250 bar; (b) Proposed NaOH-catalyzed cleavage mechanism of the β-O-4 bond involving sodium cation.

Rodriguez et al., 2017 reported a mild lignin depolymerization process using a NaOH treatment after enzymatic hydrolysis at temperatures of around 120 °C. A considerable decrease in the lignin average molecular weight and the formation of lignin-derived monomers including hydroxycinnamic acids was observed. Lavoie et al., 2011. depolymerized softwood kraft and hemp lignins pretreated by steam explosion and treated with 5 wt. % NaOH in an aqueous solution at temperatures ranging from 300 and 330 °C under pressures ranging from 9 to 13 MPa. There were 26 major compounds of low molecular weight identified by Gas Chromatography-Mass Spectrometry (GC-MS) after the reaction, in which guaiacol, catechol, and vanillin were the most abundant. The effects of different alkaline catalysts were studied by Miller et al. (2002). This study reported that strong bases (e.g. NaOH, KOH) convert more of the lignin to low molecular
weight products than weak bases (Li OH, Ca(OH)₂, Na₂CO₃). The maximum conversion was accomplished when the mole ratio of NaOH/lignin was between 1.5 and 2 for 1 hr reaction time at 330 °C at a lignin substrate concentration of 10wt. %. A longer reaction time, e.g. 2 hours, did not improve the extent of the reaction. Recently, Rößiger et al. (2018) reviewed the history, the challenges and perspectives relating to base-catalyzed depolymerization of lignin.

2.7.2 Acid-catalyzed hydrolytic de-polymerization of lignin

Acid treatment is one of the earliest techniques used to deconstruct wood components and separate lignin. Hewson et al. (1943) conducted a series of treatments on maple wood meal by using different combinations of acids and alcohols, including HCl/ethanol and formic acid/ethylene glycol to separate lignin into water-soluble and water-insoluble components at a low temperature range. They concluded that this low temperature approach was not sufficient to break the complex lignin structure into monomeric compounds for further usage. More recently, different types of acids were investigated for lignin depolymerisation including mineral and Lewis acids, zeolites and ionic liquids. Gasson et al. (2012) recently investigated acid-catalyzed lignin de-polymerization at higher temperatures. Different ratios of formic acid to ethanol were employed in a continuously stirred tank reactor (CSTR). They found that methoxyphenol, catechol, and phenol were obtained as the major components when the reaction temperature was raised to the 360 to 400 °C range. The critical reaction pathway for the formation of phenolic products was primary lignin degradation via the cleavage of β-O-4 bonds catalyzed by acid (Forchheim et al., 2012). Experimental details of acid-catalyzed lignin de-polymerization reactions are summarized in Table 2-2. Acidic or alkaline approaches alone aiming to produce monomeric compounds are considered ineffective due to competing re-polymerization and condensation reactions of the cleaved lignin fragments (Wang et al., 2013). Thus, acid catalyzed de-polymerization of lignin is usually combined with other methodologies, e.g., using an acid/ethanol solution system with metallic catalyst enhancers (Xu et al., 2012). Generally, acid-catalyzed de-polymerization focused on the cleavage of the β-O-4 bonds in lignin. Formic acid or other acids provided a source of hydrogen cation in the hydrolysis by forming H₃O⁺ on the β-O-4 bond or the
cationic aromatic rings. Co-catalysts palladium or platinum were usually used to increase the selectivity of the cleavage (Liguori and Barth, 2011). Since formic acid can decompose to form hydrogen gas, lignin de-polymerization using the formic acid/ethanol solution system was believed to take place via the reductive de-polymerization mechanism (Huang et al., 2014), which is discussed further in the subsequent section.

**Table 2-2  Acid–catalyzed de-polymerization of wheat straw lignin (Wang et al., 2013).**

<table>
<thead>
<tr>
<th>Acid-alcohol aqueous solution</th>
<th>Reaction conditions</th>
<th>Yield (wt. %) of main products: Methoxyphenols, Catechols, Phenols</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>T (°C)</td>
<td>P (MPa)</td>
</tr>
<tr>
<td>10 wt.% formic acid- 77wt% ethanol</td>
<td>360</td>
<td>25</td>
</tr>
<tr>
<td>10 wt.% formic acid- 77wt% ethanol</td>
<td>380</td>
<td>25</td>
</tr>
<tr>
<td>10 wt.% formic acid- 81wt% ethanol</td>
<td>380</td>
<td>25</td>
</tr>
</tbody>
</table>

Deepa and Dhepe (2014) conducted a series experiments to depolymerize alkali lignin, bagasse lignin, and organosolv lignins on various solid acid catalysts. They stated that, efficient conversion of lignins into value-added aromatic monomers was achieved, in particular, the SiO$_2$-Al$_2$O$_3$ catalyst presented exceptionally high yields of 60% for organic solvent soluble extracted lignins at 250 °C within 30 min.

Recently Kristianto et al. (2017) reported that the addition of Ru/C catalyst and formic acid to ethanol solvent enhanced the depolymerization efficiency of concentrated acid hydrolysis lignin significantly compared to its solvothermolysis without any additives.

At higher formic acid contents and increased reaction time at 350 °C in the presence of Ru/C increased the resulting bio-oil yield and also reduced the oxygen content of the bio-oil. Furthermore, Singh and Ekhe (2015) investigated the effect of solid acids on lignin depolymerization. The group established a one-pot process using Cu/Mo loaded ZSM-5 catalyst for the production of alkyl phenols using methanol as a hydrogen donor, and water as co-solvent. Kraft lignin was almost fully converted to alkyl phenols (>95%) at 220 °C for 7 h, with only a small amount of char (<0.5%) being formed. The products were then analyzed using a GC-MS/FID system, which showed 3-methoxy- 2,5,6-trimethyl phenol (M11) as the predominant product with a high selectivity (70.3%) for
the reaction catalyzed by Cu/Mo-ZSM-5 at a solvent ratio of 1:1 (methanol/H₂O). It should be noted here that, the bulky nature of biomass and the acidic reaction conditions are the main reason for re-polymerization and self-condensation reactions of lignin under processing conditions eventually leading to a complex pool of aromatics (Li et al., 2012).

2.7.3 Oxidative de-polymerization of lignin

Lignin depolymerization by oxidation was confirmed as a selective and economically viable approach that is widely applied to pulp bleaching processes. Various sophisticated strategies for oxidative depolymerization of lignin model compounds or lignin have been developed, including electrochemistry, photocatalysis, and the use of heterogeneous catalysts or ionic liquids. Valuable monomers were thus produced from lignin degradation at high selectivity (Sun et al., 2018).

Lignin depolymerization via oxidation especially employing oxygen, hydrogen peroxide, or peroxyacids may grow significantly in the future since oxidative methods are already widely employed in the papermaking industry for pulp bleaching. Moreover, most of oxidation approaches used today are likely environmentally friendly and conducted under mild conditions. However, oxidation approaches need sufficient selectivity to avoid overoxidation of the substrate to gaseous products.

In contrast to other strategies, oxidative depolymerization involving free radicals during oxidation may lead to additional functionalities to the already complex lignin- derived aromatic compounds. Preferably, an oxidation approach should enable efficient depolymerization under mild conditions, directly converting lignin to specific fine chemicals bearing alcohol, aldehyde, or carboxylic acid group moieties (Chatel et al., 2014). Oxidative degradation of lignin is inspired by nature, where enzymes achieve decomposition of lignocellulose residues by employing specific manganese-containing peroxidases as oxidants (Hofrichter, 2002). Another example is the production of vanillin from lignin by oxidative reactions using copper catalysis.
By far, this is the only methodology currently used at a commercial scale to obtain aromatic chemicals from lignin (Bjørsvik et al., 2002). Rahimi et al. (2013) developed selective oxidation methodology using a two-step process under aerobic conditions (Figure 2-10), i.e., in CH₃CN-water solution with 4-acetamido-TEMPO/HNO₃/HCl catalyst at 65 °C (Step 1), and in formic acid-water solution with HCO₂Na catalyst at 110 °C (Step 2), resulting in β-O-4 linkage cleavage.

However, the oxidative cleavage of β-O-4 ketone-containing model compounds and lignin were not at the desired level due to the instability of the formed products under these oxidative conditions.

Oxidative lignin depolymerization pathways can yield valuable chemicals such as simple aldehydes (vanillin, syringaldehyde, p-hydroxybenzaldehyde) or acids (vanillic acid and syringic acid) (Lalitendu et al., 2017). Depending on the oxidation stage, various carboxylic acids having aromatic and non-aromatic structures with mono- or di-carboxyl functional groups can be produced (Kang et al., 2019). Hydrogen peroxide, molecular oxygen and other oxidants in the presence or absence of a catalyst have been investigated extensively. Hydrogen peroxide is the simplest peroxide incorporating a single oxygen – oxygen bond. It is used as an oxidizer, bleaching agent and antiseptic. Concentrated hydrogen peroxide is a potent oxidizing agent, because of the nature of its unstable
peroxide bond. The reactions of hydrogen peroxide with lignin are of great significance to the pulp and paper industry since it is extensively used as an efficient bleaching reagent in this industry. Hydrogen peroxide is favorably removing chromophoric structures present in residual lignin. However, it is incapable of degrading the lignin structural network. Consequently, to degrade and remove the residual lignin, hydrogen peroxide must be activated. This activation is usually achieved by adding organic or mineral acids. Crestini et al. (2006) reported kraft lignin and lignin model compound degradation using H$_2$O$_2$ as an oxidant on methylrhenium trioxide (CH$_3$ReO$_3$) catalyst. Their study reported that depolymerized lignin compounds with increased aliphatic-OH, syringol-OH, guaiacyl-OH, p-hydroxy phenyl- OH, and COOH group were produced at room temperature.

Ozonolysis of lignin was first reported in 1913 (Danby et al., 2017). The early focus was on ozone’s ability to attack aromatic rings, thereby resulting in complete delignification. The application of ozone for determining lignin structure, particularly of the aliphatic side chains, has been widely studied (Akiyama et al., 2002). Batch ozonolysis of lignin has been reported to yield oxygenated aromatics but only at short reaction times (between 1 and 8 min), beyond which overoxidation products might dominate.

To minimize overoxidation Quesada et al. (1998) suggested to control the ozonolysis of the cleaved functional groups and the lignin backbone in two ways: (a) using short residence times in a continuously stirred reactor and (b) choosing a solvent that inhibits ozone’s tendency to oxidize aromatic moieties. Short chain organic acids are often used as solvents for organosolv extraction of lignin from biomass. The effect of the solvent has been studied by Rahimi et al., 2014. They found that the use of formic acid significantly improves aromatic monomer yields via novel depolymerization strategies based on the existence of C$_{\gamma}$- and C$_{\alpha}$-hydroxy species in the $\beta$-O-4 linkage.

Danby et al. (2018) proposed a continuous ozonolysis process for grass lignin in acidic media. In a two-step process, a continuously stirred tank reactor was used, where ozone was bubbled through an acidic solution of lignin for a short period of time at a low temperature (70 °C), followed by membrane separation. The resulting products were mainly vanillin and 4-hydroxybenzaldehyde, constituting about approximately 7 wt. % of
the amount of lignin used. Ozone is often considered a “green” alternative to less sustainable oxidants.

2.7.4 Reductive de-polymerization of lignin

Reductive treatment of lignin dates back to early works on structural elucidation, when lignin was treated in the presence of CuCr catalysts under relatively severe reaction conditions (250−260 °C, 220−240 bar), to obtain aliphatic compounds (mainly 4-propylcyclohexanol) which were isolated and characterized mainly based on boiling or melting points and elemental analyses (Bower et al., 1941). Reductive de-polymerization of lignin through selective hydrogenolysis of the aromatic carbon-oxygen (C-O) bonds in aryl ethers is another effective route for the generation of fuels and chemical feedstocks from biomass or coal Sergeev and Hartwig (2011) reported very effective cleavage of diarylethers using Ni (COD)2 - bis(cyclooctadiene) nickel and an NHC ligand in the presence of base under a 1 bar hydrogen atmosphere at 80-100 °C, producing arene and phenol products at excellent yields (Figure 2-11).

![Successful cleavage of lignin model compounds in H2 atmosphere with nickel catalyst.](image)

**Figure 2-11** Successful cleavage of lignin model compounds in H2 atmosphere with nickel catalyst.

Different hydride donors can be applied including silane reducing agents, aluminum hydride donors or hydrogen gas with the addition of AlMe₃, aryl-alkyl ethers and benzylic ethers (Sergeev and Hartwig, 2011). These catalytic systems were more active for aryl substrates with electron withdrawing substituents. Since formic acid can decompose to form hydrogen gas (HCOOH → H₂ + CO₂), lignin de-polymerization using formic acid as a solvent or catalyst was believed to take place via the reductive de-
polymerization mechanism as well. It has been demonstrated that the hydrogen formed in-situ from hydrogen-donating solvents, i.e., formic acid, is more effective for reductive degradation of lignin than external hydrogen gas sources (Huang et al., 2014). Reductive depolymerization requires catalysts efficient for selective scission of C–O bonds. A stepwise reductive deoxygenation of the aromatic monomers that are obtained post depolymerization commonly leads to a decrease in complexity of the product mixtures, increasing the selectivity to defined aromatic compounds. These exceptional features make the approach attractive toward structure elucidation (Barta et al., 2010).

Galkin et al. (2014) developed an efficient catalyst system for the cleavage of C–O bonds in lignin β-O-4 linkages of model compounds by using Pd/C and formic acid as a reducing agent under mild reaction conditions (80 °C in air). Remarkably, this research group found that the addition of catalytic amounts of a hydrogen source (e.g., HCOOH, NH₄HCO₂, 2-propanol, and NaBH₄) was sufficient to promote the redox neutral cleavage of the β-O-4 linkage. Furthermore, under relatively mild reaction conditions Barta et al., 2014 described an efficient reductive system for lignin depolymerisation which displayed high isolated yield for specific aromatic compounds at 140–180 °C. In this work, organosolv lignin substrate extracted from candlenut shells was depolymerized to well-defined aromatic monomers over copper doped porous metal oxide (CuPMO) in the presence of hydrogen gas (50 bar). The key product at 140 °C was 4-propanolcatechol that was isolated by column chromatography at 43.3% yield - the total monomer yield reached 63.7%. Very recently, Monsigny et al. (2018) presented an efficient catalytic reduction of lignin model compounds as well as softwood and hardwood lignins by using iridium-based Brookhart’s catalyst and hydrosilanes (R₃SiH) as a reductant. This catalyst displayed increased stability and selectivity in comparison to the B(C6F5)₃/hydrosilane system and it enabled a convergent reductive depolymerization of wood lignins to isolable mono-aromatics. The oxidative depolymerization of lignin offers a highly efficient entry to the solubilization of lignin. A difficulty in this approach remains the isolation of pure aromatics (Zakzeski et al., 2010). In contrast, mild reductive routes that would converge towards monoaromatics derivatives of the constituting monolignols by replacing C–O bonds with C–H bonds, are quite rare. Thus, more investigations are needed toward this approach (Galkin et al., 2014).
2.7.5 Ionic-liquid catalyzed depolymerisation of lignin

Ionic liquids (ILs) have been proposed as solvents for lignocellulose fractionation due to their special and highly tunable solvent properties (Verdía et al., 2014). The limitations related to ILs are the cost as well as the ease of product separation and solvent recyclability. Interestingly, George et al. (2015) reported the synthesis of several ethylammonium sulfate ILs resulting in efficient delignification without significant reduction of cellulose crystallinity. In addition, a production cost close to conventional organic solvents was revealed. Furthermore, ILs can act as reaction media for lignin dissolution and depolymerization due to the incorporation of acidic or other catalytic properties. Ionic Liquids (ILs) are salts that are in the liquid state at room temperature (Zhu et al., 2011). Jia et al. (2010) reported a method for the β-O-4 bond cleavage of two lignin model compounds, guaiacylglycerol-β-guaiacyl ether (GG) and veratrylglycerol-β-guaiacyl ether (VG), using an ionic-liquid: 1-butyl-3-methylimidazolium chloride ([Bmim][Cl]) with metal chlorides as a co-catalyst. Figure 2-12 shows a simplified reaction pathway. They concluded that Iron (III) chloride, copper (II) chloride and aluminum (III) chloride are the most effective in cleaving the β-O-4 bond in GG. An interesting conclusion is that more β-O-4 bond cleavage of GG occurs when there is an increase in available water.

![Figure 2-12](image-url)  
**Figure 2-12** Formation of Hibbert's ketones following β-ether cleavage in IL-catalyzed lignin de-polymerization.

Diop et al. (2015) depolymerized lignin successfully by thermal treatment of kraft lignin in butyl-1,8-diazabicyclo [5.4.0] undec-7-enium chloride ([DBUC4+] [Cl-]) without a catalyst. A range of temperatures were investigated (150, 200, and 250 °C) for 1 h. The
average molecular weight of the lignin collected after 1 h of reaction time decreased by 23, 70, and 58 % for the treatment at 150, 200, and 250 °C, respectively. FTIR spectra showed the cleavage of β-O-4 bonds in kraft lignin. Also, ¹H NMR spectra exhibited demethylation of all treated kraft lignins. Moreover, the ³¹P NMR analysis proved that demethylation of the treated kraft lignin contributed to the formation of catechol groups. The mechanism of lignin depolymerization through ionic liquid (ILs) pretreatment was recently considered and preferential lignin dissolution was often assumed to occur due to the chemical nature of lignin compared to that the ionic liquid. For example, the benzene ring of the H structure is presumed to be first attacked by acidic protons, H⁺ to generate an important cationic intermediate, which results in the final product, phenol, through the rupture of C–Ar bonds in benzyl (Moreau et al., 2002). The main advantages of employing ionic liquid media are that the low molecular weight (volatile aromatic) products can be separated by distillation and the by-products of degradation can be precipitated with water or be separated by selective membrane technologies (Long et al., 2015). Other advantages of using (ILs) in this and other research fields relate to them being non-flammable, non-volatile, and recyclable. ILs have been shown to dissolve wood, cellulose, and lignin, which opens up new opportunities in biomass conversion (Fort et al., 2007).

2.7.6 Biological and biochemical depolymerization of lignin.

Biological and biochemical approaches are quite promising for lignin valorization, since they can overcome the high heterogeneity of the recalcitrant lignin on some occasions even better than traditional chemical strategies (Beckham et al., 2016). The aromatic compounds obtained from lignin depolymerization and catabolism offer a strategy that should be considered equivalent to biomass-derived polysaccharide depolymerization and fermentation or chemical conversion. In nature, lignin is depolymerized by fungi and bacteria that generally use powerful oxidative enzymes. Linger et al. (2014) reported using a natural aromatic-catabolizing organism, Pseudomonas putida KT2440, to convert both aromatic model compounds and heterogeneous, lignin-enriched streams derived from pilot-scale biomass pretreatment into medium chain-length polyhydroxy alkanoates. In the same study, they concluded that the use of aromatic catabolic pathways enables the
valorization of lignin by overcoming its inherent heterogeneity to produce fuels, chemicals, and materials. In particular, Linger et al., 2014 demonstrated a two-step approach using metabolically engineered “Pseudomonas putida KT2440”, to convert both lignin model compounds and lignin-enriched streams derived from pilot-scale biomass pretreatment into medium chain-length polyhydroxyalkanoates (PHAs) at a yield of 34–39%. They further proved that mcl-PHAs can be depolymerized to alkenoic acids, which are precursors for various chemical applications. Also, alkenoic acids can be converted to alkanes by a bimetallic catalyst. In the same study, they introduced a modification of the aforementioned aromatic-catabolizing organism to show an integrated scheme for the conversion of lignin via biologically derived muconic acid to adipic acid that is one of the most widely produced dicarboxylic acids. Hence, biological and biochemical concepts for lignin valorization offer a versatile path forward for the production of fuels, chemicals, and materials from lignin.

2.8 Nitrolignin

Nitration is a general type of chemical process for the introduction of nitro groups into organic compounds. It is a significant reaction in many applications including: wood protection, dyes, drugs, explosives, solvents, and additives to fuels and oils. Despite its 150-year history, the nitration reaction continues to attract the attention of many researchers today. Lignin is nitrated readily with HNO₃, as confirmed in the 1920s by several authors (Calvo-Flores et al., 2015) and it was also found to react with gaseous NO₂. Diluted HNO₃ has generally been used for lignin nitration. Normally, nitration is conducted in a non-aqueous medium, and the nitrolignin produced is isolated, by precipitation, using water addition. Nitrolignin is soluble in common organic solvents similar to those used for halolignins. Nitrolignins incorporate nitrogen in the form of nitro groups on the aromatic ring, as has been established by the identification of monomeric nitroaromatic compounds (Dence et al., 1971). Glycol-lignin was successfully nitrated by adding it to a mixture consisting of acetic anhydride/fuming HNO₃ (4:1) at a temperature below 0 °C. Also, acetylation occurred simultaneously. The nitrated lignin could be reduced with sodium amalgam in alkaline solution, resulting in a reduction product which could be diazotized. The latter when coupled with β-naphthol
disulfonic acid generated a product that dyed silk and wool a brownish color when mordanted with tannic acid (Hibbert and Rowley, 1930). Another example of nitrolignin preparation was by Phelps, 1909, who produced a yellow dyestuff by the treatment of lignosulfonic acid with HNO₃.

### 2.9 Concluding Remarks

As discussed above, lignin represents an important renewable resource for use in several high-value applications. Despite nearly a century of research and development aiming to convert lignin into valuable products, lignin in most current and planned biorefinery contexts remains underutilized, most often being burned to generate heat and power. Currently only 2% of the annually produced lignin is commercialized, mainly in the lignosulphonate form. Although with much lower reactivity, crude lignin can be used in a certain application at a low substitution rate. However, the drive towards effective lignin valorization processes has witnessed a significant resurgence in the past decade, catalyzed by an improved understanding of lignin chemistry, structure, and reactivity and plasticity in parallel with new catalytic and biological approaches to valorize this important widely available biopolymer. The lignin macromolecule contains a variety of functional groups that have an impact on its reactivity. Lignin mostly contains methoxyl groups, phenolic hydroxyl groups, and a few terminal aldehyde groups. Only a small portion of the phenolic hydroxyl groups are free since most are involved in linkages to neighboring phenylpropane units. Thus, it is essential to identify cost-effective routes for improving lignin reactivity. One of the most promising strategies for increasing the reactivity of lignin is lignin depolymerisation. So far, kraft lignin (KL) has been depolymerized into oligomers and monomers via hydrolytic depolymerization (using water) or reductive depolymerization (using hydrogen) in various solvents and catalysts. The most commonly used solvents include water, water-ethanol co-solvent, water-ethanol-formic acid, methanol, and acetone, etc. Also, a range of various homogeneous, heterogenous, metallic, commercial and industrial catalysts have been tested for the depolymerization of lignin. However, most of the depolymerization processes reported in the literature operate at high temperature and pressure (as high as 8-12 MPa). These high temperature-pressure processes are associated with high capital/operating costs and
several more challenges in large-scale industrial applications.
To address this problem, this project focused on developing cost-effective and industrially saleable approaches for lignin depolymerisation that can easily be integrated into pulp mill operations. In this respect, it represents a step forward in terms of helping to widen the range of applications in which lignin could be used while increasing the substitution rates at which lignin can replace petroleum-based products.

2.10 References


Chapter 3

3 Effects of Process Parameters on Hydrolytic Treatment of Black Liquor for the Production of Low Molecular Weight Depolymerized Kraft Lignin.

The information presented in this Chapter is based on the paper “Effects of Process Parameters on Hydrolytic Treatment of Black Liquor for the Production of Low Molecular Weight Depolymerized Kraft Lignin”, which was published in Molecules 23.10 (2018): 2464-2481. The sections in Chapter 3 present the results towards the completion of objective 1 of this PhD project.

3.1 Abstract

The present research work aimed at hydrolytic treatment of kraft black liquor (KBL) at 200-300 °C for the production of low molecular weight depolymerized kraft lignin (DKL). Various process conditions such as: reaction temperature, reaction time, initial kraft lignin (KL) substrate concentration, presence of a catalyst (NaOH), capping agent (phenol) or co-solvent (methanol) were evaluated. The research demonstrated effective depolymerization of KL in KBL at 250-300 °C with NaOH as a catalyst at a NaOH/lignin ratio of about 0.3 (w/w) using diluted KBL (with 9 wt.% KL). Treatment of the diluted KBL at 250 °C for 2 h with 5% addition of methanol co-solvent produced DKL with a weight-average molecular weight (Mw) of 2340 Da, at approx. 45 wt.% yield, and a solid residue at a yield of ≤1 wt.% . A longer reaction time favored the process by reducing the Mw of the DKL products. Adding a capping agent (phenol) helped reduce re-polymerization/condensation reactions thereby reducing the Mw of the DKL products, enhancing DKL yield and increasing the hydroxyl group content of the lignin. For the treatment of diluted KBL (with 9 wt.% KL) at 250 °C for 2 h, with 5% addition of methanol co-solvent in the presence of NaOH/lignin ≈ 0.3 (w/w), followed by acidification to recover the DKL, the overall mass balances for C, Na and S were measured to be approx. 74%, 90% and 77%, respectively. These results represent an important step towards developing a cost-effective approach for valorization of kraft black liquor for chemicals.
3.2 Introduction

An increasing global population with limited resources is probably one of the greatest challenges that humanity faces at the present time. A large part of the problem is that our economy is based on fossil resources that are not renewable or sustainable (Calvo-Flores et al., 2015). Potential solutions to the growing global demand for energy/chemicals and the associated environmental problems include the development of alternative, renewable sources for energy, chemicals, and materials. In relation to energy, several alternative sources can be considered including: nuclear, solar and wind power. In the case of chemicals and materials, however, the only renewable alternative to fossil resources is biomass. So far, most research work focused on the use of the cellulose and/or hemicellulose components of biomass. However, lignin should not be ignored since it constitutes approximately 30 wt. % of the dry weight of softwoods and about 20 wt. % of hardwoods. It is estimated that the planet currently contains $3 \times 10^{11}$ metric tons of lignin with an annual biosynthetic rate of production of approximately $2 \times 10^{10}$ tons (Whittaker et al., 1975; Kaplan, 1998).

The removal of lignin from wood through various chemical pulping processes has experienced tremendous growth over the last century due to increased demand for cellulose fibers. Lignin is a complex biopolymer, amorphous and cross-linked in three dimensions. It is comprised mainly of three monolignols as the basic building blocks, namely: p-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol, which are phenylpropane (C9) units differing from each other in the substitutions at the 3- and 5-ring positions. These lignols are linked into lignin aromatic centers in the form of phenyl propanoids, namely p-hydroxyphenyl (H), guaiacyl (G) and syringyl (S) units, respectively. Different types of lignins (i.e., softwood, hardwood, grasses) contain different amounts of methoxyl groups depending on how much of each of the three lignols has been incorporated into the lignin macromolecules (Xu et al., 2014); (Heitner et al., 2016). It is generally accepted that the biosynthesis of lignin stems from the polymerization of the three types of phenylpropane units or monolignols discussed above (Chakar et al., 2004). The most common linkages between lignin building blocks are
aromatic or aliphatic ether bonds. The main linkages in softwood lignin are: β-O-4, 5-5’, α-O-4, β-5, 4-O-5, β-1 and β-β, with the β-O-4 linkage being the dominant one, comprising more than 50% of the linkages in softwood lignin (Pu et al., 2008).

Over the last few years, much effort has been made to explore the use of lignin as an alternative feedstock to produce various chemicals and materials such as bio-based polyurethane (BPU) foams, bio-based phenol-formaldehyde (BPF) foams/resins, and epoxy resins. For example, kraft lignin (KL) was shown by several researchers to be a suitable partial replacement for petroleum-based polyols in the preparation of polyurethane (PU) foams as well as phenol in the preparation of phenol formaldehyde (PF) resins (Mahmood et al., 2016); (Cheng et al., 2012). In these two applications, however, the lignin substitution level is commonly less than 30 wt.% and 50 wt.%, respectively, because of the high lignin Mw and the resulting reduced solubility and reactivity as well as the increased viscosity of the reaction medium. In fact, replacing bisphenol A or B with untreated kraft lignin in the preparation of epoxy resins is not even feasible because of the high lignin Mw.

To address this problem, several strategies were developed for lignin depolymerization. Alkali-catalyzed hydrolysis is one of the main approaches reported in the literature for the production of depolymerized lignin products. For example, Roberts et al. examined the de-polymerization of lignin using sodium hydroxide as a catalyst in aqueous media (Roberts et al., 2011). The mechanism of the cleavage of the phenyl ether linkage was investigated using a model compound incorporating a β-O-4 linkage. A transition state involving a hydroxide ion and a sodium cation was proposed, leading to several possible monomeric aromatics. However, re-condensation of the monomeric aromatics caused the formation of products of a wide molecular weight range sometimes larger than the original lignin molecular weight. Using a capping agent such as phenol was recommended to suppress these side reactions, and this was confirmed in other studies (Yuan et al., 2010); (Toledano et al., 2014). Rodriguez et al. reported a mild lignin depolymerization process using a NaOH treatment after enzymatic hydrolysis at mild temperatures of around 120 °C. A considerable decrease in the lignin average molecular weight and the formation of lignin-derived monomers including hydroxycinnamic acids.
were observed (Rodriguez et al., 2017). Lavoie et al. depolymerized softwood kraft and hemp lignins pretreated by steam explosion and treated with 5wt. % of NaOH in an aqueous solution at temperatures ranging from 300 and 330 °C under pressure ranging from 9 to 13 MPa. There were 26 major compounds of low molecular weight identified by Gas Chromatograph (GC)-MS after the reaction, in which guaiacol, catechol, and vanillin were the most abundant (Lavoie et al., 2011).

Recently, Rößiger et al. (2018) reviewed history, challenges and perspectives relating to base-catalyzed depolymerization of lignin. In particular, these investigators emphasized the importance of avoiding lignin repolymerization by scavenging and/or deactivating of reactive lignin-derived intermediate species containing phenol, carbonyl, or alkene functionalities. Boric acid and phenol were suggested as possible capping agents based on previous work by Roberts et al. (2011) and Toledano et al. (2014). These studies also discussed the benefits of conducting lignin depolymerization in a flow reactor as an additional approach for minimizing lignin repolymerization and improving the technology readiness level as well as the economics of the process. Acid-catalyzed hydrolytic depolymerization of lignin is one of the earliest techniques used to break down wood components and separate lignin. Hewson et al. conducted a series of treatments on maple wood meal by using different combinations of acids and alcohols, including HCl/ethanol and formic acid/ethylene glycol, to separate lignin into water-soluble and water-insoluble components at low temperatures (Hewson et al., 1943). They concluded that this approach was not sufficient to break down the complex lignin structure into monomeric compounds for further usage. Gasson et al. (2012) recently investigated acid-catalyzed lignin depolymerization. This study showed that lignin depolymerization in ethanol with formic acid can be carried out quickly and efficiently under high temperature and pressure conditions.

One of the most promising strategies for lignin depolymerization is oxidative degradation as conducted in natural systems where enzymes achieve decomposition of lignocellulose residues by employing specific manganese-containing peroxidases as oxidants (Hofrichter, 2002) or pure molecular oxygen. Another example is the production of vanillin from lignin by oxidative reactions using a copper catalyst this is, in fact, the
only methodology currently used at the commercial scale to obtain monoaromatic chemicals from lignin (Bjørsvik et al., 2002). Another promising approach for lignin depolymerization is by ionic liquids. Ionic Liquids (ILs) are salts that are in the liquid state at room temperature (Zhu et al., 2011). Jia et al. (2010) reported a method for the β-O-4 bond cleavage of two lignin model compounds, guaiacylglycerol-β-guaiacyl ether (GG) and veratrylglycerol-β-guaiacyl ether (VG), using an ionic-liquid, namely: 1-butyl-3-methylimidazolium chloride ([Bmim][Cl]) with metal chlorides as a co-catalyst. Recently, a new approach was reported for extracting lignin from woody biomass at high yield, high purity, and low molecular weight, using a deep eutectic solvent (DES).

A eutectic system is a homogeneous mixture of two solid-phase chemicals that form a joint superlattice at a particular molar ratio, called the eutectic composition. The joint superlattice then melts at the eutectic temperature, a temperature lower than the melting points of the individual components (Lyman et al., 2017). Alvarez-Vasco et al. developed a DES for the extraction of up to 95% of lignin from woody biomass at high yield (up to 78% from poplar and 58% from D. fir). The resulting lignin product had several distinctive characteristics: lower and narrowly distributed molecular weight compared to Mill Wood Lignin (MWL) as well as a very low number of ether linkages, representing a new type of lignin (Alvarez-Vasco et al., 2016). Kraft black liquor (KBL) is a complex aqueous solution containing several components.

The black liquor chemical composition depends on the type of the raw wood material processed, i.e., softwoods (e.g., pine), hardwoods (e.g., poplar and eucalyptus) or fibrous plants (e.g., bamboo) (Cardoso et al., 2009). Generally, black liquor is composed of water, organic and inorganic compounds. Inorganic compounds mostly originate from the white liquor used in pulping. Organic compounds are mostly derived from both lignin and carbohydrates in wood. Inorganics and degraded carbohydrates are soluble in water. They are present as salts of low-molecular-weight inorganic and organic compounds. The degraded carbohydrates are present as sodium salts of various saccharinic acids and/or lactones (Horntvedt, 1968). Black liquor properties are affected by the level and composition of these compounds (organic and inorganic constituents).
KL is not soluble in water, but it is soluble in black liquor because of its high content of residual alkali (see Table 3-1). To date, most of the known studies reported on lignin depolymerization used lignin as the substrate. This means that the lignin had to be re-dissolved in a solvent, depolymerized and recovered again in the depolymerized form using a lignin recovery process for a second time. This inevitably would lead to significantly high capital and operating costs associated with lignin depolymerization and recovery. To reduce or eliminate the costs associated with the recovery of depolymerized lignin, this research aimed at depolymerizing KL in black liquor rather than depolymerizing purified lignin itself. Thus, this approach could be more cost-effective than other lignin depolymerization techniques. In particular, we tried to exploit the presence of several well-known nucleophilic agents in black liquor (Sixta, 2006) (e.g., hydrosulfide, mercaptide and hydroxide anions) to depolymerize lignin thereby minimizing the cost associated with purchased chemicals. Furthermore, we made sure that any chemicals added to black liquor (e.g., NaOH, phenol, methanol) are fully compatible with the kraft recovery cycle since the filtrate from lignin recovery will, ultimately, be directed to the mill chemical recovery system. The purpose of this paper is to present the main features of our approach for depolymerizing lignin in black liquor as well as the effects of various reaction parameters on depolymerized lignin Mw, yield and main structural features.

In contrast to previous studies reported in the literature, our objective was not necessarily to depolymerize lignin to the monomeric or dimeric form but to depolymerized products with sufficiently low Mw to allow for increased substitution ratios in several applications such as phenol and polyol replacement in phenolic resins and polyurethane materials, respectively.

3.3 Materials and methods

The softwood kraft black liquor (KBL) used in this study was provided by the FPInnovations Bioeconomy Technology Centre, Thunder Bay, Ontario, Canada which is located at the site of a Resolute kraft pulp mill. The composition of this liquor is provided in Table 3-1 while Table 3-2 presents the elemental composition of this liquor. Other chemicals used include: solid sodium hydroxide (96%), sulfuric acid (99%), acetone
(99.5%), d6-DMSO, d-chloroform, HPLC-grade tetrahydrofuran (THF), all CAS reagent grade, purchased from Sigma–Aldrich and used without further purification.

### 3.3.1 Methodology

The KBL hydrolytic depolymerization experiments were carried out in a 100 mL Parr reactor (Model 4848, Parr Instrument Company, Moline, IL, USA). A typical run employed 50 g of KBL (27.9 wt. % solids), 2 g of NaOH catalyst, 18 g of water for dilution, under N₂ at 1 MPa (initial pressure). The experiments were conducted under pre-selected conditions at temperatures ranging from 200 °C to 350 °C and reaction times ranging from 0.5 h to 3 h. In a typical experiment, the KBL was charged into the reactor and the reactor was sealed. The reactor was first vacuum-purged 2 to 3 times with N₂ in order to ensure complete removal of any air or oxygen present inside the reactor. Subsequently, the reactor was pressurized with N₂ to a pressure of 1 MPa and a leak test was conducted. The reactor was then heated up at a heating rate of about 5 °C/min under stirring at 300 rpm. The reaction time was recorded from the point at which the target temperature was reached. After completion of the reaction, the reactor was rapidly cooled in icy water to stop further reactions. After the reactor system reached near room temperature, the gas produced was collected into a gas bag and quantified using Micro-GC with a thermal conductivity detector (TCD). The reaction products were then acidified to pH = 2 using sulfuric acid thereby inducing the lignin to precipitate out of solution in the form of suspended colloidal particles. After allowing the depolymerized kraft lignin (DKL) particles to coagulate to larger particles, the slurry was filtered to produce a DKL cake and a filtrate. The solid cake of DKL products was collected and washed with distilled water. The acidic filtrate which contained low molecular weight compounds was collected and analyzed for total carbon content (TC) and carboxylic acids content using HPLC. The dry filter cake composed of DKL and solid residues (SR) was dissolved in acetone aided by 5.0 min of sonication, followed by filtration to separate the acetone-soluble phase containing DKL from the acetone-insoluble phase, which was the solid residue (SR) retained on the filter paper. The solid residues were then dried at 105 °C for 6 hrs and weighed to obtain the SR yield (%). The acetone-soluble phase was processed using rotary evaporation under reduced pressure at 50 °C wherein acetone was
removed and a powder or viscous-liquid DKL product was collected. The purified, dry depolymerized lignin product was then tested for various properties including molecular weight distribution. The latter was measured after acetobromination of the lignin and injection of a small volume of acetobrominated lignin dissolved in THF into an organic phase (THF) size exclusion chromatographic (SEC) system with on-line refractive index (RI) and UV detectors as described in ref. (Baumberger et al., 2007). The average molecular weight of the DLKs was measured with a Waters Breeze GPC system with an on-line UV detector at 270 nm; The GPC system was equipped with a 1525 binary pump, and a Waters Styrylgel HR1 column. The system was operated at a column temperature of 40 °C using tetrahydrofuran (THF) as the eluent at a flow rate of 1 mL min−1. linear polystyrene standards were used for molecular weight calibration. The molecular weight range of linear polystyrene standard was 100 to 1 million g/mol. All yields (Gas, Aqueous phase, SR and DKL) (%) were calculated based on the initial dry black liquor solids content. The detailed work-up procedure for products separation is illustrated in Figure 3-1. Each experiment was conducted three times to ensure that relative experimental errors are not more than 5-10%.

**Table 3-1** Softwood kraft black liquor composition (oven dry basis) from Eastern Canadian mill.

<table>
<thead>
<tr>
<th>Properties</th>
<th>Unit</th>
<th>Method used</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total solids</td>
<td>%</td>
<td>27.9</td>
</tr>
<tr>
<td>Sulfated ash</td>
<td>% as NaOH</td>
<td>32.1</td>
</tr>
<tr>
<td>Organic: inorganic ratio</td>
<td>wt. ratio</td>
<td>2.12</td>
</tr>
<tr>
<td>Effective alkali</td>
<td>% as Na₂O</td>
<td>0.951</td>
</tr>
<tr>
<td>Sulfide</td>
<td>% as S²⁻</td>
<td>2.8</td>
</tr>
<tr>
<td>Active alkali</td>
<td>% as Na₂O</td>
<td>3.66</td>
</tr>
<tr>
<td>UV lignin</td>
<td>%</td>
<td>42</td>
</tr>
<tr>
<td>Total sugars</td>
<td>%</td>
<td>3.13</td>
</tr>
<tr>
<td>Soap</td>
<td>%</td>
<td>0.27</td>
</tr>
<tr>
<td>HHV</td>
<td>Btu/lb</td>
<td>6,599</td>
</tr>
<tr>
<td>Inorganic compounds (S &amp; Na)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na</td>
<td>%</td>
<td>16.05</td>
</tr>
<tr>
<td>Total S</td>
<td>%</td>
<td>3.76</td>
</tr>
<tr>
<td>Total S / Total Na weight ratio</td>
<td>wt. ratio</td>
<td>0.23</td>
</tr>
</tbody>
</table>

Based on EPA 3015A

Calculated value
Chloride % 0.15 Based on TAPPI T-699
Sodium chloride % 0.25 Calculated value
Carbonate % 3.32 Based on TAPPI T-699
Sodium carbonate % 5.87 Calculated value
Thiosulfate % 0.87 Based on TAPPI T-699
Sodium thiosulfate % 1.23 Calculated value
Sulfite % 0.19 Based on TAPPI T-699
Sodium sulfite % 0.86 Calculated value
Sulfate % 0.55 Based on TAPPI T-699
Sodium sulfate % 0.81 Calculated value

1 Technological Association of the Pulp and Paper Industry (US);
2 FPInnovations
3 Environmental Protection Agency (US)

Table 3-2 Elemental analysis of softwood black liquor.

<table>
<thead>
<tr>
<th>Element</th>
<th>%</th>
<th>N (%)</th>
<th>C (%)</th>
<th>H (%)</th>
<th>S (%)</th>
<th>O (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>0.03</td>
<td>37.32</td>
<td>3.93</td>
<td>1.64</td>
<td>57.08</td>
</tr>
</tbody>
</table>

*a On dry basis; b By difference

Figure 3-1 Work-up procedure for products separation following the depolymerization of lignin in black liquor.
3.3.2 Gas phase analysis

The gaseous product was mainly composed of H\(_2\), CO, CH\(_4\), CO\(_2\) and C2 – C3 compounds and its yield was very low (<1 wt.%) due to the relatively low reaction temperatures. Thus, in this study, the yield of gaseous product and the yield of aqueous phase were lumped together and reported as Yield of (Gas + Aqueous phase), calculated simply by difference from the initial weight of the black liquor solids used.

3.3.3 FTIR analysis

FTIR spectroscopy was employed using a Nicolet-6700 Fourier Transform Infrared Spectrometer with a universal ATR accessory for the dry samples of KBL (control) and DKL to understand the changes in functional groups of the lignin structure. Spectra from 800 to 4000 cm\(^{-1}\) were collected for the sample powders in absorbance mode with 64 scans per spectrum at 4 cm\(^{-1}\) resolution.

3.3.4 \(^{31}\)P NMR Spectroscopy analysis

The hydroxyl group content of the lignin and modified lignin samples was measured using quantitative \(^{31}\)P NMR spectroscopy. The samples were derivatized with 100 L of 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane (TMDP). A (30-40 mg) of derivatized samples, were dissolved in 500 μL of anhydrous pyridine and deuterated chloroform (1.6:1, v/v) and mixed with 100 L of a solution of N-hydroxy-5-norbornene-2,3-dicarboxylic acid imide (10 mg mL\(^{-1}\)) and chromium (III) acetylacetonate (5 mg mL\(^{-1}\)) as internal standard and relaxation agent. The solution was thoroughly mixed and transferred to a sealed 5-mm NMR tube. All NMR experiments were carried out at 298 K on a Varian Inova 500 NMR Spectrometer. (Hosseinaei et al., 2017). \(^{31}\)P NMR spectra were acquired using an inverse-gated decoupling pulse sequence with a 90-pulse angle, 25 s relaxation delay, and 256 scans.
3.4 Results and Discussion

As mentioned before, the main objective of this work was to develop a cost-effective approach for depolymerizing lignin. In this context, instead of attempting to depolymerize separated/purified kraft lignin (KL), we focused on depolymerizing lignin in black liquor for the purpose of reducing by more than 50% all costs associated with the KL separation/purification process. To achieve this objective, we evaluated the effects of various process parameters on DKL reaction yield, $M_w$ and main functional groups. In particular, we evaluated the effects of the following parameters: reaction temperature, reaction time, initial KL substrate concentration, capping agent (phenol), co-solvent (methanol) and catalyst (sodium hydroxide). The DKL products were then characterized by GPC-UV, FTIR, $^{31}$P NMR and elemental analysis.

3.4.1 Effects of temperature

In order to evaluate the effect of temperature on DKL’s Mw and reaction yield, black liquor and sodium hydroxide catalyst were added to the Parr reactor as described above and the reactor was heated to various temperatures in the 200-350 °C range for 1h to depolymerize the lignin contained in the black liquor. Other experimental conditions in this experiment were as follows: NaOH/lignin ratio of 0.3:1 (w/w) and, black liquor substrate containing 13 wt. % lignin. The purified, dry DKL product was then tested for various properties including molecular weight distribution.
Figure 3-2 Effects of temperature on molecular weight distribution of DKLs (A) and reaction yields (B) after treatment of black liquor at temperatures ranging from 200 to 350 °C for 1 h.

As clearly shown in Fig. 3-2A, an increase in the reaction temperature from 200 to 350 °C led to a shift in the molecular weight distribution to the right in the GPC chromatogram obtained by injecting a THF solution of this lignin, following acetobromination, into a GPC system, i.e., it moved towards a lower weight-average molecular weight (M<sub>w</sub>). This suggests that under the conditions of this reaction, the hydrolysis of kraft lignin was promoted at higher temperatures. Figure 3-2B displays the effects of reaction temperature
in the 200-350 °C range on the yields for DKL, solids residue (SR) and gas and aqueous products. As seen in this figure, the reaction yield of DKL decreases with increasing temperature. Hence, the optimum temperature range in terms of achieving a reasonably high degree of lignin depolymerization while maintaining a reasonably high DKL yield appears to be between 200 to 250 °C. The results presented here could be attributed to the fact that the lignin depolymerization reaction is endothermic (Cheng et al., 2012). Hence, as the temperature rises, more intramolecular linkages are cleaved thereby producing lower molecular weight compounds (e.g., lignin monomers and oligomers) that are soluble in the aqueous phase. The solid residues (SR) yield decreased in the range of 200 °C to 250 °C then significantly increased after 300 °C. The latter behavior was also observed by Yuan et al. (2010) in the hydrolytic de-polymerization of pure kraft lignin under alkaline conditions. This is probably due to: (a) re-polymerization of the intermediate products to form stable C–C linkages, (b) cross-linking between the side chains of the oligomeric products and the phenol reactive sites with aldehydes in a manner similar to a phenol-formaldehyde crosslinking reaction (Chakar et al., 2004).

Based on the above results, in all subsequent experiments, the reaction temperature was fixed at 250 °C in order to achieve a reasonably high degree of lignin depolymerization while maintaining a reasonably high DKL yield.

3.4.2 Effects of reaction time

In order to evaluate the effect of reaction time on DKL’s Mw and the product yields, black liquor and sodium hydroxide were heated to 250 °C to depolymerize the KL contained in the black liquor for various lengths of reaction time ranging from 0.5h to 3 h, where the NaOH/lignin ratio was fixed at 0.3:1 (w/w) and the black liquor substrate contained 13 wt.% KL. Fig. 3-3A illustrates the effects of reaction time on molecular weight distribution of DKLs for two different reaction times (0.5h and 2h). As seen in this figure, the GPC-UV signal shifted toward lower molecular weights in the case of the longer reaction time.
Figure 3-3 Effects of reaction time on MW of DKLs (A) and reaction yields (B) after treatment of black liquor from 0.5 to 3 h at 250 °C.

Fig. 3B shows the effects of reaction time on yields of DKL, SR and (Gas+ Aqueous phase). As seen in this figure, under the conditions of this experiment, there was a slight decrease in DKL yield, accompanied by a slight increase in SR yield (%) with increasing reaction time. This is likely due to the re-polymerization of the intermediate products and cross-linking between the side chains of the oligomeric products being promoted at longer reaction times (Yuan et al., 2010). The optimal reaction time appears to be at 1-2 h. Consequently, the reaction temperature and time were fixed at 250 °C and 1-2 h in
order to achieve a reasonably high degree of lignin depolymerization while maintaining a reasonably high DKL yield. Table 3-3 presents the experimental run # and the associated reaction conditions used in each run.

Table 3-3 Experimental run # and the associated reaction conditions for the depolymerization of lignin in black liquor at 250 °C.

<table>
<thead>
<tr>
<th>Run #</th>
<th>Temp. (°C)</th>
<th>Catalyst</th>
<th>Time (h)</th>
<th>Co-solvent *</th>
<th>Capping agent b</th>
<th>Lignin concentration in black liquor</th>
</tr>
</thead>
<tbody>
<tr>
<td>K2</td>
<td>250</td>
<td>−</td>
<td>1</td>
<td>−</td>
<td>−</td>
<td>13% c</td>
</tr>
<tr>
<td>K6</td>
<td>250</td>
<td>NaOH/lignin ≈ 0.3 (w/w)</td>
<td>1</td>
<td>−</td>
<td>−</td>
<td>13%</td>
</tr>
<tr>
<td>K7</td>
<td>250</td>
<td>NaOH/lignin ≈ 0.3 (w/w)</td>
<td>2</td>
<td>−</td>
<td>−</td>
<td>13%</td>
</tr>
<tr>
<td>H2</td>
<td>250</td>
<td>NaOH/lignin ≈ 0.3 (w/w)</td>
<td>2</td>
<td>5%d</td>
<td>−</td>
<td>9%</td>
</tr>
<tr>
<td>H9</td>
<td>250</td>
<td>NaOH/lignin ≈ 0.3 (w/w)</td>
<td>1</td>
<td>−</td>
<td>5%e</td>
<td>9%</td>
</tr>
<tr>
<td>H10</td>
<td>250</td>
<td>−</td>
<td>2</td>
<td>5%</td>
<td>−</td>
<td>13%</td>
</tr>
<tr>
<td>H26</td>
<td>250</td>
<td>NaOH/lignin ≈ 0.3 (w/w)</td>
<td>2</td>
<td>−</td>
<td>−</td>
<td>13%</td>
</tr>
<tr>
<td>LS_3</td>
<td>250</td>
<td>−</td>
<td>2</td>
<td>−</td>
<td>−</td>
<td>13%</td>
</tr>
<tr>
<td>LS_4</td>
<td>250</td>
<td>−</td>
<td>2</td>
<td>5%</td>
<td>−</td>
<td>13%</td>
</tr>
<tr>
<td>H1</td>
<td>250</td>
<td>NaOH/lignin ≈ 0.3 (w/w)</td>
<td>2</td>
<td>−</td>
<td>−</td>
<td>9%</td>
</tr>
<tr>
<td>H31</td>
<td>250</td>
<td>NaOH/lignin ≈ 0.3 (w/w)</td>
<td>2</td>
<td>−</td>
<td>−</td>
<td>9%</td>
</tr>
<tr>
<td>H48</td>
<td>250</td>
<td>NaOH/lignin ≈ 0.3 (w/w)</td>
<td>2</td>
<td>−</td>
<td>2%</td>
<td>9%</td>
</tr>
</tbody>
</table>

*a Capping agent: phenol; b Co-solvent: methanol; c Lignin concentration is expressed as % in black liquor; c, d the co-solvent and capping agent concentrations are expressed as % on a dry lignin basis.

3.4.3 Effect of initial lignin concentration in black liquor on DKL’s $M_w$

In order to evaluate the effects of initial KL concentration on the DKL’s $M_w$, black liquor and sodium hydroxide were heated to 250 °C for 2h at a NaOH/lignin ratio of 0.3:1 (w/w) for both the original and the diluted black liquor substrates (13 wt.% and 9 wt.% KL concentrations). $M_w$ distributions of the DKL products obtained from the black liquor samples with different initial KL concentrations are illustrated in Fig. 3-4. As seen in this figure, the $M_w$ declined when the initial KL concentration was reduced, suggesting that diluting black liquor with more water facilitated the hydrolytic splitting of ether linkages in KL during the de-polymerization process at 250 °C, likely because water dilution enhanced the accessibility of the lignin molecules to the various reactants in black liquor. It should be noted here that diluting black liquor to too low levels are not economically
attractive since it would result in a higher energy consumption and reduced DKL recovery from black liquor.

![Graph showing UV/Absorbance against Elution Time for 13% and 16% Lignin substrates.]

**Figure 3-4** Effect of the initial KL concentration on M_w of DKLs from treatment of black liquor with two different initial lignin concentrations (13wt.% and 9wt.%) at 250 °C for 2 h.

### 3.4.4 Effects of capping agent

The effects of capping agent (phenol) on M_w of DKL and product yield were investigated under the following conditions: black liquor with 9 wt.%, KL, catalyst NaOH/lignin ratio of 0.3:1 (w/w), phenol concentration of 0-5 wt.% (on a dry lignin basis), 250 °C and 2h. As shown in Table 3-4, following the addition of the phenol capping agent at a 1 wt.% charge, the M_w of the DKL dropped from 7050 Da to 1200 Da. Furthermore, the polydispersity index, which is a measure of the tightness of the molecular weight distribution, improved significantly as well by decreasing from 14.6 to 1.9 although the DKL yield declined slightly from 33.1% to 29.2 wt. %, accompanied by a small increase in SR yield from 0.40 wt.% to 0.63 wt.% . When further increasing the phenol charge to the 2 and 5 wt.% levels, respectively, did not lead to further changes in M_w, polydispersity index or yield of DKL product, but the yield for solid residues declined to as low as 0.16 wt.%. Similar effects of phenol in hydrolytic depolymerization
of lignin in water–phenol mixtures were reported by Okuda et al. (2004). The above positive results obtained with addition of a small amount of phenol in drastically reducing the \( M_w \) of the DKL could be ascribed to the capping of active fragments/intermediates, thereby suppressing the cross-linking reactions Okuda et al., 2004. On the other hand, some low \( M_w \) lignin depolymerization products capped by phenol could remain soluble during the precipitation process, which might explain the slightly reduced DKL yield when using the phenol capping agent. The capping effects of phenol in lignin depolymerization under alkaline conditions is likely to be due to the reaction of phenol with reactive \( \alpha \)-positions in lignin fragments thereby inhibiting their self-condensation while facilitating lignin fragmentation through neighboring group participation reactions (Gierer, 1977).

Table 3-4 Effects of phenol addition to black liquor on \( M_w \), polydispersity and yield of DKL at 250 °C for 2 h.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Capping agent(phenol) (wt.% w.r.t. lignin)</th>
<th>Yield (wt.%) ( ^{a} )</th>
<th>Molecular weight of DKL by GPC-UV</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>DKL SR ( M_w ) (Da) ( M_n ) (Da) PDI ( ^{b} )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H1</td>
<td>0</td>
<td>33.1 0.40 7050 480 14.6</td>
<td></td>
</tr>
<tr>
<td>H31</td>
<td>1</td>
<td>29.2 0.63 1200 622 1.9</td>
<td></td>
</tr>
<tr>
<td>H48</td>
<td>2</td>
<td>29.1 0.16 1170 560 2.1</td>
<td></td>
</tr>
<tr>
<td>H9</td>
<td>5</td>
<td>30.5 0.16 1185 599 2.0</td>
<td></td>
</tr>
<tr>
<td>Kraft lignin</td>
<td>-</td>
<td>- - 10000 5000 2.0</td>
<td></td>
</tr>
</tbody>
</table>

\(^{a}\) On a dry lignin basis in black liquor; \(^{b}\) Polydispersity index (PDI) = \( M_w/M_n \)

3.4.5 Effects of co-solvent

The effects of co-solvent (methanol) on \( M_w \) of DKL and product yield were investigated under the following conditions: black liquor with 13 wt. % KL, 250 °C, NaOH/lignin ratio of 0.3:1 (w/w), 2 h and methanol content of 5 wt. % (w.r.t. the KL content in black liquor). As shown in Table 3-5, following the addition of methanol co-solvent at 5 wt. % loading, in the absence of added NaOH, the \( M_w \) of the DKL product dropped from 7050 Da to 2340 Da, the PDI decreased significantly from 14.6 to 3.5, and more importantly, the DKL yield increased from 30.1% to 42.92%. In the presence of 30 wt. % NaOH
catalyst (on a dry lignin basis), more interestingly, the \( M_w \) of the DKL product was reduced to as low as 1500 Da and a PDI as low as 2.3 was obtained. However, the DKL yield dropped to 32.1%. In general, a high concentration of NaOH produced DKL products with a lower \( M_w \), while leading to the loss of some low \( M_w \) compounds in the DKL recovery process, which probably accounts for the reduced DKL yield. Thus, the black liquor alkali system with methanol as a co-solvent proved to effectively depolymerize KL into lower-molecular-weight DKL products. The alcohol-water system most likely improved the solubility of the reaction intermediates, thereby preventing repolymerization of the intermediates (Xu et al., 2008; Brittain et al., 2018). In addition, based on prior work in this area, it appears that methanol contributes to lignin depolymerization by: (a) donating a proton to reactive carbanion intermediates that are formed in the reaction and (b) reacting with lignin through a solvolysis reaction involving sodium methoxide (Brittain et al., 2018).

**Table 3-5** Effects of methanol addition to black liquor on \( M_w \), polydispersity and product yields at 250 °C for 2 h.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Co-solvent (methanol) (wt.% w.r.t. lignin)</th>
<th>Cat. (NaOH)/lignin (w/w)</th>
<th>Yield (wt.%)&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Molecular weight of DKL by GPC-UV</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>DKL (Da)</td>
</tr>
<tr>
<td>H1</td>
<td>0</td>
<td>0.3</td>
<td>33.1</td>
<td>7050</td>
</tr>
<tr>
<td>H10</td>
<td>5</td>
<td>0</td>
<td>42.9</td>
<td>2340</td>
</tr>
<tr>
<td>H2</td>
<td>5</td>
<td>0.3</td>
<td>32.1</td>
<td>1500</td>
</tr>
<tr>
<td>Kraft Lignin</td>
<td></td>
<td></td>
<td></td>
<td>10000</td>
</tr>
</tbody>
</table>

<sup>a</sup> On a dry basis in black liquor; <sup>b</sup> Polydispersity index (PDI) = \( M_w/M_n \)

### 3.4.6 Characterization of depolymerized lignins

The FTIR spectra of lignin from untreated kraft black liquor (KL) and DKL samples produced at selected reaction conditions were analyzed for qualitatively monitoring the changes in functional groups. For example, Figure 3-5 compares the FTIR spectrum of the control KL with the DKL products from experimental runs K6 and K7 (using black liquor containing 13 wt. % KL under the reaction conditions of 250 °C, NaOH/lignin = 0.3 (w/w) for 1h and 2h, respectively). As shown in this figure, the DKL samples displayed a significantly stronger absorbance than the original lignin in the 3200–3550...
cm⁻¹ wavenumber range, attributed to the stretching of aromatic and aliphatic O–H groups, which suggests an increase in the hydroxyl group content of the DKL samples as compared to the control kraft lignin. Furthermore, the DKL samples present a weaker FTIR signal around 1115 cm⁻¹ compared to the control. Since this signal could be attributed to ether linkages in lignin (Huang et al., 2014), the reduction in this signal can be considered as suggestive evidence that, during hydrolytic treatment of black liquor under the indicated conditions, lignin depolymerization occurs mainly through the cleavage of ether linkages. DKL samples also show reduced FTIR signals at 1420 cm⁻¹ which are attributed to symmetric bending vibrations of C–H bonds in methoxyl groups (Durie et al., 1960), suggesting removal of the methoxyl functional groups from the lignin during the hydrolytic depolymerization process. Similarly, the increase in signal in the 1691-1707 cm⁻¹ absorption range most likely corresponds to an increase in unconjugated carbonyl groups (e.g. aldehyde /ketone groups) (Kline et al., 2010).

![FTIR spectra](image)

**Figure 3-5** FTIR spectra for the KL control and the DKLs from experimental runs K6 and K7 using black liquor containing 13 wt. % KL under the reaction conditions of 250 °C, NaOH/lignin ≈ 0.3 (w/w) for 1h and 2h, respectively.

Table 3-6 presents the main types and content of hydroxyl groups (e.g., carboxylic acid hydroxyl, aliphatic hydroxyl, non-condensed phenolic hydroxyl and condensed phenolic hydroxyl) of various depolymerized lignin samples compared to the control. The
identification of these groups was conducted based on the NMR chemical shifts for these functional groups as shown in Table 3-7 (Li et al., 2017). According to the results obtained from the $^{31}$P NMR spectra, the DKL samples exhibit considerably higher amounts of non-condensed phenolic hydroxyl groups (138.3–140.3 ppm and 137.3–138.3 ppm) compared to the control, as illustrated in Figure 3-6. As shown above by FTIR, this increase is likely to occur as a result of cleavage of ether linkages ($\beta$-O-4, $\alpha$-O-4, etc.) during lignin depolymerization (Zinovyev et al., 2017). For example, in the DKL sample from Run #H9 with a Mw = 1185 Da, the non-condensed phenolic group content is 7.8 mmol/g while for the control it is only 3.4 mmol/g. This result is likely due to the combined effects of the catalyst (NaOH) and the capping agent (phenol) used in Run #H9. It is worth pointing out here that when phenol was used as a capping agent (5 wt. % phenol w.r.t. dry mass of lignin) in Run #H9, the resulting DKL had a higher non-condensed free Ph-OH and Guaiacyl-OH (G) content, compared to DKL products obtained from other depolymerization conditions- this suggests that phenol could be participating in capping free radicals generated in the lignin depolymerization process thereby suppressing the condensation reactions (Ahvazi et al., 1998; Crestini et al., 2017). Even in the absence of added phenol, however, the non-condensed free Ph-OH and Guaiacyl-OH (G) content of the depolymerized lignins produced in our experiments is considerably higher than what one would expect from the hydrolysis of ether bonds. Since, according to the literature, KL contains about 7.4 $\beta$-O-4 ether linkages per 100 units, if these linkages were to be fully cleaved, this would lead to an additional 0.41 mmol of non-condensed phenolic hydroxyl groups/g of lignin. Since, in our work, the original lignin contained 3.38 mmol/g of non-condensed phenolic hydroxyl groups, following depolymerization, the total content of such groups in depolymerized lignin should not have exceeded 3.84 mmol/g of lignin. The fact that it ranges from 4.015 to 5.79 mmol/g in the depolymerized samples (excluding the sample from Run #H9 in which phenol was added) this would suggest that mechanisms other than ether cleavage are leading to the creation of free phenolic groups in depolymerized lignin. Given that black liquor contains, in addition to acid-precipitable KL, a considerable amount of lignin fragments of lower Mw that cannot be precipitated at pH = 2, it is possible that, under alkaline conditions, such fragments react with precipitable lignin in the alpha position.
(very much like phenol) thereby creating additional p-hydroxyphenyl-OH and/or guaiacyl-OH groups. Based on the results shown in Table 3-6, it appears that using methanol as an additive also leads to an increased content of p-hydroxyphenyl groups in depolymerized lignin. For example, Run #K7 could be taken as a very good control experiment for Run #H2 since the only difference between them is the presence of 5% methanol on a lignin basis in the latter case. In this case, whereas Run #K7 resulted in 1.191 mmol/g of p-hydroxyphenyl-OH groups, Run #H2 resulted in 1.46 mmol/g of p-hydroxyphenyl-OH corresponding to a 22.6% increase.

This increase in p-hydroxyphenyl-OH groups is likely to be due to the significant reduction in M_w in the latter run to about 1500 Dalton compared to about 7050 Dalton in the case of Run #H1 which was run under very similar conditions but in the absence of methanol. Based on prior work done by Diam et al. (1978), under alkaline conditions and high temperatures, the lower M_w’s are at least partially due to the methylation of active benzyl alcohol groups in lignin molecules thereby preventing condensation reactions. As shown in Table 3-6, except for the DKL sample from H9, in all other DKL samples, the content of condensed phenolic hydroxyl groups was commonly reduced during depolymerization. This further suggests that most conditions used in these experiments appear to suppress condensation reactions of the reaction intermediates. This can be explained by the presence of hydrosulfide ions in black liquor which is known to help reduce lignin condensation during pulping, and/or the presence of methanol and phenol which are expected to act as free radical scavengers thus helping to minimize lignin condensation reactions (Argyropoulos et al., 2003). Furthermore, as shown in Table 3-6, the aliphatic hydroxyl group content in all DKL samples (150.4.3–145.5 ppm) was lower than the control. This is probably due to the fact that, under alkaline conditions, formaldehyde can be cleaved from the γ-position of the C9 lignin units (Heitner et al., 2016).

Furthermore, as demonstrated by Zinovyev et al. (2017), through fractionation of KL using ultrafiltration, the aliphatic hydroxyl group content declines with decreasing lignin molecular weight. Shen et al. also observed that the carboxyl group content of lignins produced from catalyzed depolymerization, as determined by 31P NMR, increased with decreasing molar mass. However, in this work (Table 3-6) there is no clear trend
pertaining to the carboxyl group content probably because the lignin molecular weight was reduced through chemical reactions rather than fractionation (Shen et al., 2016). Overall, the total hydroxyl group content consistently increased in the DKL samples obtained from catalytic depolymerization experiments with NaOH catalyst when compared to the control—however, the total hydroxyl group content for the DKL from non-catalytic depolymerization experiments is lower than that of the control.

Table 3-6 31P NMR analysis of hydroxyl groups in depolymerized kraft lignins.

<table>
<thead>
<tr>
<th></th>
<th>KL</th>
<th>K7</th>
<th>K6</th>
<th>K2</th>
<th>H2</th>
<th>H10</th>
<th>H9</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aliphatic-hydroxyl, mmol/g</td>
<td>Aliphatic-OH</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DPM</td>
<td>0.943</td>
<td>0.864</td>
<td>0.693</td>
<td>0.516</td>
<td>0.785</td>
<td>0.533</td>
<td>0.970</td>
</tr>
<tr>
<td>4-O-5'</td>
<td>1.061</td>
<td>1.110</td>
<td>0.994</td>
<td>0.795</td>
<td>1.112</td>
<td>0.843</td>
<td>1.303</td>
</tr>
<tr>
<td>5-5'</td>
<td>0.906</td>
<td>0.679</td>
<td>0.627</td>
<td>0.519</td>
<td>0.729</td>
<td>0.549</td>
<td>0.924</td>
</tr>
<tr>
<td>Condensed phenolic hydroxyl, mmol/g</td>
<td>DPM</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>Syringyl-OH (S)</td>
<td>2.942</td>
<td>4.605</td>
<td>3.944</td>
<td>2.928</td>
<td>4.212</td>
<td>3.274</td>
<td>5.661</td>
</tr>
<tr>
<td>Guaiacyl-OH (G)</td>
<td>0.460</td>
<td>1.191</td>
<td>1.362</td>
<td>1.087</td>
<td>1.460</td>
<td>1.393</td>
<td>2.135</td>
</tr>
<tr>
<td>p-hydroxyphenyl-OH (H)</td>
<td>0.535</td>
<td>0.483</td>
<td>0.652</td>
<td>0.229</td>
<td>0.614</td>
<td>0.417</td>
<td>0.911</td>
</tr>
<tr>
<td>Carboxylic acid hydroxyl, mmol/g</td>
<td>Benzylic-COOH</td>
<td>0.395</td>
<td>0.359</td>
<td>0.695</td>
<td>0.112</td>
<td>0.522</td>
<td>0.395</td>
</tr>
<tr>
<td></td>
<td>Terminal-COOH</td>
<td>8.527</td>
<td>9.772</td>
<td>9.378</td>
<td>7.61</td>
<td>9.75</td>
<td>7.52</td>
</tr>
<tr>
<td>Total hydroxyl, mmol/g</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 3-6 31P NMR spectra of the (A) control (KL) and DKL of the sample run# H2(B).
Table 3-7 Functional groups verses chemical shift (Li et al., 2017).

<table>
<thead>
<tr>
<th>δ(ppm) shift</th>
<th>functional structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>145.15</td>
<td>IS (internal standard)</td>
</tr>
<tr>
<td>150.4-145.5</td>
<td>Aliphatic - Alcohol</td>
</tr>
<tr>
<td>144.4-143.1</td>
<td>DPM</td>
</tr>
<tr>
<td>143.1-141.7</td>
<td>4-O-5'</td>
</tr>
<tr>
<td>141.7-140.8</td>
<td>5-5'</td>
</tr>
<tr>
<td>143.1-141.7</td>
<td>Non-cond. Ph-OH Syringyl (S)</td>
</tr>
<tr>
<td>140.3-138.3</td>
<td>Non-cond. Ph-OH Guaiacyl (G)</td>
</tr>
<tr>
<td>138.3-137.3</td>
<td>Non-cond. Free Ph-OH</td>
</tr>
<tr>
<td>136-135</td>
<td>Benzylic-COOH</td>
</tr>
<tr>
<td>135-134</td>
<td>Terminal-COOH</td>
</tr>
</tbody>
</table>

3.4.7 Carbon, sodium, and sulfur overall mass balance

As a first step in evaluating the integration of the lignin depolymerization approach reported here into pulp mill operations, we conducted, Na, S and C elemental mass balances around one of our experiments, i.e., run# H2, which related to the treatment of diluted KBL (with 9 wt.% KL) at 250 °C for 2 h, with 5% addition of methanol co-solvent in the presence of NaOH/lignin ≈ 0.3 (w/w). As previously discussed, this experiment led to DKL with a very low molecular weight (Mw = 1500 Da). Four technical chemical analysis tests were used, namely: elemental composition analysis (on a dry basis), total carbon (TC) (carbon in liquid phase) analysis, inductively coupled plasma (ICP) spectroscopy and analysis for sulphur gases using an SRI 8610C Gas Chromatograph (GC) with FPD/FID detectors (Flame Photometric/ Flame Ionization Detectors) specific for gaseous sulfur analysis. Carbon balance was evaluated based on the elemental composition analysis and TC analysis of the initial black liquor and the DKL products along the various stages of the process, namely: reaction, acidification and washing/drying. ICP and GC-FPD/FID was used to evaluate Na and S balance, respectively, along the above-mentioned stages. Figure 3-7 presents a simplified diagram of the main unit operations of the proposed process, along with the calculated results of the elemental C, Na and S balance at each stage of the process. The first stage was the reaction stage for treatment of black liquor in a Parr reactor, in which the added black liquor was found to contain 29.8 wt.% carbon, 20 wt.% Na and 5 wt.% S. The carbon recovery across the reactor was approx. 80% due to unavoidable errors in the experiment
and the fact that the carbon recovery in the gas phase was not included due to its negligibly low yield. GC-FPD/FID analysis was used to determine total reduced sulfur (TRS) compounds as well as sulphur dioxide (SO₂) in the gas phase. The (TRS) gases generated are commonly a mixture of hydrogen sulphide (H₂S), methyl mercaptan (CH₃SH), dimethyl sulphide (CH₃SCH₃) and dimethyl disulphide (CH₃S-SCH₃) while the oxidized gases are SO₂ and SO₃ (Saturnino et al., 2012). 75% of total sulfur was recovered in the liquid reaction products and 10% of the total sulfur was recovered in the gaseous products. Therefore, the overall sulfur recovery was 85 wt.%, which is reasonable considering the inevitable errors in the sulfur analysis. Sodium balance was performed by ICP analysis, and the result revealed a very high recovery efficiency (98%) in the reaction stage.

The second stage of the process was acidification of the treated black liquor using sulphuric acid to precipitate DKL from the acidified black liquor, followed by filtration of the slurry. As a result, this stage generated the main product, namely: a lignin cake (solid form) and a filtrate (liquid form). Elemental balance assessment was carried out on both phases. Carbon balance was conducted on the lignin cake employing elemental analysis and on the filtrate by TC. The elemental balance results for the second stage of the process showed high recovery efficiencies for the elements C, S and Na at 95%, 96% and 95%, respectively. In the second process stage, the elemental distributions in the two products (the solid lignin cake and the liquid filtrate) were also calculated and illustrated in Figure 3-7. 51% of C ended up in the lignin cake while 49% ended up in the filtrate. 23% of S ended up in the lignin cake and 77% in the filtrate, while 16% of Na ended up in the lignin cake and 84% in the filtrate. The third stage of the process was lignin washing and drying. The overall elemental mass balance was conducted based on dry cake analysis for C, Na and S with the element recovery efficiencies being 97, 96 and 95% respectively. The final dry DKL product had the following composition: Na: 0.042 wt.%, S: 0.4 wt.% and C: 65.95 wt.%, all on a dry lignin basis. For the entire process including treatment of diluted KBL (with 9 wt.% KL) at 250 °C for 2 h, with 5% addition of methanol co-solvent in the presence of NaOH/lignin ≈ 0.3 (w/w), followed by
acidification to recover the DKL, the overall mass balances for C, Na and S were calculated to be approx. 74%, 90% and 77%, respectively.

**Figure 3-7** Schematic diagram illustrating the main unit operations of the DKL lignin recovery process (treatment of diluted KBL (with 9 wt.% KL) at 250 °C for 2 h, with 5% of methanol co-solvent in the presence of NaOH/lignin ≈ 0.3 (w/w)) along with the results obtained for elemental mass balance across all three unit operations.

### 3.5 Conclusions

In this work, the effects of reaction temperature on the hydrolytic treatment of kraft black liquor (KBL) under catalytic (NaOH) and non-catalytic conditions were studied with both original KBL (lignin substrate concentration of 13 wt.%) and diluted KBL (lignin substrate concentration of 9 wt. %). The DKL products were precipitated from treated black liquor by lowering the pH to 2 using sulphuric acid. The obtained DKL products were characterized by GPC-UV, FTIR, $^{31}$P NMR and elemental analysis. The research demonstrated effective depolymerization of kraft lignin in KBL at 250-300 °C with NaOH as a catalyst at a NaOH/lignin ratio of about 0.3 (w/w) using the diluted KBL. Particularly low molecular weight lignins were produced by treating kraft black liquor...
under the above conditions but in the presence of a capping agent (phenol) or a co-solvent (methanol). In the latter cases, the depolymerized lignin (DKL) products obtained exhibited an $M_w$ of around 1000-2000 Da at a yield of about 30-45 % depending on the operating conditions. Compared with lignin depolymerization work reported in the literature, where technical lignin was used, direct treatment of black liquor has many advantages as it would lead to a significant reduction in capital and operating costs associated with separation of lignin from black liquor.

3.6 References


Chapter 4

4 Depolymerization of hydrolysis lignin using chemicals recoverable by the kraft recovery cycle.

The information presented in this Chapter is based on the paper “Depolymerization of hydrolysis lignin using chemicals recoverable by the kraft recovery cycle”, which to be submitted for publication. The sections in Chapter 4 present the results towards the completion of objective 2 of this PhD project.

4.1 Abstract

Lignin-rich residues obtained after enzymatic hydrolysis of woody biomass, hereinafter referred to as hydrolysis lignin (HL), are recalcitrant, heterogeneous, insoluble in most common solvents, and less reactive compared to other lignins. This is largely because such “lignins” are essentially composed of lignin covalently bonded to carbohydrates forming what is called a “lignin-carbohydrate complex (LCC)”. In order to enhance the reactivity of HL, an effective depolymerization strategy is required. In this work, a novel, cost-effective approach to produce depolymerized hydrolysis lignin (DHL) using kraft cooking liquor (white liquor (WL)) was developed. The effect of various process parameters such as reaction time, (WL: HL) ratio, and reaction temperature on lignin depolymerization was investigated using a 2-L Parr reactor under a N₂ atmosphere. Lignin was precipitated from the various DHL fractions through the addition of H₂SO₄ until pH=2 was reached. The acidified reaction products were then filtered, and the lignin captured on the filter was washed with water. The purified DHLs were then characterized by GPC-UV, ³¹P NMR, and UV-Vis spectroscopy, while the filtrates were characterized by HPLC for saccharinic and other acids. The weight-average molecular weight (Mw) value of the DHL obtained at 190 °C after treatment for 1h at a WL:HL ratio of 2:1 (w: w) in the 2-L Parr reactor was 2600 Da while the Mw of untreated HL could be not determined because it was not soluble in THF. Moreover, a significant increase in non-condensed phenolic hydroxyl and carboxylic acid group content was observed with decreasing M_w. This approach demonstrated the technical feasibility of employing WL as an inexpensive catalyst for depolymerizing HL into low M_w DHL.
fractions for use as a replacement of petroleum-based chemicals in several applications (e.g. phenol in PF resins and polyols in PU foams). Compared to various existing lignin modification approaches, the approach reported here could be more cost-effective if integrated into kraft pulp mill operations with the residual WL from our lignin depolymerisation process being recycled to the mill chemical recovery cycle. Process scale-up has been demonstrated using a 20-L circulating reactor. In this case, the Mw of the DHL produced after such a treatment at 170 °C for 2h was 2400 Da.

4.2 Introduction

It is widely recognized that continued use of fossil resources is not sustainable not only because of the finite amounts of these resources but also because of the toxicity of several fossil-derived products and their negative impact on climate change (Hook et al., 2013). Therefore, it is essential to develop sustainable technology solutions that can address these growing concerns. Renewable energy is energy obtained from natural resources that can be replenished or renewed within a human lifespan. It is viewed as a potential solution to the growing global demand for clean energy. In addition to energy, there is a need to develop chemicals and materials out of sustainable and widely available resources such as biomass. Plant biomass contains mainly three polymers: cellulose, hemicellulose and lignin along with smaller amounts of pectin, protein, extractives and ash. (Bajpai, 2016). Cellulose is a homopolysaccharide composed of β-D-glucopyranose units which are linked together by β (1-4) glycosidic bonds to form a linear polymer. Cellulose comprises about 40-45% of dry wood and, as a result of its largely crystalline structure, is resistant to hydrolysis. Hemicelluloses are heterogenous and amorphous polysaccharides composed of various monomeric sugars and sugar acids. Hemicelluloses comprise 17-25% of dry wood and can relatively easily be hydrolyzed by acids and/or enzymes to their monomeric components (Sjostrom, 2013). Lignin is a complex and amorphous biopolymer composed of non-fermentable oxygenated aromatics cross-linked in three dimensions. Lignin comprises about 28 wt.% of softwoods and 20 wt.% of hardwoods based on dry wood (Heitner et al., 2010). Lignin is composed of three phenylpropanoid building units: p-hydroxyphenylpropane, guaiacylpropane, and syringylpropane interconnected by etheric and carbon-to-carbon linkages.
Generally, in unprocessed lignin, 60% or more of these linkages are ether bonds, while the remaining linkages are carbon-carbon bonds (Xiang and Lee, 2000). Hydrolysis lignin (HL) is a byproduct from acid or enzymatic biomass pretreatment processes such as the ones employed in cellulosic sugar and/or ethanol plants. HL could be, for example, the solid residue from the enzymatic hydrolysis of woody biomass and is mainly composed of lignin (50-65 wt.%), cellulose and hemicellulose residues. Extensive research was undertaken in the former Soviet Union to find uses for acid hydrolysis lignins as they had several wood hydrolysis plants (Rabinovich, 2010). HL’s fundamental difference from kraft lignin is that it contains high amounts of bound residual polysaccharides (mostly insoluble cellulose) after acid or enzymatic hydrolysis which decreases its purity, solubility and general reactivity (Wahlström et al., 2017). Apart from incineration, several chemical modifications of HL were carried out at the time in an effort to come up with cost-effective uses of this abundantly available polymer. However, most of the HL was disposed of, because the modifications developed were too expensive, or the products made did not find suitable applications. Similar problems are faced by researchers today in developing effective uses of HL. Lignin depolymerization is one of the most promising routes recently applied to improve lignin reactivity. Several lignin depolymerization processes (via hydrolytic, reductive or oxidative routes) have been reported in the literature. For example, Nguyen et al. (2014) reported a high-pressure pilot process for the hydrolytic conversion of kraft lignin (KL) into bio-oils and chemicals in near critical water (350 °C, 25 MPa) employing a fixed-bed catalytic reactor filled with ZrO₂ pellets, while the lignin was dispersed in an aqueous solution containing K₂CO₃ (catalyst) and phenol (co-solvent). Mahmood et al. (2013) achieved the depolymerization of kraft lignin via hydrolysis, using aqueous NaOH as a catalyst. The process itself was very effective in achieving good quality depolymerized kraft lignin (DKL). However, the average molecular weight (Mw) of the DKL was >5000 g/mole after depolymerization at 250 °C, 45 min reaction time at 20 wt.% KL concentration. The Mw of DKL could be reduced to ~1500 g/mole after depolymerization at 350 °C for 45 min or at 250 °C for 2 h at 10 wt.% KL concentration. However, the reactor pressure increased from 5MPa to 16 MPa with the corresponding increase in temperature from 250 °C to 350 °C. In other work, Yuan et al. (2010) also achieved successful
depolymerization of KL into oligomers in hot-compressed water-ethanol medium with NaOH as the catalyst and phenol as a capping agent. A promising approach was reported recently for extracting lignin from woody biomass at high yield, high purity and low molecular weight, by using a deep eutectic solvent (DES). Deep eutectic solvents are systems formed from a eutectic mixture of Lewis or Brønsted acids and bases. Such mixtures have a melting point much lower than either one of the individual components. DES mixtures have been prepared, for example, from choline chloride (ChCl) and four hydrogen-bond donors – acetic acid, lactic acid, levulinic acid and glycerol (Lynamet et al., 2017; Alvarez-Vasco et al., 2016). These were demonstrated to extract lignin from woody biomass in high yield (up to 78% from poplar and 58% from Douglas fir). The resulting lignin product, DESL, had several distinctive characteristics including lower and narrowly distributed molecular weight, and the lack of ether linkages, representing a new type of lignin. So far, most lignins have been de-polymerized into oligomers and monomers via hydrolytic depolymerization (using water) or reductive depolymerization (using hydrogen) in various solvents and catalysts. The most commonly used solvents include water, water-ethanol co-solvent, water-ethanol-formic acid, methanol, acetone, etc. Also, a range of various homogeneous, heterogenous, metallic, commercial and industrial catalysts have been tested for the depolymerization of lignin. Recently, Li et al., 2018, demonstrated a new approach for lignin depolymerization and separation in the solid state, by using an acidic lithium bromide trihydrate (ALBTH) system under mild conditions (with 40 mM HCl at 110 ºC). Woody and grass biomass were treated with ALBTH. In this process, the cellulose and hemicellulose were hydrolyzed and dissolved, while solid, pure depolymerized lignin was separated efficiently at high purity. The depolymerized lignin product showed low molecular weight with a minimal degree of condensation. Despite any specific advantages that the lignin depolymerization processes described above might have, they also have several drawbacks including: operation at high-temperatures and pressures, use of expensive solvents and/or catalysts which are not easily recoverable as well as issues with scalability and industrial applicability. As a result, most depolymerization processes reported in the literature are likely to be associated with high capital and operating costs (Mahmood et al., 2015).

In contrast to the above approaches, this paper presents a simple, easily scalable process
for the depolymerization of HL using recoverable cooking liquor from the kraft process (white liquor) at relatively moderate temperatures, pressures and reaction times. Furthermore, in this paper, we discuss the scale up of this process to the 20-L reactor level. The process developed can easily be integrated into pulp mill operations, especially in the case of kraft pulp mills that already have a lignin recovery system such as LignoForce™ or LignoBoost™. It is important to note here that hydrolysis lignins are less resistant to depolymerization than kraft lignins since the former contain a significantly higher number of ether linkages and a significantly lower number of C-C bonds. This is because, during the bulk delignification stage of the kraft pulping process, the content of β-O-4 linkages in the wood chips significantly decreases for both the liquor-phase (kraft) and residual lignins in the pulp. At the final delignification stage, both lignins exhibit approximately one seventh of the native β-O-4 content in wood. The depolymerization process in the current study resembles delignification of wood chips in the kraft pulping process in which lignin is removed from the lignocellulosic matrix via lignin depolymerization.

As is the case with wood chips, raw HL contains lignin mostly in its native form which is rich in β-O-4 ether linkages (Rinaldi et al., 2016). There are two main types of lignin reactions that occur during kraft pulping under alkaline conditions. The first one is lignin degradation reactions, which lead to lignin fragments of low average molecular weight (desirable reactions). The second one is lignin condensation reactions which lead to the formation of alkali-stable linkages (undesirable reactions) (Gierer, 1970). Due to the high frequency of their occurrence in lignin, β-O-4 and α-O-4-ether linkages together comprise the most abundant connections between lignin units (up to 80%) (Rinaldi et al., 2016). Therefore, two main possible chemical pathways were proposed in an effort to elucidate the mechanism of delignification leading to lower molecular weight lignin – the first chemical pathway relates to phenolic lignin structures while the second one relates to non-phenolic lignin structures. These will be further discussed in the “Results and Discussion” section of this paper as they relate to the results obtained in this work.
4.3 Materials and Methods

The hydrolysis lignin (HL) used in this study was a by-product of the TMP-Bio process developed by FPInnovations (Yuan et al., 2010). It was derived from aspen wood and was not soluble in any solvent. HL is usually composed of 60–65 wt.% lignin, 20–25 wt.% cellulose and 5% hemicellulose. The TMP Bioprocess utilizes low-pressure mechanical refining to disintegrate the biomass feedstock (e.g. aspen wood chips) into a fibrous mass which is more amenable to enzymatic hydrolysis. The enzymatic hydrolysis results in two products: a sugar solution that is rich in glucose (C6) and xylose (C5) sugars and HL. The elemental composition (on a dry basis) of HL is 49.25 wt.% carbon (C), 6.3 wt.% hydrogen (H), 0.385 wt.% nitrogen (N) and 44.05% oxygen (O) plus ash. The average molecular weight of the soluble part of hydrolysis lignin after acetobromination of the original HL is believed to be around 8000 g/mole as analyzed by GPC-UV. However, the average molecular weight is difficult to measure due to its lack of solubility in common organic solvents. Other chemicals used include: NaOH; Na₂S; sulfuric acid, 98%; acetone, 99%; tetrahydrofuran (THF, HPLC grade); Butylated Hydroxytoluene (BHT), 99%; – Glacial Acetic Acid, 99.7%; Acetyl Bromide, 99%; Phosphoric acid, 85%; and acetonitrile, HPLC grade.

4.3.1 Methodology:

**White liquor preparation:** In this work, simulated white liquor was prepared by mixing 121 mL of NaOH solution (at a concentration of 595 g/L as Na₂O) with 224 mL of Na₂S solution (at a concentration of 156 g/L as Na₂O) with distilled water added to the mixture to produce 1L of solution. Titration (Brinkmann Titrino) of the solution was used to measure the effective alkali (EA) and sodium sulfide (Na₂S) concentration of the solutions made. Table 4-1 shows the adjusted EA and sulfide content of the white liquor made.
Table 4-1 White liquor composition.

<table>
<thead>
<tr>
<th>Properties</th>
<th>Unit</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Effective Alkali (Na₂O)</td>
<td>g/L</td>
<td>85</td>
</tr>
<tr>
<td>Sulfide (Na₂S)</td>
<td>g/L</td>
<td>35</td>
</tr>
<tr>
<td>Density</td>
<td>(g/mL)</td>
<td>1.102</td>
</tr>
</tbody>
</table>

The experiments relating to the direct hydrolysis of HL with white liquor were carried out in a batch 2-L Parr Model 4843 reactor, equipped with a pressure gauge, thermocouple, stirrer, gas lines (in and out) and sampling line. In a typical run, 100 g of HL, 100 g of white liquor (1:1(w/w)) and 500 mL of deionized water were charged to the reactor. The reactor was then closed and tightened. To ensure the complete removal of any air or oxygen present, the reactor was purged 2-3 times with N₂. Subsequently, the reactor was pressurized with N₂ to a cold pressure of 2 bar and a leak test was performed. The reactor was then heated up under stirring (670 rpm) and allowed to run over a pre-specified length of reaction time (e.g. 1 hour) after the reactor reached the set temperature (150, 170 or 190 °C). Once the pre-determined reaction time was reached, the reactor was immediately quenched with water to terminate further reactions. When the system nearly reached room temperature, all the reactor contents were collected and acidified using 1M H₂SO₄ to pH= 2, in order to precipitate out the DHL. The liquid/solid mixture was then separated by filtration. Subsequently, the solid DHL cake was washed in three stages using: a) 2 L of 0.4N H₂SO₄, b) 2 L of 0.01N H₂SO₄ and c) 2 L of distilled water. The recovered DHL was air dried for 24h. The yield was determined based on the percentage of the dry mass of depolymerized lignin to the dry mass of the initial HL. All the washing filtrates were collected for further analysis. Each experiment was conducted three times to ensure that relative experimental errors are not more than 5-10%.

4.3.1.1 3¹P NMR Spectroscopic Analysis of Modified Lignin Product

The hydroxyl group content of the lignin and modified lignin samples was measured using quantitative ³¹P NMR spectroscopy. The samples were derivatized with 100 L of 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane (TMDP). A (30-40 mg) of derivatized samples, were dissolved in 500 μL of anhydrous pyridine and deuterated chloroform (1.6:1, v/v) and mixed with 100 L of a solution of N-hydroxy-5-norbornene-
2,3-dicarboxylic acid imide (10 mg mL\(^{-1}\)) and chromium (III) acetylacetonate (5 mg mL\(^{-1}\)) as internal standard and relaxation agent. The solution was thoroughly mixed and transferred to a sealed 5-mm NMR tube. All NMR experiments were carried out at 298 K on a Varian Inova 500 NMR Spectrometer. (Hosseinaei et al., 2017). \(^{31}\)P NMR spectra were acquired using an inverse-gated decoupling pulse sequence with a 90-pulse angle, 25 s relaxation delay, and 256 scans.

### 4.3.1.2 Carboxylic acid analysis

The concentration of carboxylic acids in the filtrate was measured by high-performance liquid chromatography (HPLC). For this purpose, an Agilent 1260 system consisting of a binary pump, an autosampler, a column oven, a chromatographic column and a UV detector was used and operated with Openlab operating system software. An Allure Organic column, 4.6mm x 300mm, packed with 5µm particles from Restek was used for the chromatographic separation. Samples were diluted using a phosphoric acid solution, pH 2.6, and filtered through a 0.2 µm membrane syringe filter. 20 microliters of solution were injected into the HPLC system after system calibration with suitable standards.

HPLC analysis was carried out under the following conditions: eluent A = H\(_3\)PO\(_4\) (0.057%, pH 2.6), eluent B = Acetonitrile (ACN), Mobile phase composition at 0-5 min: H\(_3\)PO\(_4\), 99%: Acetonitrile, 1%, Mobile phase composition at 20 min: H\(_3\)PO\(_4\) 85%: ACN 15%. Run time: 40min, Pump flow rate: 1mL/min (120-130Bar), Column temperature: 30°C, and UV detector wavelength: 220 nm.

### 4.4 Results and discussion

#### 4.4.1 Effect of temperature and WL/HL ratio on lignin MW and reaction yield.

To investigate the effects of temperature and WL:HL ratio on HL depolymerization, a pre-planned set of experiments was conducted. The experiments were designed as follows: at each ratio of WL/HL (1:4, 1:2, 1:1, 2:1), three temperatures were investigated (150, 170 and 190 °C). Table 4-2 presents the experimental run # for each reaction that was conducted, and the associated conditions used.
Table 4-2. Experimental run # and associated reaction conditions for the depolymerization of HL with white liquor (HL: 100g, distilled water: 500g, Reaction time: 1h).

<table>
<thead>
<tr>
<th>Sample#</th>
<th>T (°C)</th>
<th>WL: HL (w: w) (%)</th>
<th>pH of lignin precipitation</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZHL_3</td>
<td>150</td>
<td>1:4</td>
<td>2</td>
</tr>
<tr>
<td>ZHL_1</td>
<td>170</td>
<td>1:4</td>
<td>2</td>
</tr>
<tr>
<td>ZHL_2</td>
<td>190</td>
<td>1:4</td>
<td>2</td>
</tr>
<tr>
<td>ZHL_4</td>
<td>150</td>
<td>1:2</td>
<td>2</td>
</tr>
<tr>
<td>ZHL_9</td>
<td>170</td>
<td>1:2</td>
<td>2</td>
</tr>
<tr>
<td>ZHL_5</td>
<td>190</td>
<td>1:2</td>
<td>2</td>
</tr>
<tr>
<td>ZHL_7</td>
<td>150</td>
<td>1:1</td>
<td>2</td>
</tr>
<tr>
<td>ZHL_8</td>
<td>170</td>
<td>1:1</td>
<td>2</td>
</tr>
<tr>
<td>ZHL_6</td>
<td>190</td>
<td>1:1</td>
<td>2</td>
</tr>
<tr>
<td>ZHL_10</td>
<td>150</td>
<td>2:1</td>
<td>2</td>
</tr>
<tr>
<td>ZHL_12</td>
<td>170</td>
<td>2:1</td>
<td>2</td>
</tr>
<tr>
<td>ZHL_11</td>
<td>190</td>
<td>2:1</td>
<td>2</td>
</tr>
</tbody>
</table>

Figure 4-1 shows the molecular weight distribution (GPC-UV) of DHL obtained from the experiments conducted at various reaction temperatures for a reaction time of 1h. It is clearly shown here, that an increase in the reaction temperature led to a decrease in the lignin molecular weight (Mw) for all the ratios tested. For example, at a 2:1 ratio of WL:HL, at 150 °C, the Mw was 4518 Dalton, as compared to 2686 Dalton at 190 °C. These results suggest that the cleavage of ether bonds in lignin was promoted at higher temperatures as a result of overcoming the activation energy barrier of these reactions. As also shown in Figure 4-1, the Mw decreased with increasing WL:HL ratio. This is likely because of the increasing amount of nucleophilic agents in the reaction mixture such as hydrosulphide (HS⁻), mercaptide (CH₃S⁻) and hydroxide (OH⁻) ions. As is well-known in the kraft pulping literature, lignin is likely to be depolymerized during this process through two possible mechanisms. In the case of lignin molecules in which phenolic groups are present, the depolymerization is expected to occur through the formation of a quinone methide intermediate while in the case of lignin molecules with no phenolic groups, the depolymerization is expected to occur through an oxirane intermediate. According to the first mechanism, the lignin degradation reactions start with ionization of the phenolic groups under alkaline conditions (Fengel and Wegener,
The ionization then triggers the formation of the para-quinone methide intermediate. The oxygen of the quinone group then draws the electron density to the double bond thus making the α-carbon more positive. This, in turn, shifts the electron densities of the other bonds in this conjugated system. Since HS⁻ is a powerful nucleophilic agent, it attacks the quinone methide intermediate at the C-α position and adds itself to the quinone methide structure. This is followed by an intramolecular attack of the thiol group at the neighboring β-carbon which causes formation of a thiiran intermediate. Finally, elimination of elemental sulfur (formation of polysulfide), associated with re-aromatization, yields coniferyl-type structures (Sixta, 2006). This reaction scheme ultimately leads to break up of β-ether bonds thereby depolymerizing lignin. According to the second mechanism, the reaction proceeds to fragmentation via epoxide intermediates formed by a neighboring group-assisted mechanism (Sixta, 2006). Subsequently, the epoxide formed is attacked by nucleophiles, such as HS⁻ and HO⁻, or by nucleophilic sites in carbohydrates (Heitner et al., 2010). The latter attack can produce stable lignin carbohydrate complexes (LCCs) – this is one of the reasons for the incomplete removal of lignin from the fibers during the bulk delignification stage.

Figure 4-1 Effect of temperature and WL: HL (w: w) ratio on lignin Mw.
During the above experiments, the white liquor was gradually enriched with an extremely complex mixture of dissolved lignin and carbohydrate degradation products. As shown in Figure 4-1, the Mw started to decrease dramatically when the ratio was adjusted to 1:1. This is probably because, at this WL:HL ratio, there is sufficient alkalinity in the liquor to neutralize any acidic compounds that might be generated during the cooking process thereby maintaining the pH in the optimum range for depolymerization reactions to occur. Furthermore, additional white liquor assured the presence of an excess of HO\(^-\) and HS\(^-\) ions which are the active depolymerizing agents. It is possible that the depolymerization of HL might be occurring through two chemical pathways: the first pathway might be the cleavage of linkages between lignin and carbohydrates and/or carbohydrate peeling reactions thereby reducing the size of lignin carbohydrate complexes (LCC) – this was confirmed by the decreasing carbohydrate content in the final product as the WL:HL ratio was increased. The second pathway could be lignin depolymerization. For WL:HL ratios of 1:4, 1:2, and even 1:1, no significant drop in M\(_w\) was observed, suggesting a deficiency in OH\(^-\) and HS\(^-\) ions needed for the cleavage of intramolecular ether linkages in the lignin. At the 2:1 ratio, however, a sharp decrease in M\(_w\) was observed (see Figure 4-1).

Moreover, during the cooking reaction, HO\(^-\) ions were consumed in the neutralization of organic acids being generated from carbohydrate degradation such as formic, glycolic, lactic and acetic acids. As seen in Figure 4-2, these acids reduce the pH which can, in turn, decrease lignin solubility and/or affect the reactivity of the active depolymerization agents. Therefore, an excess of white liquor was needed to keep lignin dissolved in the liquor to achieve lower M\(_w\). As is the case in kraft pulping, it is important to ensure that the liquor has a pH value >11, to avoid lignin precipitation and condensation reactions in the reaction solution. In contrast to soda pulping, in kraft pulping, as a result of the presence of hydrosulphide ions the quinone methide intermediates are largely converted to benzyl thiols thereby reducing the opportunity for condensation reactions. This might explain the reason for the absence of solid residue in our reaction products (Sarkanen and Ludwig, 1971). Figure 4-2 presents the pH before and after the reaction of HL with WL for all applied WL: HL ratios. At low ratios (1:4 and 1:2), the HO\(^-\) ions were totally
consumed as the final pH was on the acidic side. On the other hand, the final pH was alkaline at higher WL:HL ratios. The pH difference before and after the reaction is an indirect indication of white liquor consumption during the reaction. Alkali is basically consumed in three different reactions, a) hydrolysis and degradation of carbohydrates, b) neutralization of organic carboxylic acids generated by degradation of carbohydrates and c) neutralization of the phenolic groups generated by lignin depolymerization (Sarkanen and Ludwig, 1971).

**Figure 4-2.** pH of the reaction mixture before and after the reaction of HL with WL at different WL: HL (w: w) ratios and temperatures.
Figure 4-3 shows the effect of temperature and WL:HL ratio on depolymerized lignin yield after being recovered by precipitating it from the reaction products through the addition of sulphuric acid to pH = 2 and filtering the lignin slurry. As seen in this figure, the yield decreases with increasing temperature and WL/HL ratio. At a WL:HL ratio ≥ 1:1, the depolymerized lignin yield was significantly reduced. At the WL:HL ratio of 1:1, the yield declined from 63% at 150 °C to 57% at 190 °C, while at a WL:HL ratio of 2:1, the yield declined from 59% at 150 °C to 47% at 190 °C. At low WL/HL ratios (< 1:1), no significant change in reaction yield was observed with increasing temperature. Furthermore, with increasing temperature and WL:HL ratio, the lignin:carbohydrate ratio in the final product also increased suggesting the depolymerization/degradation of the carbohydrate component of the hydrolysis lignin. Whereas, the lignin content in unwashed HL was initially 48wt%, it increased to 74wt% after reaction at T = 190 °C at a WL/HL ratio of 2:1. The decrease in reaction yield can be partly attributed to carbohydrates being hydrolyzed and/or decomposed by alkali during cooking. Based on our analysis of the filtrates, various soluble organic compounds were generated during
the reaction. It appears from these analyses that carbohydrates in HL were hydrolyzed to soluble monomeric and oligomeric sugars, as well as oxidized to various saccharinic acids, simple organic acids and alcohols. The ash content of DHL was only 0.1-0.2wt% (measured at 525 °C).

### 4.4.2 Effect of reaction conditions on lignin and carbohydrate content of depolymerized hydrolysis lignin.

Table 4-3 presents the lignin content (Klason and soluble lignin) as well as the carbohydrates content of the depolymerized hydrolysis lignins produced under different conditions. As seen in Table 4-3, the carbohydrate content in the modified lignin product decreased at high temperatures and high WL/HL ratios as compared to the control. However, there was practically no change at low WL:HL ratios (1:4) and (1:2). This effect can be explained by the lack of sufficient WL required for lignin and carbohydrate depolymerization/degradation. At higher WL:HL ratios, especially at 2:1 at 150 °C and 170 °C, the carbohydrate content decreased to about 33% and 37% of the initial content, respectively. This is a result of carbohydrate degradation to soluble low molecular weight monomers, oligomers and organic acids. While the corresponding decrease at 190 °C was only 29%, it can perhaps be explained by the possible formation of alkali resistant LCC structures between lignin and carbohydrates as discussed above for the case of non-phenolic lignin moieties (Gierer, 1980). As a result of the carbohydrate content of hydrolysis lignin being degraded faster than the lignin content, the total % lignin (Klason and acid-soluble) content in DHL increased with increasing temperature and WL:HL ratio. At high WL:HL ratios, the total lignin content ranged from 71 to 84% of the total mass of DHL depending on the temperature used.
Table 4-3 Effect of reaction conditions on Carbohydrate, Klason Lignin and soluble lignin content of DHL produced.

<table>
<thead>
<tr>
<th>Temperature, °C (WL:HL ratio)</th>
<th>Sample</th>
<th>Klason lignin, %</th>
<th>Soluble lignin, %</th>
<th>Total Lignin, %</th>
<th>Carbohydrate, %</th>
<th>Total Carbohydrate reduction, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unwashed HL</td>
<td></td>
<td>48.8</td>
<td>5.7</td>
<td>54.5</td>
<td>27.6</td>
<td>82.1</td>
</tr>
<tr>
<td>150-(1:4)</td>
<td>ZHL 3</td>
<td>51.6</td>
<td>2.1</td>
<td>53.7</td>
<td>22.10</td>
<td>75.8</td>
</tr>
<tr>
<td>170-(1:4)</td>
<td>ZHL 1</td>
<td>63.1</td>
<td>4.7</td>
<td>67.8</td>
<td>24.8</td>
<td>95.4</td>
</tr>
<tr>
<td>190-(1:4)</td>
<td>ZHL 2</td>
<td>63.8</td>
<td>2.3</td>
<td>66.1</td>
<td>23.9</td>
<td>90.0</td>
</tr>
<tr>
<td>150-(1:2)</td>
<td>ZHL 4</td>
<td>55.2</td>
<td>3.7</td>
<td>58.8</td>
<td>24.6</td>
<td>83.5</td>
</tr>
<tr>
<td>170-(1:2)</td>
<td>ZHL 9</td>
<td>60.0</td>
<td>2.60</td>
<td>62.6</td>
<td>23.80</td>
<td>86.4</td>
</tr>
<tr>
<td>190-(1:2)</td>
<td>ZHL 5</td>
<td>71.6</td>
<td>2.5</td>
<td>74.1</td>
<td>25.0</td>
<td>99.0</td>
</tr>
<tr>
<td>150-(1:1)</td>
<td>ZHL 7</td>
<td>69.1</td>
<td>2.8</td>
<td>71.8</td>
<td>20.7</td>
<td>92.5</td>
</tr>
<tr>
<td>170-(1:1)</td>
<td>ZHL 8</td>
<td>67.8</td>
<td>3.6</td>
<td>71.5</td>
<td>19.2</td>
<td>90.7</td>
</tr>
<tr>
<td>190-(1:1)</td>
<td>ZHL 6</td>
<td>75.6</td>
<td>4.40</td>
<td>80.00</td>
<td>18.6</td>
<td>98.5</td>
</tr>
<tr>
<td>150-(2:1)</td>
<td>ZHL 10</td>
<td>74</td>
<td>3.5</td>
<td>77.5</td>
<td>18.5</td>
<td>89.26</td>
</tr>
<tr>
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<td>5.3</td>
<td>81.8</td>
<td>16.5</td>
<td>98.3</td>
</tr>
<tr>
<td>190-(2:1)</td>
<td>ZHL 11</td>
<td>69.3</td>
<td>5.5</td>
<td>74.60</td>
<td>20.10</td>
<td>94.70</td>
</tr>
<tr>
<td>170-(3.2:1)</td>
<td>LS_23</td>
<td>76</td>
<td>8.2</td>
<td>84.2</td>
<td>15.9</td>
<td>100.04</td>
</tr>
</tbody>
</table>

4.4.3 Soluble lignin in the filtrate.

The soluble lignin in the acidic filtrate was determined using UV absorbance at 205 nm using a hardwood lignin extinction coefficient of 110 L/g.cm (Dence, 1992). As previously, reported in the literature, certain low M_w lignins are soluble in acidic media (e.g. lignin model compound syringylglycerol-β-syringyl ether) (Yasuda et al., 2001). Figure 4-4 shows the concentration of soluble lignin in the acidic filtrate as a function of temperature and WL:HL ratio. The concentration of soluble lignin clearly increased with increasing temperature and WL:HL ratio. Lignin concentration in the filtrate dramatically increased at 190 °C, with a soluble lignin concentration of about 3500 ppm at a WL:HL ratio of 1:4, as compared to 6000 ppm at the ratio of 2:1. These results are consistent with the decreased yields of DHL obtained under these conditions.
Figure 4-4 Effect of temperature and WL: HL (w:w) ratio on soluble lignin concentration in the filtrate.

4.4.4 Low molecular weight carboxylic acids in the filtrate

As mentioned above, at the end of the reaction, the products were acidified using 1M H$_2$SO$_4$ to precipitate DHL by adjusting the pH to 2. Liquid/solid separation was conducted by filtration to give a solid cake (DHL) and an acidic filtrate. The liquid (acidic filtrate) was collected and samples were submitted for carboxylic acid analysis using HPLC. During the cooking process, lignin is known to degrade into low molecular-weight compounds which contain ionizable groups such as phenolate, catecholate and partly also carboxylate groups (Michelsen and Foss, 1996). The sodium salts of carboxylic acids mainly originate from carbohydrates and include for instance, the salts of hydroxyacids such as gluco-xyloisosaccharinic acid, lactic acid and gluconic acid. Moreover, relatively large amounts of the sodium salts of formic acid, glycolic acid, and acetic acid are formed through fragmentation reactions of carbohydrates (Sixta, 2006); (Alén and Niemelä, 1985). As is the case in the kraft pulping process, at high temperatures and under alkaline conditions at the beginning of cooking, the acetyl groups in hardwood hemicelluloses (e.g. xylan) are hydrolyzed. Furthermore, in the earlier
stages of cooking, the polysaccharide chains are peeled off directly from the reducing end groups (primary peeling). Because of the alkaline hydrolysis of glycosidic bonds that occurs at high temperatures, new groups are formed, following additional degradation (secondary peeling). As result, the cellulose yield is always reduced in cooking, but to a lesser extent than hemicelluloses which are degraded more extensively due to their low degree of polymerization and amorphous state. The peeling reactions are finally interrupted because of a termination reaction that converts the reducing end groups to stable carboxylic acid groups (Sjostrom, 2013). The total amount of low-molecular-weight carboxylic acids (after cooking) was found to be around 10wt% of the initial amount of HL. Four major carboxylic acids were detected: glycolic, formic, lactic and acetic acids. The carboxylic acid concentration was directly proportional to temperature and WL:HL ratio as shown in Figure 4-5 for lactic acid. The composition of the alkaline reaction products is affected by many parameters, such as temperature, pH, and reaction time. Whereas the formation of carboxylic acids proceeded more or less constantly during the cooking process, the most dominant acid was lactic acid with a concentration of 5500 ppm for a reaction conducted at 190 °C and a WL:HL ratio of 2:1.

For other acids (glycolic, formic and acetic) acids, there was no clear trend that could be observed -the concentration of these acids fluctuated between 1000 to 2500 ppm at different WL:HL ratios. It is worth noting here that, at low WL:HL ratios (e.g. 1:4 and 1:2), the concentration of all acids did not change much with increasing temperature.
Figure 4-5 Effect of temperature and WL: HL (w: w) ratio on lactic acid production.

4.4.5 Effect of temperature and WL:HL ratio on depolymerized lignin functional groups.

The development of Nuclear Magnetic Resonance (NMR) techniques has significantly aided the understanding of lignin structure and physicochemical behavior. Phosphorus 31 is a nucleus that is 100% naturally abundant. Lignin derivatization with phosphorus-containing reagents has dramatically grown to help us elucidate new analytical features in lignin (Crestini et al., 2017). For example, quantitative $^{31}$P NMR has offered considerable detail in identifying various aromatic groups bearing free phenolic hydroxyls, including p-hydroxyphenyls, catechols, guaiacyl units and phenols with carbon substituents at the C5 or C6 positions (Pu et al., 2011). In addition, the primary hydroxyl and carboxyl groups in lignin as well as the two diastereomeric forms of arylglycerol-β-aryl ether units (β-O-4) present in DHL can also be determined using $^{31}$P NMR (Argyropoulos, 1995).
A comprehensive analysis of hydroxyl groups in depolymerized lignin (ZHL_11) and their typical chemical shifts/integration ranges are summarized in Table 4-4. Various factors make phosphorus an ideal sensor group for NMR studies of labile groups in lignin. These are:

1- Several types of organophosphorus compounds reveal signals within narrow ranges, characteristic of the oxidation state of the phosphorus nuclei;

2- The relationships have been identified between phosphorus chemical shifts and structures that, in some cases, even reveal stereochemical information (Heitner et al., 2010).

**Table 4-4** Hydroxyl group content of depolymerized lignin (sample ZHL_11) produced at 190 °C at a WL: HL (w: w) ratio of 2:1 as analyzed by $^{31}$P NMR

<table>
<thead>
<tr>
<th>Type of hydroxyl group</th>
<th>Chemical shift, ppm</th>
<th>Area</th>
<th>mmol</th>
<th>mmol/g</th>
<th>% of total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Internal Standard</td>
<td>145.15</td>
<td>1.00</td>
<td>0.01</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aliphatic – OH</td>
<td>150.4-145.5</td>
<td>11.33</td>
<td>0.06</td>
<td>1.68</td>
<td></td>
</tr>
<tr>
<td>Total Aliphatic - OH</td>
<td></td>
<td></td>
<td></td>
<td>1.68</td>
<td>31.3</td>
</tr>
<tr>
<td>Condensed Ph-OH - DPM</td>
<td>144.4-143.1</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td></td>
</tr>
<tr>
<td>Condensed Ph-OH - 4-O-5'</td>
<td>143.1-141.7</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td></td>
</tr>
<tr>
<td>Condensed Ph-OH - 5-5'</td>
<td>141.7-140.8</td>
<td>2.32</td>
<td>0.01</td>
<td>0.34</td>
<td></td>
</tr>
<tr>
<td>Total Condensed Ph-OH</td>
<td></td>
<td></td>
<td></td>
<td>0.34</td>
<td>6.4</td>
</tr>
<tr>
<td>Non-condensed Ph-OH Syringyl (S)</td>
<td>143.1-141.7</td>
<td>13.21</td>
<td>0.07</td>
<td>1.95</td>
<td></td>
</tr>
<tr>
<td>Non-condensed Ph-OH Guaiacyl (G)</td>
<td>140.3-138.3</td>
<td>5.38</td>
<td>0.03</td>
<td>0.80</td>
<td></td>
</tr>
<tr>
<td>Non-condensed Ph-OH</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Free Ph-OH</td>
<td>138.3-137.3</td>
<td>0.65</td>
<td>0.00</td>
<td>0.10</td>
<td></td>
</tr>
<tr>
<td>Total Non-condensed Ph-OH</td>
<td></td>
<td></td>
<td></td>
<td>2.85</td>
<td>53.2</td>
</tr>
<tr>
<td>Benzylic-COOH</td>
<td>136-135</td>
<td>0.75</td>
<td>0.00</td>
<td>0.11</td>
<td></td>
</tr>
<tr>
<td>Terminal-COOH</td>
<td>135-134</td>
<td>2.54</td>
<td>0.01</td>
<td>0.38</td>
<td></td>
</tr>
<tr>
<td>Total Carboxylic-OH</td>
<td></td>
<td></td>
<td></td>
<td>0.49</td>
<td>9.1</td>
</tr>
<tr>
<td>Total Hydroxyl Group Content</td>
<td></td>
<td></td>
<td></td>
<td>5.4</td>
<td>100</td>
</tr>
</tbody>
</table>

Quantitative $^{31}$P NMR analysis was used to measure the hydroxyl group content of all DHL samples generated in this work. The results are shown in Table 4-7 in which the hydroxyl group content is presented as a function of temperature, WL/HL ratio and Mw. As seen here, no clear trend can be observed at the WL:HL ratios of 1:4 and 1:2. However, at higher WL:HL ratios, the following observations can be made:
**Aliphatic hydroxyl groups**: At higher WL:HL ratios (e.g. 1:1 and 2:1), the aliphatic hydroxyl group content (δ 150.4-145.5 ppm) decreased for both ratios (see Figures 4-6 and 4-7), as the temperatures increased. In addition, the same trend was observed with Mw (the aliphatic hydroxyl group content declined, when the Mw was reduced) as previously seen by Argyropoulos et al. (2017).

**Carboxylic acid groups**: With increasing treatment temperature and WL:HL ratio, a higher carboxyl group content was obtained. Figures 4-6 and 4-7 show that at high WL/HL ratios (e.g. 2:1 and 1:1), the carboxyl group content increased as the molecular weight, Mw, decreased. For example, for Mw= 4518 Da, the carboxyl group content was 0.18 mmole/g and it increased by about three times to 0.5 mmole/g as the Mw decreased to 2680 Da. The explanation for this trend could be that HS- ions in the white liquor can degrade enol ether structures to produce carboxyl groups in lignin (Sixta, 2006).

The phenolic hydroxyl group is one of the main functional groups of lignin, which affect its physical and chemical properties. The chemical reactivity of lignin in various modification processes is often influenced by its phenolic hydroxyl group content (e.g., in the reaction with formaldehyde for the production of lignin-based adhesives) (Olivares et al., 1988). The two main types of phenolic groups that can be quantified by 31P NMR are non-condensed and condensed phenolic hydroxyl groups.

**Non-condensed phenolic hydroxyl groups** (δ 137-143 ppm shift): These appear to follow a similar trend as the carboxylic acid groups – a higher content was observed with decreasing molecular weight. Hence, it appears that, during the depolymerization process, low molecular weight DHL was produced as a result of cleavage of β- and α-O-4 linkages. As a result, more non-condensed phenolic hydroxyl structures were generated (Potthast et al., 2017). This is also confirmed in Figures 4-6 and 4-7, where an increase in non-condensed phenolic hydroxyls groups was observed with decreasing Mw for both WL:HL ratios.

**Condensed phenolic hydroxyl groups**: These groups slightly increased with decreasing Mw as seen in Figures 4-6 and 4-7. This is likely to be due to repolymerization of phenolic fragments during the cooking process. An insignificant amount of condensed
structures such as diphenylmethane, 4-O-5', and 5-5' (Crestini et al., 2017; Heitner et al., 2010) was found in depolymerized hydrolysis lignin.

![Graph showing the effect of H-lignin depolymerization on different types of hydroxyl functional groups in lignin at a WL: HL (w: w) ratio of 2:1.](image)

**Figure 4-6** Effect of H-lignin depolymerization on different types of hydroxyl functional groups in lignin at a WL: HL (w: w) ratio of 2:1.
Effect of H-lignin depolymerization on different types of hydroxyl functional groups at a WL: HL (w: w) ratio of 1:1.

The above results are in agreement with Potthast et al. (2017) who in a series of sequential ultrafiltration experiments of kraft lignins from black liquor, found that aliphatic-OH group content decreased, and both carboxyl and phenolic-OH group content increased with decreasing molecular weight.

### 4.5 Scale-up of H-lignin depolymerization to the 20-L reactor level

Based on the results obtained from small-scale experiments, an effort was made to scale-up the process developed to the 20-L reactor level using a batch circulating reactor (see Figure 4-8). Steam was used to heat up the reactor through a jacket, and then cold water was introduced in the jacket to cool down the contents after a designated reaction time. The conditions used, and the results obtained are shown in Table 4-5. The main differences between the experiment conducted at the 20-L level versus the one conducted using the e 2-L Parr reactor are the following:
1- A double impeller agitation design was operated in the 2-L Parr reactor while a circulation mixing system was employed in the case of the 20-L reactor;

2- The HL/deionized water ratio in the Parr reactor was set to 1/5 (w/w), whereas in the circulating reactor it was 1:8 (w: w). Furthermore, the white liquor to HL ratio in the 20-L reactor was 3.2/1. These high ratios were selected for the circulation reactor to insure continuous flow of the constituents through the reactor without clogging;

3- While the residence time in the PARR reactor was 1 h, the residence time in the circulating batch reactor was 2 hours to guarantee good mixing which can often prevent heat losses and improve reaction performance.

Table 4-5  Conditions used, and results obtained from lignin depolymerization reaction in 20-L reactor

<table>
<thead>
<tr>
<th>Sample</th>
<th>HL(g)</th>
<th>DW (g)</th>
<th>WL (g)</th>
<th>Temp. (°C)</th>
<th>Mw/UV</th>
<th>pH_in</th>
<th>pH_out</th>
<th>Time (h)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LS_23</td>
<td>1000</td>
<td>8000</td>
<td>3200</td>
<td>170</td>
<td>2392</td>
<td>13.1</td>
<td>12.8</td>
<td>2</td>
<td>40, @pH=2</td>
</tr>
</tbody>
</table>

The reaction rate and degree of mixing are usually closely related to each other. For a reaction to occur, molecules need to come into close contact with each other. Having a sufficient degree of mixing is important in terms of achieving the chemical kinetics needed to produce new species, especially in mass transfer-controlled reaction systems (Shah, 2012). The results of scale-up experiments (LS_23) were compared with the results obtained for experimental run ZHL_12, since both samples were produced at the same temperature (170 °C). The average molecular weight (M_w) of the final product of experiment LS_23 was 2392 Dalton, while that for ZHL_12 was 3200 Dalton. The main reason for this is likely to be the longer reaction time and higher WL/HL ratio used in the former experiment compared to the latter. These results are in agreement with previous studies (Yuan et al., 2010). In particular, the high WL/HL ratio maintains a high concentration of HS⁻ and HO⁻ (the active depolymerization reagents) and a high pH
throughout the duration of the reaction. This leads to the cleavage of a higher number of ether bonds which, in turn, results in a lower Mw (Sarkanen and Ludwig, 1971).

In both of the above experiments, the HL starting material contained 54.5% lignin, and 27% carbohydrates. After the treatment in ZHL_12, the composition of the DHL changed to 81% lignin and 16.5% carbohydrates. A further increase in lignin content was achieved in LS_23, for which we obtained 84.2% lignin and 15.8% carbohydrates. However, the % Yield for LS_23 was 40% whereas in the case of ZHL_12 it was around 50% (see Table 4-6). $^{31}$P NMR analysis was used to determine the main functional hydroxyl groups of the DHL for ZHL_12 and LS_23. The number of carboxylic acid groups, aliphatic hydroxyl groups, phenolic hydroxyl groups, and condensed units, are presented in Table 4-6. As expected, the lower molecular weight of LS_23 resulted in higher contents of free phenolic and carboxyl groups compared to ZHL_12.

Given the high content of free phenolic groups in DHL produced from both processes, they are projected to be quite suitable for use in the manufacture of phenolic resins. The same applies to the use of these DHLs in the manufacture of polyurethane foams, where a high content of primary aliphatic hydroxyl groups is required.

Table 4-6 Table 6. $^{31}$P NMR analysis of lignin hydroxyl groups for reactions conducted at the 2-L reactor level (ZHL_12) and 20-L reactor level (LS_23)

<table>
<thead>
<tr>
<th>Sample#</th>
<th>ZHL_12</th>
<th>LS_23</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carboxylic, mmol/g</td>
<td>0.330</td>
<td>0.71</td>
</tr>
<tr>
<td>Aliphatic, mmol/g</td>
<td>2.052</td>
<td>2.06</td>
</tr>
<tr>
<td>Non-Condensed OH, mmol/g</td>
<td>2.352</td>
<td>3.03</td>
</tr>
<tr>
<td>Condensed OH, mmol/g</td>
<td>0.236</td>
<td>0.38</td>
</tr>
<tr>
<td><strong>Total OH group, mmol/g</strong></td>
<td><strong>4.970</strong></td>
<td><strong>6.18</strong></td>
</tr>
</tbody>
</table>
**Figure 4-8** Schematic diagram of 20-L reactor used for reaction scale-up.

**Table 4-7** $^{31}$P NMR results with experimental conditions.

<table>
<thead>
<tr>
<th>Sample</th>
<th>pH</th>
<th>T (°C)</th>
<th>WL/HL (g/g)</th>
<th>$M_w$ (Da)</th>
<th>$M_n$ (Da)</th>
<th>PDI (-)</th>
<th>Total non-condensed-Ph-OH (mmol/g)</th>
<th>Total aliphatic – OH (mmol/g)</th>
<th>Total condensed ph-OH (mmol/g)</th>
<th>Total carboxylic -OH (mmol/g)</th>
<th>Total - OH (mmol/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZHL_3</td>
<td>2</td>
<td>150 (1:4)</td>
<td>8564</td>
<td>4199</td>
<td>2.04</td>
<td>0.284</td>
<td>1.61</td>
<td>0.05</td>
<td>0.05</td>
<td>2.00</td>
<td></td>
</tr>
<tr>
<td>ZHL_1</td>
<td>2</td>
<td>170 (1:4)</td>
<td>6563</td>
<td>2511</td>
<td>2.61</td>
<td>0.545</td>
<td>2.58</td>
<td>0.07</td>
<td>0.07</td>
<td>3.26</td>
<td></td>
</tr>
<tr>
<td>ZHL_2</td>
<td>2</td>
<td>190 (1:4)</td>
<td>6694</td>
<td>2096</td>
<td>3.19</td>
<td>0.884</td>
<td>2.55</td>
<td>0.10</td>
<td>0.12</td>
<td>3.65</td>
<td></td>
</tr>
<tr>
<td>ZHL_4</td>
<td>2</td>
<td>150 (1:2)</td>
<td>8219</td>
<td>4138</td>
<td>1.99</td>
<td>0.290</td>
<td>2.8</td>
<td>0.0</td>
<td>0.1</td>
<td>3.1</td>
<td></td>
</tr>
<tr>
<td>ZHL_9</td>
<td>2</td>
<td>170 (1:2)</td>
<td>7660</td>
<td>3080</td>
<td>2.49</td>
<td>0.425</td>
<td>2.4</td>
<td>0.1</td>
<td>0.1</td>
<td>3.0</td>
<td></td>
</tr>
<tr>
<td>ZHL_5</td>
<td>2</td>
<td>190 (1:2)</td>
<td>6898</td>
<td>2394</td>
<td>2.88</td>
<td>0.688</td>
<td>2.7</td>
<td>0.1</td>
<td>0.1</td>
<td>3.6</td>
<td></td>
</tr>
<tr>
<td>ZHL_7</td>
<td>2</td>
<td>150 (1:1)</td>
<td>7135</td>
<td>3048</td>
<td>2.34</td>
<td>0.632</td>
<td>2.70</td>
<td>0.10</td>
<td>0.16</td>
<td>3.59</td>
<td></td>
</tr>
<tr>
<td>ZHL_8</td>
<td>2</td>
<td>170 (1:1)</td>
<td>6474</td>
<td>2356</td>
<td>2.75</td>
<td>0.881</td>
<td>2.55</td>
<td>0.11</td>
<td>0.17</td>
<td>3.72</td>
<td></td>
</tr>
<tr>
<td>ZHL_6</td>
<td>2</td>
<td>190 (1:1)</td>
<td>5770</td>
<td>1832</td>
<td>3.15</td>
<td>1.383</td>
<td>2.41</td>
<td>0.17</td>
<td>0.26</td>
<td>4.23</td>
<td></td>
</tr>
<tr>
<td>ZHL_10</td>
<td>2</td>
<td>150 (2:1)</td>
<td>4518</td>
<td>1745</td>
<td>2.59</td>
<td>1.323</td>
<td>2.38</td>
<td>0.15</td>
<td>0.18</td>
<td>4.04</td>
<td></td>
</tr>
<tr>
<td>ZHL_12</td>
<td>2</td>
<td>170 (2:1)</td>
<td>3240</td>
<td>1631</td>
<td>1.99</td>
<td>2.352</td>
<td>2.05</td>
<td>0.24</td>
<td>0.33</td>
<td>4.97</td>
<td></td>
</tr>
<tr>
<td>ZHL_11</td>
<td>2</td>
<td>190 (2:1)</td>
<td>2686</td>
<td>1542</td>
<td>1.74</td>
<td>2.847</td>
<td>1.68</td>
<td>0.34</td>
<td>0.49</td>
<td>5.35</td>
<td></td>
</tr>
</tbody>
</table>
4.6 Conclusions

In this work, we developed a novel, cost-effective approach to produce depolymerized hydrolysis lignin (DHL) using recoverable white liquor (WL) from the kraft recovery cycle. The weight-average molecular weight ($M_w$) of the lignin was significantly reduced from non-measurable levels to 2600 Dalton at 190 °C for 1h at a WL:HL ratio of 2:1 (w: w). Moreover, a significant increase in non-condensed phenolic hydroxyl and carboxylic acid group contents was observed with decreasing $M_w$. We found that effective hydrolysis lignin depolymerization can be achieved at WL:HL ratio ≥ 1:1, below this ratio, minimal lignin depolymerization was observed. The approach developed could be significantly more cost-effective if integrated into kraft pulp mill operations where fresh WL can be utilized with the residual WL recovered using the existing chemical recovery system. Process scale-up was demonstrated using a 20-L circulating reactor, in which case, the Mw of the DHL produced after treatment at 170 °C for 2h was 2400 Dalton. Further investigation is needed to better understand the effect of mixing hydrodynamics on lignin depolymerization.

4.7 References


Chapter 5

Environmentally friendly depolymerization of softwood and hardwood kraft lignins using hydrogen peroxide in ambient conditions and products characterization

The information presented in this Chapter is based on the paper “Environmentally friendly depolymerization of softwood and hardwood kraft lignins using hydrogen peroxide in ambient conditions and products characterization”, which is to be submitted for publication. The sections in Chapter 5 present the results towards the completion of objective 3 of this PhD project.

5.1 Abstract

Depolymerization of lignin is a promising approach towards valorization of lignin for chemicals and materials. The present study demonstrated an environmentally friendly and cost-effective approach to depolymerization of softwood (SW) and hardwood (HW) kraft lignins under ambient conditions or mild temperatures as low as 35 °C using concentrated hydrogen peroxide (H$_2$O$_2$) without using a catalyst, additive or solvent. The degree of lignin depolymerization could be simply controlled by reaction time, and, no further separation process is needed at the completion of the treatment. The obtained depolymerized lignin products were comprehensively characterized by GPC-UV, FTIR, $^{31}$P NMR, TGA, Py-GC/MS and elemental analysis. The weight-average molecular weights (Mw) of the depolymerized lignins obtained from SW or HW lignin at a Lignin/H$_2$O$_2$ mass ratio of 1:1 after treatment for 120 h at room temperature (≈ 25 °C) were approximately 1420 Da. The contents of carboxylic acid groups in the obtained depolymerized lignins were found to significantly increase, compared with those of the untreated raw lignins. Moreover, the depolymerized lignin products have lower thermal decomposition temperatures than those of the raw lignins, as expected owing to the greatly reduced Mw. These findings represent a novel solution to lignin depolymerization for chemicals such as polyols that can be utilized as a bio-substitute for petroleum-based polyols for polyurethane production.
5.2 Introduction

The forestry and agricultural sectors worldwide are generating considerable amount of lignocellulosic materials in the form of residues, an attractive carbon-neutral source for fuels and chemicals, which can be an economically significant alternative to fossil fuels. Recently, significant advances have been achieved in the development of economically feasible biorefineries involving the fractionation of lignocellulose into its three major constituents (i.e., cellulose, hemicellulose and lignin), and full valorization of these constituents (Ragauskas et al., 2014). It should be noted here, that biomass is the only renewable source of carbon for chemicals and materials (McKendry, 2002).

Kraft pulping is the dominant chemical pulping process in the world. In this process, lignin and hemicellulose are dissolved by sodium hydroxide (NaOH) and sodium sulfide (Na$_2$S) to form black liquor, which is subsequently, concentrated and burned in the recovery system to recover chemicals and heat, both of which are crucial to the functioning of a kraft mill. In North America, however, there are many mills which have an operation bottleneck in the capacity of their recovery system. Hence, removing a portion of the lignin from the black liquor can be an effective way to increase the production of pulp without enormous capital spending. Moreover, the isolated portion of lignin can provide an additional value-added revenue stream for the mill by valorizing lignin for bio-products.

Lignin is an aromatic heterogeneous biopolymer, with a three-dimensional crossed linked network structure (Calvo-Flores et al., 2015). The structural diversity of lignin arises mainly from the combination of three linked phenylpropane derivatives that are the main building blocks of lignin’s complex architecture. The three building blocks are lignols: $\beta$-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol, all of which are phenylpropane (C$_9$ units) differing from each other in the substitutions at the 3 and 5 positions. These lignols are linked into a lignin aromatic network in the form of phenyl propanoids, namely $\beta$-hydroxyphenyl (H), guaiacyl (G) and syringyl (S) units, respectively. Different sources of lignin (e.g., softwood, hardwood, grasses, etc.) contain different amounts of methoxyl groups depending on how much of each of the three lignols is incorporated into the lignin macromolecules (Xu et al., 2014; Heitner et al.,
Technical lignins, e.g., kraft lignin extracted from the pulping process, usually have a large molecular weight and a three-dimensional crossed linked network structure as described above, which make it less reactive in applications as, for example, chemical replacement of petroleum-based products in materials such as polyurethanes, due to the steric hindrance (Mahmood et al., 2016). It has been demonstrated that degradation or depolymerization can be an effective and promising approaches to enhance the reactivity of lignin for bio-based materials applications (An et al., 2019). The major lignin degradation methods can be categorized according to the mechanism of lignin network depolymerization, namely, oxidative, solvolytic, hydrogenolytic or hydrolytic reactions, which will be briefly reviewed below.

Lignin structures were initially recognized by oxidation reactions. The types of linkages between the precursors were investigated 50 years ago (Morohoshi et al., 1979). Freudenberg et al. (1965) confirmed lignin’s aromatic nature by oxidizing it with nitrobenzene in an alkaline medium at 160–180 °C for 2–3 hours. In their experiments, benzaldehydes were recovered as a main product with minor amount of benzoic acids. In this reaction, nitrobenzene was considered to act as a two-electron-accepting oxidant and produce quinone methide intermediates from phenolic units of lignin (Freudenberg et al., 1965).

Several solvolytic depolymerization studies have been reported in the literature, involving different solvent mixtures (including glycerol, THF, methyl-THF, and γ-valerolactone (GVL)) and different types of catalysts (e.g., oxalic acid, HCl, Lewis acids metal chlorides, and ammonia) (Sun, et al., 2018; Rößiger et al., 2017). Acid-catalyzed solvolytic treatment is one of the earliest techniques used to deconstruct wood components and separate lignin. Hewson et al. (1943) conducted a series of treatments on maple wood meal using different combinations of acids and solvents, including HCl/ethanol and formic acid/ethylene glycol to separate lignin into water-soluble and water-insoluble components at a low temperature range. It was concluded that this approach, at a low temperature was not sufficient to de-polymerized the complex lignin structure into monomeric/oligomeric compounds. Gasson et al. (2012) investigated formic acid-catalyzed lignin depolymerization at higher temperatures in alcohol solvents.
Different ratios of formic acid to ethanol were employed in a pressurized autoclave reactor. They found that methoxyphenol, catechol, and phenol were obtained as the major components when the reaction temperature was raised to the 360 to 400 °C range. The primary reaction pathway for the lignin degradation to form phenolic products was believed via cleaving of the β-O-4 bonds catalyzed by acid (Forchheim et al., 2012).

Recently, Kristianto et al. (2017) reported highly effective lignin depolymerization in ethanol solvent in the presence of formic acid and Ru/C. A higher formic acid content and prolonged reaction times at 350 °C in the presence of Ru/C increased the bio-oil (depolymerized lignin) yield and reduced the oxygen content in the bio-oil owing to hydrotreatment effects of the hydrogen generated in-situ from formic acid decomposition.

In other work by the authors’ group, Mahmood et al., (2013) achieved the depolymerization of Kraft lignin via hydrolysis using aqueous NaOH as a catalyst. The process itself was very effective and achieved a high yield (70-90%) of depolymerized kraft lignin (DKL) with a weight-average molecular weight (Mw) of ~1500 g/mole at 250 - 350 °C for 2h. However, it was a high-pressure process and the reactor pressure varied from 5 MPa to 16 Mpa at 250 - 350 °C. In contrast to the above-described researches work, oxidative depolymerization of lignin is a low-temperature and pressure process, offering a simpler and more energy/cost-effective approach to depolymerization of lignin at room temperature with a high product yield. Various sophisticated strategies have been reported for oxidative depolymerization of lignin model compounds or lignin, including: electrochemical, and photocatalytic approaches as well as the use of heterogeneous catalysts or ionic liquids. Valuable monomers with high selectivity were produced from lignin oxidative degradation approaches (Sun et al., 2018).

In fact, oxidative technologies were already widely established and have been used for a long time for bleaching in the pulp and paper industry. Some of these oxidative technologies (e.g. using chlorine) are no longer in use due to, more stringent environmental regulations relating to the production of chlorinated dioxin, and furans.

Oxidative approaches to lignin depolymerization, especially utilizing molecular oxygen, hydrogen peroxide, peroxyacids or ozone are potential to become important and
economically feasible lignin delignification technologies (Ma et al., 2015), as the reaction pathways can yield valuable chemicals such as simple aldehydes (vanillin, syringaldehyde, p-hydroxybenzaldehyde) or acids (vanillic acid and syringic acid) (Das Lalitendu et al., 2017). Depending on the extent of oxidation, various carboxylic acids having aromatic and non-aromatic structures with mono- or di-carboxyl functional groups can be produced (Kang et al., 2019).

Hydrogen peroxide, molecular oxygen and other oxidants in the presence or absence of a catalyst have been investigated extensively. Crestini et al. (2006) reported the degradation of kraft lignin and model compounds using H$_2$O$_2$ as an oxidant and methylrhenium trioxide (CH$_3$ReO$_3$) as a catalyst, producing degraded lignin compounds containing aliphatic-OH, syringol-OH, guaiacyl-OH, p-hydroxy phenyl-OH, and COOH groups at room temperature.

Oxidative lignin depolymerization is advantageous and environmentally friendly owing to its mild reaction conditions, but it confronted with the challenge of maintaining sufficient selectivity while avoiding over-oxidation of the substrate to gaseous products (CO or CO$_2$). In addition, lignin oxidation can result in depolymerization and functionalization of complex lignin can be achieved directly via oxidation in one pot by converting lignin to explicit fine chemicals bearing alcohol, aldehyde, or carboxylic acid functional groups. Therefore, this exclusive feature of oxidatively depolymerized lignin (low molecular weight and functionalized) could be utilized directly for industrial applications without further modification.

Sun and Argyropoulos (1996) investigated the reactivity and the efficiency of several oxidants: chlorine dioxide, ozone, dimethyldioxirane and alkaline hydrogen peroxide with lignin using quantitative $^{31}$P NMR. They found that guaiacyl phenolic units were the most vulnerable sites in all the oxidative treatments, and chlorine dioxide and ozone were the most efficient reagents towards the formation of carboxylic acids. The elimination of condensed phenolic structures at a given reagent charge was in the order of: ozone > chlorine dioxide > alkaline hydrogen peroxide. However, hydrogen peroxide treatment is an environmentally friendly approach, in which molecular oxygen and water are generated from hydrogen peroxide decomposition (Kadla et al., 2001).
Hydrogen peroxide (H\textsubscript{2}O\textsubscript{2}) is the simplest peroxide with an oxygen – oxygen single bond. It has been widely used as an oxidizer, bleaching agent and antiseptic reagent.

Concentrated hydrogen peroxide is a potent oxidizing agent due to its unstable peroxide bond. H\textsubscript{2}O\textsubscript{2} has been commercially used as an efficient bleaching reagent in pulp and paper industry. It can effectively remove chromophoric structures present in lignin, but it is incapable of degrading the lignin structure network.

To degrade lignin, H\textsubscript{2}O\textsubscript{2} must be used together with organic acids or mineral acids. Moreover, the solutions of hydrogen peroxide in water are non-ideal, as the volume of a solution is less than the sum of the volumes of the components, and there is an appreciable heat effect upon mixing. Furthermore, the vapor pressures of the solutions do not follow Raoult’s law (Robinette,1956). H\textsubscript{2}O\textsubscript{2} is a very weak acid that remains undissociated at pH < 9.0. At higher pH levels, hydroperoxide anions appear, and they are commonly considered to be the reactive species in oxidation reactions under alkaline conditions (Xiang et al., 2000).

As is well known, the chemical composition of softwoods (SW) is different from hardwoods (HW) with respect to cellulose, hemicellulose and lignin content. The type of linkages predominant in these two types of wood are shown in and so does that Table 5-1.

**Table 5-1** General compositions of softwood and hardwood, and their lignin linkage types (Doelle et al., 2018; Basker et al., 2012).

<table>
<thead>
<tr>
<th></th>
<th>Hardwood</th>
<th>Softwood</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Chemical composition (wt.%)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cellulose</td>
<td>42</td>
<td>45</td>
</tr>
<tr>
<td>Hemicellulose</td>
<td>27</td>
<td>30</td>
</tr>
<tr>
<td>Lignin</td>
<td>28</td>
<td>20</td>
</tr>
<tr>
<td>Extractives</td>
<td>3</td>
<td>5</td>
</tr>
<tr>
<td><strong>Lignin linkage types (Number/100 phenylpropane units)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>β-O-4</td>
<td>43-50</td>
<td>50-65</td>
</tr>
<tr>
<td>α-O-4</td>
<td>6-8</td>
<td>4-8</td>
</tr>
<tr>
<td>β-5 + α-O-4</td>
<td>9-12</td>
<td>4-6</td>
</tr>
<tr>
<td>β-β</td>
<td>2-4</td>
<td>3-7</td>
</tr>
<tr>
<td>5-5′</td>
<td>10-25</td>
<td>4-10</td>
</tr>
<tr>
<td>4-O-5′</td>
<td>4</td>
<td>6-7</td>
</tr>
</tbody>
</table>
In addition, hardwoods contain mainly a mixture of syringyl (S) and guaiacyl (G) units, whereas softwoods contain mainly guaiacyl (G) units. SW and HW lignins also differ in the relative amounts of linkages between the phenylpropane units (Table 5-1) (Sixta, 2006). In the pulping delignification process, the G-based lignin structural network are more resistant to cleavage, therefore they contribute to a lower depolymerization during pulping. Essentially, the efficiency of pulping is directly proportional to the amount of syringyl (S) units in lignin (Gonzalez et al., 1999). Furthermore, guaiacyl (G) units have a free C-5 position available for carbon-carbon interunit bonds (condensation), which makes them amenable to lignin re-polymerization (Gutiérrez et al., 2006). From Table 5-1, the linkage β-O-4 (arylglycerol-β-aryl ether) is, clearly the most frequent linkage type, accounting for more than 50% of the linkages in lignin (Basker et al., 2012). The dominant weak β-O-4 linkages in lignin provide opportunities for cleavage by many processes (Mahmood et al., 2015a; Lancefield et al., 2015). Other linkages are more resistant to chemical degradation (Adler, 1977).

In softwoods, the G type lignins contain more resistant linkages as those involving the C5 of aromatic nuclei of (β-5, 5–5’ and 4-O-5’) than S type lignins (hardwood lignins) due to the availability of the C5 position for coupling. This is could be the reason for the higher condensation degree frequency of C–C linkages between aromatic rings in softwood lignins than in hardwood lignins (Basker et al., 2012).

### 5.3 Materials and Methods

#### 5.3.1 Materials

Two types of kraft lignin (KL), softwood kraft lignin (SKL) from Western Canadian mill and a hardwood kraft lignin (HKL) from a central Canadian mill were used in this study. Both kraft lignins were separated from kraft black liquor using FPInnovations’s LignoForce™ process. Briefly, the black liquor was oxidized with molecular oxygen at 80 °C, and then the pH was reduced using CO₂ and H₂SO₄ followed by filtration and

<table>
<thead>
<tr>
<th></th>
<th>β-1</th>
<th>3-7</th>
<th>5-7</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-6, C-2</td>
<td>3</td>
<td>2-3</td>
<td></td>
</tr>
</tbody>
</table>
washing with dilute H₂SO₄. As a result, the products both lignins were in H-form (protonated lignin), and both substrates SWL and HWL in pure water solutions have a pH value of around 4.0. The low pH of the reaction medium would affect lignin degradation in hydrogen peroxide (Xiang et al., 2000). Hydrogen peroxide can act as a nucleophilic or an electrophilic agent depends on the pH of the solution (relatively stable at acidic conditions). Thus, in this work, the oxidation reactions were carried out under acidic environment. Table 5-2 displays the elemental analysis and the physical properties for SKL and HKL. All other chemicals used in the study, such as hydrogen peroxide 50% water solution, were ACS reagent-grade chemicals purchased from Sigma-Aldrich and used as received.

### Table 5-2 Elemental analysis and the physical properties for SKL and HKL.

<table>
<thead>
<tr>
<th></th>
<th>SKL</th>
<th>HKL</th>
</tr>
</thead>
<tbody>
<tr>
<td>Elemental analysis (wt.% d.b.)¹</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>65.2</td>
<td>63.2</td>
</tr>
<tr>
<td>H</td>
<td>5.52</td>
<td>5.41</td>
</tr>
<tr>
<td>N</td>
<td>0.20</td>
<td>0.02</td>
</tr>
<tr>
<td>O²</td>
<td>26.7</td>
<td>28.7</td>
</tr>
<tr>
<td>Ash³</td>
<td>0.83</td>
<td>0.44</td>
</tr>
<tr>
<td>Total S</td>
<td>1.51</td>
<td>2.25</td>
</tr>
<tr>
<td>Mₘₙ, UV detector (Da)</td>
<td>6041</td>
<td>2718</td>
</tr>
<tr>
<td>PDI UV detector (-)⁴</td>
<td>3.3</td>
<td>3.0</td>
</tr>
<tr>
<td>Mₘₙ, MALLS detector (Da)</td>
<td>9997</td>
<td>10374</td>
</tr>
<tr>
<td>PDI MALLS detector (-)</td>
<td>2.0</td>
<td>2.0</td>
</tr>
</tbody>
</table>

¹On dry basis; ²By difference; ³Ashing in air at 575°C; ⁴Polydispersivity index (PDI = Mₘₙ/Mₙ);

### 5.3.2 Oxidative treatment of SKL and HKL.

The oxidative treatment of kraft lignins SKL and HKL was conducted in a 150 mL beaker at ambient conditions. In a typical run, 6 g (or 4.5 g or 3 g) of 50% H₂O₂ were added slowly to 3 g of SKL or HKL on dry basis, the ratio of H₂O₂/KL was kept at 1:1 w/w (or 1:0.75 w/w or 1:0.5 w/w, respectively). The mixture was then uniformly mixed at ambient temperature to obtain a homogenous slurry. The mixture was kept inside the fume hood at ambient temperature, or in an oven under controlled temperature (not
exceeding 35 °C if a shorter reaction time was desired). The sample mass was monitored with time until a final dry product was obtained. The recovered modified KL was air dried for 24h. The yield was determined based on the percentage of the dry mass of modified KL to the dry mass of the initial KL.

5.3.3 Product characterizations

**Elemental analysis:** Elemental composition of the samples, i.e., CHNS (carbon, hydrogen, nitrogen and sulfur), was analyzed using a CHNS-O flash elemental analyzer 1112 series (Thermo), using 2,5-Bis (5-tert-butyl-benzoxazol-2-yl) thiophene (BBOT) as the calibration standard. The composition of oxygen % was calculated by difference (\(= 100\% - C\% - H\% - N\% - S\% - Ash\%\)).

**GPC analysis:** The average molecular weights and molecular weight distributions of SKL and HKL, and the de-polymerized lignin products were measured with a Waters GPC–UV (gel permeation chromatography–UV detector 270 nm) instrument equipped with Waters Styrage HR1 column at 40 °C, using THF as the eluent at 1 mL min-1 and linear polystyrene standards for molecular weight calibration. All the sample were derivatized by acetylation before injecting into GPC.

**FTIR analysis:** Fourier-transform infrared spectroscopy (FTIR) was employed to investigate the functional group structures of the dry samples of SKL (control) and HKL (control) and depolymerized lignin products and their changes during the de-polymerization process. The FTIR analysis was performed on a Nicolet-6700 FTIR with universal ATR accessory.

**31P NMR:** The hydroxyl group content of the lignin and modified lignin samples was measured using quantitative 31P NMR spectroscopy. The samples were derivatized with 100 L of 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane (TMDP). A (30-40 mg) of derivatized samples, were dissolved in 500 μL of anhydrous pyridine and deuterated chloroform (1.6:1, v/v) and mixed with 100 L of a solution of N-hydroxy-5-norbornene-2,3-dicarboxylic acid imide (10 mg mL-1) and chromium (III) acetylacetonate (5 mg mL-1) as internal standard and relaxation agent. The solution was thoroughly mixed and transferred to a sealed 5-mm NMR tube. All NMR experiments were carried out at 298 K
on a Varian Inova 500 NMR Spectrometer. (Hosseinaei et al., 2017). $^{31}$P NMR spectra were acquired using an inverse-gated decoupling pulse sequence with a 90-pulse angle, 25 s relaxation delay, and 256 scans.

**TGA analysis:** Thermal gravimetric analysis (TGA) analysis of the lignin and depolymerized lignin products was performed using a PerkinElmer Pyris 1,1 TGA in nitrogen atmosphere. The dry samples weighing approximately 10 mg was heated in a N$_2$ flow at 20 mL/min from 25 °C to 600 °C at 10 °C /min. The weight loss % and the rate of weight loss (DTG) of the samples were recorded.

**Py-GC/MS:** Py-GC-MS: analysis was conducted on an Agilent 6890B GC coupled a 5973A MSD using 30 m × 0.25 mm × 0.25 µm DB-5 columns with temperature programming as follows: 1 min hold at an initial temperature of 50 °C followed by a 30 °C min$^{-1}$ ramp to the final temperature of 350 °C with 1 min hold. Py-GC/MS analysis was done using the Double-Shot mode. Pyrolysis of samples (∼100 µg) was performed with a py2020i microfurnace pyrolyzer / AS1020 autosampler (Frontier Laboratories). The compounds were identified by comparing their mass spectra with those of the NIST library.

### 5.4 Results

#### 5.4.1 General observations and product yields

In the present work, lignin was treated with concentrated H$_2$O$_2$ (50%) at ambient temperature (25 °C). The treatment needed 120 h at room temperature (25 °C) for completion, hence, we accelerated the treatment by increasing the temperature to 35 °C, which reduced the treatment time to about 80 h, Treatment temperatures above 35 °C should be avoided to prevent burning the reaction slurry. A homogenous shiny reddish powder of de-polymerized lignin product at a very high yield (> 95± 3%) was obtained in all treatment runs (see Figure 5-1).

Furthermore, it was observed that during treatment of the hardwood lignin, the reaction mixture expanded and foamed, while the foaming was not significant during the softwood lignin treatment. The foam formation was likely due to the release of gases
release from the reaction system. The gas formation could be due to cleavage of the methoxy groups of the syringyl structures in hardwood lignin, producing CH$_4$. In addition, decomposition of unreacted or residual H$_2$O$_2$, forming O$_2$ and water vapor, could also contribute to the foam formation, in particular, in the presence of metals ion catalysts (Marzzacco, 1999). Homogenous powder products of de-polymerized lignins were obtained and the products have a high solubility in water or acetone.

![SKL and HKL reaction mixture during oxidative treatment (a) and depolymerized lignin sample after the treatment (b).](image)

**Figure 5-1** SKL and HKL reaction mixture during oxidative treatment (a) and depolymerized lignin sample after the treatment (b).

The mass loss of the reaction mixture (lignin and H$_2$O$_2$) vs. treatment time was monitored during the treatment where 5 g dry base (d.b.) SWL or HWL and 10g H$_2$O$_2$ 50 (wt.%) were used, as illustrated in Figure 5-2. As shown in this Figure, the mass loss rate from the HWL treatment was faster than that of the SWL treatment. After 5 days, however, almost the same degree of mass loss was achieved in both treatments with HWL or SWL. The faster mass loss with HWL might be due to the higher reactivity of HWL (containing more syringyl nuclei) compared to SWL (containing more guaiacyl nuclei) in the treatment (Shimada et al.,1997).
5.4.2 Elemental analysis

Elemental analysis of the SKL, HKL and the depolymerized lignin products were conducted to investigate the changes in the composition of the lignins during the treatment. Table 5-3 presents the elemental contents (wt.% on dry basis) of C, H, N, S, ash and O of the original SKL, HKL, and depolymerized lignin samples at various lignin/H$_2$O$_2$ mass ratios (1:1, 1:0.75 and 1:0.5). As seen here, the changes in H, N, and S were negligible in all de-polymerization treatments with H$_2$O$_2$ at all mass ratios, while the carbon contents in both SKL and HKL were significantly reduced, accompanied by a marked increase in oxygen content in the depolymerized lignin products. This result suggests that the oxidative depolymerization of lignin would lead to the cleavage of methoxyl groups to form methanol (accounting for the decrease in carbon content), while the oxidative depolymerization would also create more oxygen functional groups, e.g., COOH and –OH in the depolymerized lignin products, as expected.
Table 5-3  Elemental compositions of the original SKL, HKL, and depolymerized lignin samples at various lignin/H$_2$O$_2$ mass ratios (1:1, 1:0.75 and 1:0.5)

<table>
<thead>
<tr>
<th>Elemental composition, wt. % (d.b.)</th>
<th>Original lignin</th>
<th>De-polymerized lignins</th>
<th>Original lignin</th>
<th>De-polymerized lignins</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>SKL  1:1</td>
<td>1:0.75</td>
<td>1:0.5</td>
<td>HKL  1:1</td>
</tr>
<tr>
<td>C</td>
<td>65.2</td>
<td>50.5</td>
<td>53.9</td>
<td>57.4</td>
</tr>
<tr>
<td>H</td>
<td>5.5</td>
<td>4.9</td>
<td>4.7</td>
<td>5.0</td>
</tr>
<tr>
<td>N</td>
<td>0.2</td>
<td>0</td>
<td>0.06</td>
<td>0.06</td>
</tr>
<tr>
<td>S</td>
<td>1.51</td>
<td>1.79</td>
<td>1.27</td>
<td>1.29</td>
</tr>
<tr>
<td>Ash$^1$</td>
<td>0.83</td>
<td>0.83</td>
<td>0.83</td>
<td>0.83</td>
</tr>
<tr>
<td>O$^2$</td>
<td>26.8</td>
<td>42.0</td>
<td>39.2</td>
<td>35.4</td>
</tr>
</tbody>
</table>

1 Assuming the depolymerized lignin has the same ash content as the original lignin; 2 By difference

5.4.3 FTIR analysis

Fig. 5-3 presents FTIR spectra of the original SKL (Fig. 5-3A), HKL (Fig. 5-3B), and depolymerized lignin products of various lignin/H$_2$O$_2$ mass ratios (1:1, 1:0.75 and 1:0.5). As shown in the Figures, there are five major differences in the spectra of the depolymerized lignin products when compared with those of the original lignins (SKL or HKL) as displayed at wavenumbers 1727, 1515, 1460, and 1272 (cm$^{-1}$). The IR absorbance at wavenumber 1727 (cm$^{-1}$) can be attributed to non-conjugated C=O stretching vibration for carboxyl group (Fan et al., 2012). The intensity of this IR peak increases rapidly when increasing the amount of H$_2$O$_2$ in the treatment. This implies that the oxidation of lignin by H$_2$O$_2$ generates more C=O functional groups such as -COOH in the depolymerized lignin products.

The peaks at 1600 cm$^{-1}$ and 1515 cm$^{-1}$ can be ascribed to C=C in aromatic structures (Fan et al., 2012). These peaks have reduced intensity in the depolymerized lignin products compared with these in the original SKL or HKL, indicating that the oxidative treatment did reduce the lignin’s aromatic structure content. This suggests lignin depolymerization as a result of oxidative ring opening.

The band at 1460 cm$^{-1}$ can be ascribed to C-H bending in methylene groups (Kline et al., 2010). As seen in this Figure, the peaks at 1460 cm$^{-1}$ are of approximately similar intensities for the SKL or HKL controls and the de-polymerized lignin samples at the lignin/H$_2$O$_2$ mass ratio of 1:0.5. However, this peak was not observed in the
de-polymerized lignin samples at ratios of 1:0.75 and 1:1, suggesting that under severe oxidation addition, the generation of electrophilic hydroxonium ion HO⁺ could lead to the breaking double bonds, yielding various aldehyde or ketone groups.

The band at 1270 cm⁻¹ is assigned to guaiacyl C-O stretching. The peak intensity decreases in the two depolymerized lignin products from the oxidative treatments at 1:0.5 and 1:0.75 ratios, while the peak disappears in the product at the 1:1 ratio, suggesting that the oxidative depolymerization of lignin would lead to the cleavage of methoxyl groups, resulting in reduction in oxygen content in the de-polymerized lignin products, as suggested previously in Table 5-3. As shown in Fig. 5-3B, in the HKL sample, syringyl ring breathing is represented by the wavenumber 1330 cm⁻¹ (Calvo-Flores et al., 2015). This peak disappeared during the oxidation treatment in all depolymerized samples using different lignin; peroxide ratios, suggesting oxidative cleavage of methoxyl groups. Furthermore, the syringyl structure at the wavenumber 1118 cm⁻¹ belonging to aromatic C–H in plane deformation of these structure (Kubo et al., 2005) was also observed in the HKL sample, but it was not detected for any of the treated hardwood lignins, again indicating cleavage of methoxyl groups during the oxidative treatment.
Figure 5-3 FTIR spectra of the original SKL (A), HKL (B), and depolymerized lignin products with various lignin/H₂O₂ mass ratios (1:1, 1:0.75 and 1:0.5).

5.4.4 Molecular weight distribution by GPC

The molecular weights and distributions of the original lignins (SKL and HKL) and depolymerized lignin products, after acetobromination, were measured by GPC-UV using a method as described by Baumberger et al. (2007). Fig. 5-4 displays the weight average molecular weight (Mₖ) of SKL and HKL, and the de-polymerized kraft lignin (DKL) products. As clearly shown, the molecular weight of hardwood kraft lignin (Mₖ=2750 Da) is much lower than that of softwood kraft lignin (Mₖ = 6050 Da), as commonly reported in the literature (Calvo-Flores et al., 2015; Sarkanen et al., 1971).

As also clearly shown in Figure 5-4, an increase in the H₂O₂/ KL mass ratio in the oxidative treatment led to a dramatic decrease in the molecular weight especially for softwood kraft lignin. For instance, the Mₖ dropped from 6050 Da (for SKL) to 1400 Da for the DKL from the treatment of SKL at 1:1 H₂O₂/ KL mass ratio at room temperature for 120 h, while the Mₖ was reduced from 2750 Da (for HKL) to 1415 Da for the DKL from the treatment of HKL under the same conditions. Despite the slightly higher β-O-4 linkage content in hardwood lignin compared to softwood lignin, the rate of cleavage of
benzyl ether bonds of syringyl nuclei (rich in hardwood lignin) was found to be slower than that of guaiacyl nuclei (more prevalent in softwood lignin) in acidic medium (Shimada et al., 1997).

Figure 5-4  Weight average molecular weight ($M_w$) of SKL and HKL, and the depolymerized kraft lignin (DKL) products at different lignin to peroxide ratios.

Thus, the lignin depolymerization products were a low molecular weight compared to the control lignin. Furthermore, their solubility in water at a low pH was remarkably high. As discussed previously, the lignin oxidative depolymerization via H$_2$O$_2$ treatment could involve the production of phenolic oligomers by cleavage of ether bonds and demethoxylation of syringyl and guaiacyl nuclei. Extensive oxidation could produce ring opening products, and therefore, muconic acids and their derivatives are likely anticipated in the products (Ma et al., 2015; Chen et al., 2018).

5.4.5 Functional group analysis using $^{31}$P NMR

One of the most important functional groups in lignin is hydroxyl groups, especially free phenolic groups, as the physical and chemical properties of lignin and depolymerized lignin are affected by the content of hydroxyl groups. $^{31}$P NMR spectroscopy is a unique
tool in the measurement of lignin hydroxyl groups, providing quantitative information for various types of major hydroxyl groups. After sufficient phosphitylation with phosphorous-based reagents, different hydroxyl groups in lignin belonging to aliphatic, carboxylic, guaiacyl, syringyl, p-hydroxyphenyl, catechols as well as guaiacyl group with carbon substituents at the C5 position, can be readily quantified with $^{31}$P NMR spectroscopy (Pu et al., 2011).

Fig. 5-5 presents contents of different hydroxyl functional groups as a function of $M_w$ of SKL and HKL. The carboxylic acid group is typically associated with extensive oxidation, hence among all different types of hydroxyl groups, the carboxylic hydroxyl content dramatically increased with decreasing $M_w$ (due to extensive oxidation) at a higher $H_2O_2$/lignin ratio. For example, carboxylic-OH groups exist in both the SKL and HKL controls at relatively low levels (i.e. 0.3 – 0.4 mmol/g). These levels increase to 2 mmol/g in DKL derived from either SKL or HKL after treatment at the 1:1 $H_2O_2$/lignin mass ratio. This could be attributed to extensive oxidation of lignin by $H_2O_2$. 

![Graph showing hydroxyl content vs. $M_w$](image-url)
Figure 5-5 Contents of different hydroxyl functional groups vs. $M_w$ for SKL and DKL derived from SKL (A) and HKL and DKL derived from HKL (B).

As shown in Fig. 5-5A, aliphatic hydroxyl is the dominant hydroxyl group in softwood kraft lignin due to the presence of phenylpropane units in the lignin structure, represented by either the primary-OH (in $\gamma$-C atom of the side chain) and secondary-OH (in $\alpha$-C atom) groups.

In lignin oxidative depolymerization with permanganate and ionic liquid, resulted a decrease in aliphatic OH and an increase in phenolic hydroxyl groups (Zakis, 1994; Lucia et al., 2000). The reduction of the aliphatic OH could be attributed to a dehydration of the primary or secondary-OH groups (Wen et al., 2014). As shown in Fig. 5-5A, the content of aliphatic OH group in SKL decreased slightly with increasing the extent of oxidation, dropping from 1.5 mmol/g in the original lignin to 1.27 mmol/g in the DKL with 1420 Da (corresponding to the 1:1 $H_2O_2$/SKL mass ratio). Similar trend was observed with oxidative de-polymerization of hardwood kraft lignin for which the aliphatic OH content dropped from 2 mmol/g for the HKL to 1.6 mmol/g in the DKL with 1415 Da, corresponding to the 1:1 $H_2O_2$/HKL mass ratio, (Fig.5-5B).

The condensed hydroxyl structures in lignin comprise diphenylmethanes, diphenyl ethers, and 5,5’-biphenolic moieties (Granata et al., 1995). Softwood lignins with high content of
guaiacyl (G) units have a more condensed and cross-linked structure than hardwood lignins because the C5 position in hardwood lignin is occupied by methoxyl group, as shown in Figs. 5-5A and 5-5B. As shown in Fig. 5-5A for SKL, the total condensed OH groups decreased gradually from 1.55 mmol/g in the original softwood kraft lignin to 1.14 mmol/g in the DKL from the oxidative treatment of SKL at 1:1 H₂O₂/SKL mass ratio. This decrease could be explained by the scission of \( \beta-O-4 \) linkages that led to non-condensed moieties. On the contrary, the total content of condensed hydroxyl groups in hardwood kraft lignin were increased from 0.43 mmol/g in the original HKL to 0.711 mmol/g in the DKL from the oxidative treatment of HKL at 1:1 H₂O₂/SKL mass ratio (Fig. 5-5B). This suggests that during oxidative depolymerization, demethoxylation could occur, converting syringyl (S) to guaiacyl (G) structures. Subsequently, repolymerization of the G structure at the C5 position would take place, accounting for the increase in the condensed OH structures in DKL.

Non-condensed phenolic OH groups in lignin consist of syringyl phenolics, guaiacyl phenolics and p-hydroxy phenyl. In softwood lignin, the major non-condensed phenolic hydroxyls are guaiacyl phenolics with a minor amount of p-hydroxy phenyl. The total content of phenolic OH groups increased from 1.18 mmol/g in the original SKL to 2.09 mmol/g in the DKL at 0.5:1 H₂O₂/SKL mass ratio, which is likely due to the reduction in condensed OH contents (Fig. 5-5A), but it decreased back to 1.27 mmol/g in the DKL at 1:1 H₂O₂/SKL mass ratio. In contrast, the total content of phenolic OH groups in HKL (3.34 mmol/g) is much higher than that of SKL (1.18 mmol/g), as hardwood lignins contain more syringyl phenolics than softwood lignins. The total content of non-condensed phenolic OH groups in HKL dropped to 2.79 mmol/g in the DKL at 1:1 H₂O₂/HKL mass ratio, likely due to oxidative ring cleavage, which is in good agreement with the reduced aromatic structure in the DKLs as shown by the FTIR results (Fig. 5-3).

### 5.4.6 TGA analysis

The thermal stability of original kraft lignins and the depolymerized kraft lignins (DKL) were investigated using thermal gravimetric analysis (TGA) plots and the derivative of the TG curves (DTG) under a nitrogen environment, as illustrated in Figs. 5-6 (SKL) and 5-7 (HKL). The thermal degradation of lignin is a complex process because the structure
contains various oxygen functional groups with different decomposition pathways, including competitive and/or consecutive reactions.

As shown in the Figures Figs. 5-6 and 5-7, generally both SKL and HKL lignins started to decompose at 200-300 °C, while the maximum decomposition occurred around 350-400 °C. Various aromatic hydrocarbons could form from lignin decomposition, such as phenolics, hydroxyphenolics and guaiacyl-/syringyl-type compounds, most products having phenolic –OH groups (Brebu et al., 2010; Wittkowski et al., 1992). The weight loss at temperatures < 100 °C for all samples in both Figures can be ascribed to the loss of water contained in the KL or DKL samples (Domínguez et al. 2008). The lignin decomposition temperatures depend on its molecular structure. Lignins with higher molecular weights incorporating a significant number of intermolecular β-O-4 and C-C bonds, would have a high thermal stability and, as a result, higher decomposition temperatures (El-Saied, and Nada, 1993). Depolymerization of kraft lignins using a low and a high H₂O₂/lignin mass ratio produced DKL products with reduced M_w (Fig.5-4). Consequently, the DKL products from either SKL (Fig. 5-6) or HKL (Fig. 5-7) have a much lower decomposition temperature than that of the original lignins. For instance, the initial decomposition and the maximum decomposition temperature of SKL control with Mw of 6,050 Da were (280 and 370 °C, respectively), shifted lower to 173 and 270 °C, respectively for the DKL (Mw = 1,420 Da) obtained at a H₂O₂/lignin mass ratio of 1:1 (Fig. 5-6). Same conclusions can be obtained when comparing the thermal decomposition temperatures of HKL and DKL (Fig. 5-7). This decrease in decomposition temperatures can be attributed to the greatly reduced M_w (Wang et al., 2018).
Figure 5-6  TGA curves (A) and DTG plots (B) of SKL and its de-polymerized products.
Figure 5-7  TGA curves (A) and DTG plots (B) of HKL and its de-polymerized products.
5.4.7 Py-GC/MS analysis

Py-GC/MS analysis was conducted for the DKL products from oxidative depolymerization of SKL (Table 5-4) and HKL (Table 5-5) at room temperature at a 1:1 H$_2$O$_2$/KL mass ratio. The results of Py-GC/MS analysis can reveal key compounds of the volatile fraction of the DKL samples at 350 °C, identified by their mass spectra referring to the NIST library. It should be noted that the small peaks with an area less than 1.5 % of the total area are not included in the Tables. As shown in both Tables, the detectable compounds are mainly aromatic and aliphatic compounds such as guaiacol-type, phenol-type, catechol-type, and their oxygen substitution derivatives (carboxylic acids, esters and alcohols). Various types of phenolic compounds can be generated via the cleavage of β-aryl etheric bonds present in both softwood and hardwood samples (Zhao et al., 2014). Meanwhile, some aliphatic compounds (e.g., 1-Butene, 3,3-dimethyl- and Adipic acid, di(oct-4-yl ester)) can form from the demethoxylation reaction especially in hardwood samples (Ház et al., 2013). The demethoxylation cleavage reaction was confirmed in this work by FTIR analysis (Fig. 5-3).

Moreover, the Py-GC/MS analysis results also confirmed that the SKL and HKL were extensively oxidatively depolymerized by H$_2$O$_2$ at ambient temperature, producing low-molecular aromatic/phenolic compounds that can be utilized for bio-based phenolic resins, polyurethane resins and dispersants (Siddiqui et al., 2017; Mahmood et al., 2016).

Table 5-4 Py-GC/MS analysis results for the DKL product from oxidative depolymerization at room temperature and 1:1 H$_2$O$_2$/SKL mass ratio

<table>
<thead>
<tr>
<th>Pk#</th>
<th>RT</th>
<th>Area%</th>
<th>Library/ID</th>
<th>$M_w$</th>
<th>Qual</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.36</td>
<td>2.35</td>
<td>Acetic acid, methyl ester</td>
<td>74</td>
<td>72</td>
</tr>
<tr>
<td>2</td>
<td>0.84</td>
<td>7.5</td>
<td>Acetic acid</td>
<td>60</td>
<td>86</td>
</tr>
<tr>
<td>3</td>
<td>3.71</td>
<td>1.6</td>
<td>Furfural</td>
<td>96</td>
<td>91</td>
</tr>
<tr>
<td>4</td>
<td>5.44</td>
<td>1.7</td>
<td>Propanedioic acid, dimethyl ester</td>
<td>132</td>
<td>83</td>
</tr>
<tr>
<td>5</td>
<td>8.37</td>
<td>10.5</td>
<td>Phenol, 2-methoxy- (Guaiacol)</td>
<td>124</td>
<td>97</td>
</tr>
<tr>
<td>6</td>
<td>10.63</td>
<td>3.01</td>
<td>2-methoxy-5-methylphenol</td>
<td>138</td>
<td>90</td>
</tr>
<tr>
<td>7</td>
<td>10.79</td>
<td>4.68</td>
<td>1,2-Benzenediol</td>
<td>110</td>
<td>95</td>
</tr>
<tr>
<td>8</td>
<td>15.93</td>
<td>3.67</td>
<td>1,4-Benzenediol, 2-methoxy-</td>
<td>140</td>
<td>95</td>
</tr>
<tr>
<td>9</td>
<td>17.6</td>
<td>2.53</td>
<td>Benzoic acid, 4-hydroxy-3-methoxy-methyl ester</td>
<td>182</td>
<td>96</td>
</tr>
<tr>
<td>10</td>
<td>17.78</td>
<td>2.07</td>
<td>Homovanillic alcohol</td>
<td>168</td>
<td>80</td>
</tr>
</tbody>
</table>
Table 5-5  Py-GC/MS analysis results for the DKL product from oxidative de-polymerization at room temperature and 1:1 H\textsubscript{2}O\textsubscript{2}/HKL mass ratio

<table>
<thead>
<tr>
<th>Pk#</th>
<th>RT</th>
<th>Area%</th>
<th>Library/ID</th>
<th>M\textsubscript{w}</th>
<th>Qual</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
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<td>11.55</td>
<td>Acetic acid, Methyl ester</td>
<td>74</td>
<td>64</td>
</tr>
<tr>
<td>2</td>
<td>0.61</td>
<td>14.13</td>
<td>Acetic acid</td>
<td>60</td>
<td>90</td>
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<tr>
<td>3</td>
<td>3.7</td>
<td>6.91</td>
<td>Furfural</td>
<td>96</td>
<td>94</td>
</tr>
<tr>
<td>4</td>
<td>5.45</td>
<td>8.93</td>
<td>Propanedioic acid, dimethyl ester</td>
<td>132</td>
<td>83</td>
</tr>
<tr>
<td>5</td>
<td>9.45</td>
<td>3.64</td>
<td>1-Butene, 3,3-dimethyl-</td>
<td>84</td>
<td>50</td>
</tr>
<tr>
<td>6</td>
<td>15.92</td>
<td>2.69</td>
<td>1,4-Benzenediol, 2-methoxy-</td>
<td>140</td>
<td>80</td>
</tr>
<tr>
<td>7</td>
<td>16.44</td>
<td>4.27</td>
<td>2-Naphthyl methyl ketone</td>
<td>170</td>
<td>22</td>
</tr>
<tr>
<td>8</td>
<td>17.6</td>
<td>5.48</td>
<td>Benzoic acid, 4-hydroxy-3-methoxy- methyl ester</td>
<td>182</td>
<td>94</td>
</tr>
<tr>
<td>9</td>
<td>17.77</td>
<td>2.07</td>
<td>2-Propanone, 1-(4-hydroxy-3-methoxyphenyl)-</td>
<td>180</td>
<td>80</td>
</tr>
<tr>
<td>10</td>
<td>18.18</td>
<td>4.5</td>
<td>Benzoic acid, 4-hydroxy-3-methoxy-</td>
<td>213</td>
<td>93</td>
</tr>
</tbody>
</table>

5.5  Discussion

As described previously, SWL and HWL lignins used in this work were both acids washed, and both substrates were in the H-form (protonated lignin), with a pH value of around 4.0 in pure water. Thus, in this work, the oxidation reactions were carried out under acidic conditions, and the low pH of the reaction medium would affect lignin degradation mechanism in hydrogen peroxide (Xiang et al., 2000). H\textsubscript{2}O\textsubscript{2} can act as a nucleophilic or an electrophilic agent depends on the pH of the solution (relatively stable under acidic conditions).

Oxidation of lignin under acidic conditions could resemble oxidation of aromatic and olefinic structures with peroxy acids (prepared by treating the corresponding carboxylic
acid with hydrogen peroxide) (Sarkanen et al., 1971). Under acidic environment, H₂O₂ can form hydroxonium ion HO⁺ which is a strongly electrophilic oxidant (Geger, 1986) by the reaction of either mineral acid (e.g., sulfuric acid) or carboxylic acids (e.g., acetic acid, formic acid) with H₂O₂ as follows (Ma et al., 2015; Sun et al., 2000):

\[
\text{H}_2\text{O}_2 + \text{H}^+ \leftrightarrow \text{HO}^+ + \text{H}_2\text{O} \quad (1)
\]

The electrophilic HO⁺ ion is highly reactive towards electron-rich sites such as olefinic, carbonyl and aromatic ring structures (lignin) (Johanson, 1980). Oki, et al. (1980) suggested that in proxy oxidation system on lignin model compounds, the major reactions were demethoxylation and β-ether cleavage. As such, depolymerization of lignin could be achieved using acidic system of hydrogen peroxide via OH⁺ ions. Although a considerable interest was paid in applying peroxy acid for lignin removal from lignocellulosic biomass, there has been very little effort made towards applying peroxy acid chemistry to converting lignin to value-added products. This work successfully demonstrated a cost-effective approach to convert kraft lignin into low molecular weight compounds at close to 100% yield by oxidative degradation of lignin in slurry of acidic kraft lignin powder with concentrated H₂O₂ at ambient temperature. As shown in Eq. (1), the formation of HO⁺ ion from H₂O₂ is reversible reaction, therefore, apparently, high concentrations of the reactant (H₂O₂) would be favorable for the formation of HO⁺ ion and hence promote lignin depolymerization at room temperature (Evstigneev, 2013).
Although the mechanism of lignin degradation via \( \text{H}_2\text{O}_2 \) has not been reported, the reaction mechanism for the room-temperature \( \text{H}_2\text{O}_2 \) depolymerization of acidic kraft lignin could resemble the reaction scheme for the reaction of model compounds with \( \text{OH}^+ \) at low pH (Gierer, 1986), as illustrated in the above Scheme 1 (Fig. 5-8) involving mainly \( \text{OH}^+ \) oxidative ring opening and cleavage of \( \beta \)-aryl ether bonds.

5.6 Conclusions

This work successfully demonstrated a cost-effective approach to converting kraft lignin into low molecular weight compounds at close to 100\% yield by oxidative degradation of lignin in slurry of acidic kraft lignin powder with concentrated \( \text{H}_2\text{O}_2 \) at ambient temperature. The obtained depolymerized kraft lignin (DKL) products were comprehensively characterized by GPC-UV, FTIR, \(^{31}\text{P} \) NMR, TGA, Py-GC/MS and elemental analysis. The characterization results suggest effective depolymerization of softwood and hardwood lignins. The DKL products have a \( M_w \) of around 1400 Da at 1:1 \( \text{H}_2\text{O}_2/\text{KL} \) mass ratio with high phenolic and carboxylic groups content. Py-GC/Ms results disclosed the presence of highly oxygenated fragments with functional groups such as phenols, carboxylic acids, esters, ketones, and aldehydes in the DKL products. The novelties of this oxidative lignin de-polymerization approach are that it operates at room
temperature without needing heat, and it does not require a catalyst when acid-washed kraft lignins, and the approach can be readily scaled-up to an industrial level.

5.7 References


Chapter 6

6 Oxidative Depolymerization of Lignin with Nitric Acid at Ambient Condition

The information presented in this Chapter is based on the paper “Oxidative Depolymerization of Lignin with Nitric Acid at Ambient Condition” will to be submitted for publication. The sections in Chapter 6 present the results towards the completion of objective 4 of this PhD project.

6.1 Abstract

Lignin is a renewable natural aromatic polymer, and kraft lignin is produced in a large amount in the kraft pulping plants. However nearly 98% of kraft lignin is burned as a waste or a low-value material. In this work, we demonstrated an innovative and cost-effective strategy to produce depolymerized kraft lignin (DKL) of lower molecular weights from softwood kraft lignin (SKL) and hardwood kraft lignin (HKL) via oxidative de-polymerization using nitric acid at ambient condition (room temperature and 1 atm). This novel approach has the following features: ambient process conditions, no requirements of heat, catalyst, additives or solvents, and no need of product purification. Thus, there is a high potential for scale-up of the process. The obtained DKL products were characterized extensively by GPC-UV, FTIR, TGA, Py-GC/MS, potentiometric titration and elemental analysis. Treatment of SKL or HKL at KL/HNO₃ mass ratio of 1:4(w/w) at room temperature for 84 h resulted in DKL products with a weight-average molecular weights (Mₘ) of 1350 Da, much lower than that of the original lignin. In addition, the DKL products have a significant increase in carboxyl acid group contents, and the DKL products have much lower decomposition temperatures. It was confirmed
that nitration of lignin structure occurred during the HNO$_3$-oxidative de-polymerization, as evidenced by the presence of 5% N content in the DKL products.

6.2 Introduction

Due to the environmental and depleting resources concerns, it is an inevitable trend to move from the non-sustainable fossil-based economy to sustainable bio-economy – production of bioproducts (bioenergy, biofuels, bio-based chemicals and materials) from bio-renewable feedstocks. Compared with other bio-renewable feedstocks, lignocellulosic biomass such as forestry/agricultural residue can be a promising renewable raw material for the production of bioproducts, as it is widely and abundantly available without competition with food supply (Abejón et al., 2018). Lignocellulosic biomass is primarily composed of carbohydrate polymers (cellulose and hemicellulose), and aromatic polymers (lignin). Lignin is the second most abundant natural polymer after cellulose (Ragauskas et al., 2014). It can be separated from wood, annual plants such as wheat straw, cornstalk or other agricultural residues (e.g., sugarcane bagasse) by different pulping (extraction) processes (Laurichesse et al., 2014). Lignin constitutes around one fourth of the mass of a woody plant. It is an amorphous binding material that protect cellulose fibers, give stiffness and strength to wood and protect carbohydrates from oxidative degradation, also, make the plant cell wall hydrophobic (Guadix-Montero et al., 2018). Lignin molecular structure is a crosslinked network of three basic monolignols (phenylpropane units) as the building blocks, i.e., p-hydroxyphenyl lignin (H unit, derived from p-coumaryl alcohol), guaiacyl lignin (G unit, from coniferyl alcohol), and syringyl lignin (S unit, from sinapyl alcohol). The main difference among these monolignols is the number of methoxy groups that attached to the aromatic ring (none, one or two methoxy groups in the p-coumaryl (H), coniferyl (G) and synapyl (S) alcohol respectively) (Guadix-Montero et al., 2018). Softwood lignins are generally considered to consist of more guaiacylpropane units while hardwood lignins contain both guaiacyl and syringylpropane units (Önnerud et al., 2002).
The lignin polymer monolignols are connected via different bonds that configure a compound with high resistance to chemical modification and depolymerization. Ether linkages, especially β-aryl ether (β-O-4), are most prevalent in lignin, followed by the 4-O-5 and α-O-4 aryl ether bonds and other linkages such as biphenyl linkages 5-5, phenylcoumaran β-5, diarylpropane β-1 and β-β (Abejón et al., 2018). In addition, there are a variety of functional groups, such as methoxyl, phenolic hydroxyl, aliphatic hydroxyl, benzyl alcohol, noncyclic benzyl ether, and carbonyl groups that control the reactivity of lignin (Chen and Wan, 2017).

As such, the aliphatic and aromatic units of lignin are connected mainly by two types of inter-unit linkages (C–C and C–O linkages), and an energetic lignin depolymerisation approach should be able to break down both types of inter-unit linkages, while the bond energies of C–C linkages are higher than those of C–O linkages, and under certain conditions can produce new C–C inter-unit bonds (via condensation reactions) (Guadix-Montero et al., 2018).

A considerable amount of investigation has been explored on lignin depolymerization through thermochemical approaches such as pyrolysis (Kawamoto et al., 2007), reductive (Barta et al., 2010), and hydrolytic de-polymerization (Kristianto et al., 2017), however most of these routes struggling high cost due to their process conditions (high temperatures and pressures, and expensive catalyst) and the product separation complications. Thus, developing novel processes for lignin depolymerization at ambient condition (room temperature and 1 atm) without the need of product separation is especially promising for conversion of lignin into bio-products on an industrial scale.

There were some previous reports on nitric acid pulping of lignocellulosic biomass, although this pulping method was eventually refused for industrial use due to the environmental problems (Grushnikov et al., 1970). Tewari and Singh (1988) observed that nitration with nitric acid introduced higher nitrogen content in substrate lignin and led to reduction in methoxyl content, phenolic hydroxyl content, but a significant increase in carboxyl content. A possible mechanism for dealkylation was proposed by Bunton et al. (1950), as illustrated in Scheme 1 (Fig. 6-1). It consists g of two stages: the first stage
is slow nitrosation or nitration, forming a quinonoid oxonium ion, and second stage results in the removal of methyl group (Scheme 1).

![Scheme 1](image)

**Figure 6-1** Scheme 1. Mechanism of oxidation with NO+ (Bunton et al., 1950).

According to the above mechanism, the treatment introduces NO or NO₂ functional group into the lignin’s aromatic ring. Kalisch (1967) described that delignification in nitric acid pulping occurred through the following two steps: a) the high molecular weight lignin was fragmented by hydrolytic splitting of ether linkages (depolymerized) and produced lower molecular weight lignin fractions, and b) oxidation and nitration reactions of nitric acid and lignin led to oxidation of the side chain of coniferyl complex and nitration of the benzene ring. Chudakov et al. (1966) oxidized several lignins with hot 30% nitric acid and obtained malic/oxalic acids. They speculated that both acids were derived from quinones formed from oxidation of non-condensed lignin unit. Kee (1968) prepared nitrolignin by reacting birch and spruce dioxane lignins with aqueous nitrous acid, and the work found that 76 and 80%, respectively, of the total nitrogen was presented in nitro(R-NO₂) groups, and the yield of isolated oxalic acid attained 1-2% at 70 °C for both lignins. In another more recent study, Khabarov et al. (2016) investigated the nitration of sulfate lignin by nitric acid in an aqueous dioxane medium under homogeneous conditions. They proposed that it’s possible to synthesize nitrated lignin containing one nitro group per 1.5-2 phenylpropane units. At low consumptions of nitric acid, the nitration started after an induction period, the duration of which decreased with increasing temperature. Lignin depolymerization increases the reactivity and solubility of lignin, moreover improves the substitution ratio in various applications such as incorporating lignin polymer in many bio-based materials (e.g., phenolic and polyurethane resins) (Siddiqui et al., 2017; Mahmood et al., 2016).

Driven by development of bio-economy and in particular the necessity to find sustainable
alternatives to fossil fuel feedstock to produce chemicals and fuels, lignin depolymerisation for bio-based aromatics has received extensive and increasing attention. The aim of the present study was to explore kraft lignin depolymerization using nitric acid at ambient conditions (room temperature and atmospheric pressure) to produce nitro-lignins of lower molecular weights.

6.3 Materials & Methods

6.3.1 Materials

Two types of kraft lignin (KL), both provided by FPInnovations, were used in this study. They are softwood kraft lignin (SKL) from West Fraser’s Hinton Pulp Mill, and hardwood kraft lignin (HKL) from Resolute’s Thunder Bay mill. Other chemicals used in the study include nitric acid 69%, hydrochloric acid (1N), acetone (99.5%), d6-DMSO, d-chloroform, HPLC-grade tetrahydrofuran (THF), are all CAS reagent grade chemicals, purchased from Sigma–Aldrich, and used as received.

6.3.2 Methodology

The HNO₃-oxidative treatment of kraft lignins was accomplished in 200 mL beaker at ambient conditions (25 °C and 1 atm). In a typical run, 5g of SKL or HKL was mixed with stirring slowly with 15g of 35% HNO₃ at for SKL (or HKL)/ HNO₃ mass ratio of 1/3 (w/w) to obtain homogenous slurry, where the Run# was designated as SKL-1/3-35% or HKL-1/3-35%. Subsequently, the slurry was soaked inside a fume hood at room temperature for various lengths of time. The slurry weight was monitored with time until a final dry product was obtained (i.e. the weight of the sample became constant). The recovered modified KL was air dried for 24h. The yield was determined based on the percentage of the dry mass of modified KL to the dry mass of the initial KL. Experimental conditions and results are presented in Table 1.
Table 6-1 Experimental run # and the associated reaction conditions for the depolymerization of kraft lignin at room temperature, along with the elemental composition and yield of the DKL products.

<table>
<thead>
<tr>
<th>Run #</th>
<th>KL/HNO\textsubscript{3}</th>
<th>%H</th>
<th>%S</th>
<th>%C</th>
<th>%O</th>
<th>%N</th>
<th>Yield%</th>
</tr>
</thead>
<tbody>
<tr>
<td>-</td>
<td>SKL (control)</td>
<td>-</td>
<td>5.5</td>
<td>1.5</td>
<td>65.2</td>
<td>27.2</td>
<td>0.2</td>
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<tr>
<td>-</td>
<td>HKL (control)</td>
<td>-</td>
<td>5.4</td>
<td>2.2</td>
<td>63.2</td>
<td>24.9</td>
<td>0.02</td>
</tr>
<tr>
<td>SKL-1/3-35%</td>
<td>5 g SKL, 15g HNO\textsubscript{3} 35%</td>
<td>1/3</td>
<td>2.7</td>
<td>1.1</td>
<td>43.8</td>
<td>46.9</td>
<td>5.45</td>
</tr>
<tr>
<td>SKL-1/3-25%</td>
<td>5 g SKL, 15g HNO\textsubscript{3} 25%</td>
<td>1/3</td>
<td>3.6</td>
<td>1.0</td>
<td>50.14</td>
<td>40.3</td>
<td>4.8</td>
</tr>
<tr>
<td>SKL-1/3-15%</td>
<td>5 g SKL, 15g HNO\textsubscript{3} 15%</td>
<td>1/3</td>
<td>3.6</td>
<td>1.2</td>
<td>53.8</td>
<td>37.9</td>
<td>3.4</td>
</tr>
<tr>
<td>HKL-1/3-35%</td>
<td>5 g HKL, 15g HNO\textsubscript{3} 35%</td>
<td>1/3</td>
<td>2.7</td>
<td>1.6</td>
<td>42.5</td>
<td>47.9</td>
<td>5.06</td>
</tr>
<tr>
<td>HKL-1/3-25%</td>
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<td>1/3</td>
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<td>1.74</td>
<td>45.9</td>
<td>44.2</td>
<td>4.53</td>
</tr>
<tr>
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<td>5 g HKL, 15g HNO\textsubscript{3} 15%</td>
<td>1/3</td>
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<td>41.05</td>
<td>3.39</td>
</tr>
<tr>
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<td>5 g SKL, 20g HNO\textsubscript{3} 35%</td>
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<td>48.3</td>
<td>5.63</td>
</tr>
<tr>
<td>SKL-1/4-25%</td>
<td>5 g SKL, 20g HNO\textsubscript{3} 25%</td>
<td>1/4</td>
<td>3.3</td>
<td>0.9</td>
<td>45.33</td>
<td>45.0</td>
<td>5.3</td>
</tr>
<tr>
<td>SKL-1/4-15%</td>
<td>5 g SKL, 20g HNO\textsubscript{3} 15%</td>
<td>1/4</td>
<td>3.8</td>
<td>1.02</td>
<td>50.0</td>
<td>40.6</td>
<td>4.4</td>
</tr>
<tr>
<td>HKL-1/4-35%</td>
<td>5 g HKL, 20g HNO\textsubscript{3} 35%</td>
<td>1/4</td>
<td>3.0</td>
<td>1.7</td>
<td>39.17</td>
<td>51.2</td>
<td>4.8</td>
</tr>
<tr>
<td>HKL-1/4-25%</td>
<td>5 g HKL, 20g HNO\textsubscript{3} 25%</td>
<td>1/4</td>
<td>3.6</td>
<td>1.16</td>
<td>43.8</td>
<td>46.8</td>
<td>4.6</td>
</tr>
<tr>
<td>HKL-1/4-15%</td>
<td>5 g HKL, 20g HNO\textsubscript{3} 15%</td>
<td>1/4</td>
<td>3.7</td>
<td>1.76</td>
<td>45.8</td>
<td>44.5</td>
<td>4.1</td>
</tr>
</tbody>
</table>

In this work, we focused on lignin depolymerization at room temperature using different concentrations of HNO\textsubscript{3} and KL/ HNO\textsubscript{3} mass ratios. The total reaction time was 84 h at room temperature, but it could be accelerated by operating at a slightly higher temperature, e.g., 45 °C. The treatment should be done inside the fume hood, due to the decomposition of the HNO\textsubscript{3} (Eq. 1) to form brown gas (NO\textsubscript{2}) since the beginning of the treatment (see Fig. 6-2b), when the temperature of the reaction content was climbed to 70 °C, followed by settling of the slurry to yield a reddish DKL powder (Fig. 6-2a), and dropping of the temperature gradually to room temperature.

\[
4 \text{HNO}_3 \rightarrow 2 \text{H}_2\text{O} + 4 \text{NO}_2 + \text{O}_2
\]  

The KL/HNO\textsubscript{3} mass ratios (1/3 or 1/4) were selected according to the Mw of the DKL products. A set of preliminary experiments were carried out at a ratio KL/HNO\textsubscript{3} of 1:2 (w/w) with HNO\textsubscript{3} concentration 35%, the Mw of the DKL was measured to be 2521, 2077 Da for SKL and HKL respectively. Thus, we increased the amount of nitric acid added in the treatment in order to produce DKL products with a lower Mw. Each
experiment was repeated three times to ensure that relative experimental errors are not more than 5–10%.

![Image of a typical depolymerized kraft lignin product and NO₂ gas](image)

**Figure 6-2** (a) Picture of a typical depolymerized kraft lignin product, (b) NO₂ (reddish-brown gas) collected in a collecting bag (b).

### 6.3.3 Product characterizations

**Fourier-Transform Infrared Spectroscopy (FTIR) Analysis:** FTIR spectroscopy was employed using a Nicolet-6700 Fourier Transform Infrared Spectrometer with a universal attenuated total reflection (ATR) accessory for the dry samples of SKL and HKL (controls) and DKL products to understand the changes in functional groups of the lignin structure. Spectra from 800 to 4000 cm⁻¹ were collected for the sample powders in absorbance mode with 64 scans per spectrum at 4 cm⁻¹ resolution.

**GPC analysis:** The average molecular weights of SKL, HKL (controls) and the DKL products were measured with a GPC (gel permeation chromatography) instrument, using THF eluent (1 mL min⁻¹) and linear polystyrene standards with an Mw from 100 to 1 million g/mol for molecular weight calibration. All the sample were derivatized before injecting into GPC. UV detector was used at wave length 270 nm.

**TGA analysis:** Thermal gravimetric analysis (TGA) analysis of the lignin and depolymerized lignin products was performed using a PerkinElmer Pyris 1,1 TGA in nitrogen atmosphere. In a typical measurement, a 10 mg dry sample was heated in a N₂ flow at 20 mL/min from 25 °C to 600 °C at 10 °C /min. The weight loss % (TGA) and the
differential thermogravimetric (DTG) of the samples were recorded and plotted continuously verses the temperatures.

**Elemental analysis:** Elemental analysis of the original and depolymerized kraft lignin was performed using a CHNS Flash Elemental Analyzer 1112 series (Thermo) for determining the elemental compositions of CHNS (carbon, hydrogen, nitrogen and sulfur) in the lignin samples (Table 6-1). The composition of oxygen was calculated by difference. All samples were analyzed for elemental contents, and the nitrogen, oxygen and carbon contents were found to depend on reaction conditions, while elements such as S and H did not change significantly.

**Potentiometric titration:** A solution was prepared containing 0.25g of lignin sample, 100 mL of demineralized water, free of carbonates, and correspondingly 1M sodium hydroxide of a pH value above 12 (large excess). After being stirred until total dissolution (around 30 min for most of the samples to ensure complete dissolution), the solution was transferred to the titration vessel on which pH electrode and HCl injector are installed. The pH electrode was calibrated before titration at pH 4.7 and 10. The solution was titrated back with 1M HCl to pH=2, using a 721 Net Titrino (Metrohm Swiss) with a combined pH electrode monitored by TiN 2.4 software.

**Calculations:** Carboxyl group content was determined by titration, calculated from Eq. (2). Similar calculation was done for phenolic hydroxyl group by Eq. (3).

\[
\text{Carboxyl content (mmol/g-sample)} = \frac{(V_3 - V_2) \times N(HCl)}{W}
\]  
\[ (2) \]

\[
\text{Phenolic hydroxyl content (mmol/g-sample)} = \frac{(V_2 - V_1) \times N(HCl)}{W}
\]  
\[ (3) \]

Where: \( V_1 \) = titration volume, first inflection point (EP1) (mL).

\( V_2 \) = titration volume, second inflection point (EP2) (mL).

\( V_3 \) = titration volume, third inflection point (EP3) (mL).

\( N(HCl) \) = normality of HCl (mmol/mL)

\( W \) = weight of sample (g) on dry basis.
**Py-GC/MS:** Py-GC-MS analysis with (~100 µg sample was conducted on a py2020i microfurnace pyrolyzer / AS1020 autosampler (Frontier Laboratories) coupled with an Agilent 6890B GC - 5973A MSD. The GC-MS was equipped with 30 m × 0.25 mm × 0.25 µm DB-5 columns with temperature programming as follows: a 1 min hold at an initial temperature of 50 ºC followed by a 30 ºC min⁻¹ ramp to the final temperature of 350 ºC with 1 min hold. Analysis by py-GC/MS was done using the Double-Shot mode, and the compounds were identified by comparing their mass spectra with those of NIST library.

6.4 Results and discussion

In this work, upon the completion of the HNO₃ treatment the depolymerized lignin DKL products obtained were homogenous shiny brownish fluffy powder of (see Fig.6-2a). Interestingly, the depolymerized lignins, especially those from the tests of HKL-1/4-35% and SKL-1/4-35%, have very good solubility in water at a low pH value (≤ 2), and most of the DKL products are soluble in methanol, ethanol and acetone, depending on the HNO₃ acid concentration and the KL/HNO₃ ratio used in the treatment. The yield of the depolymerized lignin product was also very high (> 90± 5%), as shown in Table 6-1.

6.4.1 Elemental analysis

Table 6-1 displays the C, H, N, S and O contents of both SKL and HKL lignin substrates and DKL products from these two substrates at various KL/HNO₃ mass ratios. The results clearly illustrate significant changes in the elemental compositions of the depolymerized lignin products compared with the original lignin substrates, as summarized below:

(a) The DKL products have a substantially higher N% content, in particular from the tests when more HNO₃ was added. For example, the N% content is 0.2% and 0.02% for SKL and HKL, respectively. Whereas, the N% content of DKL from the tests of SKL-1/3-35% and HKL-1/3-35% increased to 5.0-5.5%.

(b) The O% content of DKL products increased dramatically when increasing the HNO₃ addition in the treatment. For instance, O% content increased to approx. 48% in DKL
obtained from the test of HKL-1/3-35%, almost double that of the HKL. This result evidences the oxidation of lignin with nitric acid that contributed to the degradation/depolymerization of lignin in the treatment, resulting in nitrophenols, organic acids, CO$_2$ etc. (Sobolev, 1961).

(c) In contrast, the C% content of both lignins decreased substantially while increasing the HNO$_3$ addition in the treatment, which is expected due to the increases in both N and O contents in the DKL products. The initial C% content of SKL or HKL was 63-65%, and it decreased to around 43% in the tests of both SKL-1/3-35% and HKL-1/3-35%. On the other hand, %C reduction might result from the cleavage of methoxyl group to form CO$_2$ during the treatment (Khabarov et al., 2016; Sobolev et al., 1961; Kee, 1968).

The above results conclusively prove the occurrences of both nitration and oxidation reactions of the lignin with nitic acid at room temperature, leading to degradation/depolymerization of lignin via cleavage of alkyl aryl ethers linkages. As such, these reactions could account for the low molecular weights of the DKL products, and their good solubility in water at a low pH (e.g. especially for the DKL products from the tests of HKL-1/4-35% and SKL-1/4-35%).

6.4.2 FTIR analysis

IR spectra were collected to characterize the functional structure of the original lignins (SKL and HKL) and their de-polymerized products after the HNO$_3$ treatment under various conditions (different HNO$_3$ acid concentrations), as illustrated in Fig. 6-3.
Figure 6-3 FTIR spectra of the original KL and its de-polymerized products from the HNO₃ treatment under various conditions: SKL (A) and HKL (B).

As shown in Fig. 6-3A (SKL and its DKL products), the band 1266–1270 cm⁻¹ represents guaiacyl (G) ring plus methoxyl C–O stretching (Jahan et al., 2007), with a strong absorbance peak for the original SKL sample at 1270 cm⁻¹. Although this peak was still observable its intensity is weakened in the depolymerized lignin samples, in particular from the tests using a higher concentration of HNO₃. This could be explained by the removal of methoxyl C–O bonds in the depolymerized lignin samples due to the oxidative cleavage of the bond to form CO₂.
The infrared absorption nitratated groups in DKL is characterized by the bands at approximately 1350 and 1550 cm\(^{-1}\), which can be assigned to aromatic nitro group (Sarkanen et al., 1971), as clearly shown in Fig. 6-3A. This is an ample evidence of introducing nitro functional group to lignin during the HNO\(_3\) treatment of kraft lignin. The depolymerized lignin samples also show reduced absorbance signals at 1425 cm\(^{-1}\) (that can be attributed to stretching vibration of C–C aromatic skeleton), suggesting degradation of aromatic skeletal during nitric acid treatment (Tejado et al., 2007).

Furthermore, the aromatic skeleton C=C stretching is represented by the absorption at 1515 and 1600 cm\(^{-1}\) (Kline et al., 2010). As displayed in Fig. 6-3A, strong peaks at 1515 and 1600 cm\(^{-1}\) in the original SKL, while these peaks were greatly reduced in the DKL samples, suggesting the rupture of the aromatic ring of the depolymerized lignins. The intensity of the peak at 1720 cm\(^{-1}\), attributed to non-conjugated C=O stretching vibration for carboxyl group (Heitner et al., 2016), increases drastically in the DKL samples when compared with the SKL control, evidencing the oxidation of lignin during the treatment.

Furthermore, as well known, the \(\beta\)-O-4 interunit linkages are the major type of structural linkage in lignins. As shown in Fig. 6-3A, the SKL original lignin possesses two clear peaks at 1030 and 1070 cm\(^{-1}\), while these absorbance signals were disappeared in the DKL samples from SKL-1/3-35%, SKL-1/3-25%, SKL-1/3-15%. This result may provide an evidence for that during the HNO\(_3\) treatment a considerable cleavage of ether linkages occurs, resulting in formation of low molecular weight DKL products (Derkacheva et al., 2008).

Fig. 6-3B illustrates IR spectra of HKL and its de-polymerized products from the HNO\(_3\) acid treatment suing different acid concentrations. Although the IR spectra in HKL and its de-polymerized samples are similar as those observed in Fig. 6-3A with the SKL, prominent differences were recognized in Fig. 6-3B at the bands of 1118 cm\(^{-1}\) and 1213 cm\(^{-1}\), related to hardwood syringyl structure. The band at 1123-1110 cm\(^{-1}\) can be attributed to aromatic C-H deformation of syringyl unit. As shown in Fig. 6-3B a strong peak is observed at 1213 cm\(^{-1}\) in the HKL sample, while this peak is gradually weakened in the DKL samples when increasing the HNO\(_3\) concentration, which might suggest cleavage of the methoxyl functional groups in the lignin during the HNO\(_3\) acid treatment.
(Tewari et al., 1988). The absorption band at 1213 cm\(^{-1}\) in the original HKL sample can be assigned to C-O stretching of guaiacyl and syringyl structure (Sameni et al., 2016), while this peak is weakened in the depolymerized samples, also suggesting cleavage of the methoxyl group (Sarkanen et al., 1971).

In summary, the FTIR analysis could prove the nitration and oxidation reactions occurring in HNO\(_3\) acid treatment of SKL or HKL at room temperature. In fact, the introduction of nitrogen functional group could be further confirmed by elemental analysis (Table 6-1) and Py-GC/MS whose results are to be discussed in a latter section.

To confirm decomposition of HNO\(_3\) during the HNO\(_3\) acid treatment process, the mixed sample of HKL-1/4-35% was placed in a TGA sample hold, heated up under N\(_2\) atmosphere up to 37 °C and soaked at this temperature for about 30 min, when the gas was analyzed online with a TGA/FTIR coupled system in various time intervals. Fig. 6-4 displays the TGA/FTIR spectra collected for the gas emitted from the treatment of HKL-1/4-35% at 37 °C in N\(_2\) flow. As clearly shown in the Figure 6-4, a strong peak that can be ascribed to the IR absorbance of NO\(_2\) was detected in the gas emission between 9-12 min, which verifies the decomposition of HNO\(_3\) during the HNO\(_3\) acid treatment process (via reaction: \(4 \text{HNO}_3 \rightarrow 2 \text{H}_2\text{O} + 4 \text{NO}_2 + \text{O}_2\)).
Figure 6-4 TGA/FTIR spectra of the gas emitted from the treatment of HKL-1/4-35% at 37 °C in N₂ flow.

6.4.3 GPC analysis

It should be noted that the results of GPC analysis reported here can only be considered as relative molecular weights due to the calibration with linear polystyrene standards, while lignin is a non-linear branched structure. Figures 6-5 and 6-6 illustrate effects of HNO₃ concentration (15%, 25%, or 35%) on weight-average molecular weight (Mₘ) of the de-polymerized products derived from SKL and HKL from HNO₃ treatment at KL/HNO₃ mass ratio of 1/3 and 1/4, respectively. Generally, the Mₘ of DKL is lower when a higher HNO₃ concentration was used. For instance, as shown Fig. 6-5A the Mₘ of the SKL (6050 Da) was reduced markedly by 70% to 1850 Da at 35% NHO₃ concentration. The degree of Mₘ reduction for HKL (originally Mₘ = 2750 Da) was much lower that for SKL.
Similar observations can be obtained from Fig. 6-6, where the HNO₃ treatment was carried out at KL/HNO₃ mass ratio of 1/4. Comparing the results in Fig. 6-6 and those in Fig. 6-5, it is obvious that more HNO₃ addition produced DKL products with a smaller M_w. For example, at KL/HNO₃ mass ratio of 1/4 with 35% HNO₃ acid, the M_w is as low as 1357 Da and 1310 Da for the DKL from SKL and HKL, respectively.

**Figure 6-5** Effects of HNO₃ concentration on weight-average molecular weight (M_w) of the de-polymerized products derived from SKL (A) and HKL (B) from HNO₃ treatment at KL/HNO₃ mass ratio of 1/3.
Figure 6-6 Effects of HNO$_3$ concentration on weight-average molecular weight ($M_w$) of the de-polymerized products derived from SKL (A) and HKL (B) from HNO$_3$ treatment at KL/HNO$_3$ mass ratio of 1/4.

This reduction in $M_w$ of both SKL and HKL during HNO$_3$ treatment can be explained by the cleavage of β-O-4’ linkages and methoxyl groups in the lignin during the nitric acid treatment, resulting in a considerable decrease of molecular weights.
6.4.4 TGA analysis

Thermal stability is an important property of polymeric materials, as thermal degradation occurs in polymeric materials at elevated temperatures. Depolymerized lignin can be valuable candidates for various applications such as in many bio-based polymer materials (e.g., phenolic and polyurethane resins) (Siddiqui et al., 2017; Mahmood et al., 2016) or simply in lignin/fossil polymer blends. Thus, Thermal stability of the DKL products derived from HNO3 treatment of SKL and HKL lignins were investigated by TGA-DTG (Differential Thermal Analysis). Typical results are shown in Figs. 6-7 and 6-8, which display TGA thermograms and DTG curves of DKL products obtained from the HNO3 treatment of SKL (Fig. 6-7) and HKL (Fig.6-8) at KL/HNO3 ratio of 1/4 with 35% and 15% acid concentrations. As clearly shown in these two Figures, TG curves of depolymerized KL products showed a faster degradation rate and lower degradation peak temperatures than the original KLs, suggesting reduced thermal stability of the depolymerized lignin products. Table 6-2 lists the thermal degradation peak temperatures of DKL products obtained from the HNO3 treatment of SKL and HKL at KL/HNO3 ratio of 1/4 and 1/3 with 35% and 15% acid concentrations. DKL products from the tests at KL/HNO3 ratio of 1/4 have lower decomposition temperatures than those from the treatments at KL/HNO3 ratio of 1/3. For example, the DKL from SKL-1/4-35% has a decomposition peak temperature at 138 °C, much lower than that of SKL-1/3-35% (156 °C).

As previously reported, lignin molecular structure was composed of mostly aromatic rings with various branching, which would degrade at temperatures between 100 to 800 °C (Yang et al., 2007; Jiang et al., 2018). This reduction in decomposition temperatures of de-polymerized lignin products may attribute their lower Mw, compared with the original KLs. Generally, molecules of a lower Mw would lead to a lower decomposition temperature and higher volatility.
Figure 6-7 TGA thermograms (A) and DTG curves (B) for SKL and the DKL products from the SKL-1/4-35% and SKL-1/4-15 % treatments.
Figure 6-8: TGA thermograms (A) and DTG curves (B) for HKL and the DKL products from the SKL-1/4-35% and SKL-1/4-15% treatments.
Table 6-2 Thermal degradation peak temperatures of DKL products obtained from the HNO$_3$ treatment of SKL and HKL at KL/HNO$_3$ ratio of 1/4 and 1/3 with 35% and 15% acid concentrations

<table>
<thead>
<tr>
<th>Sample #</th>
<th>Degradation peak temp. (°C)</th>
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</thead>
<tbody>
<tr>
<td>SKL</td>
<td>369</td>
</tr>
<tr>
<td>SKL-1/3-15%</td>
<td>251</td>
</tr>
<tr>
<td>SKL-1/3-35%</td>
<td>156</td>
</tr>
<tr>
<td>SKL-1/4-15%</td>
<td>161</td>
</tr>
<tr>
<td>SKL-1/4-35%</td>
<td>138</td>
</tr>
<tr>
<td>HKL</td>
<td>337</td>
</tr>
<tr>
<td>HKL-1/3-15%</td>
<td>251</td>
</tr>
<tr>
<td>HKL-1/3-35%</td>
<td>156</td>
</tr>
<tr>
<td>HKL-1/4-15%</td>
<td>158</td>
</tr>
<tr>
<td>HKL-1/4-35%</td>
<td>139</td>
</tr>
</tbody>
</table>

6.4.5 Phenolic Hydroxyl and Carboxyl Group Determination by (Potentiometric Titration)

Potentiometric titration can be an effective and fast method for measurement of the contents of phenolic hydroxyl and carboxyl groups in lignin and its degraded products. Potentiometric titration was done using excess amount of NaOH to neutralize the phenolic and carboxyl acid groups, followed by back titration with 0.1N HCl (Serrano et al., 2018). The results are illustrated in Figs. 8 and 9, where the contents of carboxylic and phenolic hydroxyl groups of the DKL products obtained from the HNO$_3$ treatment of SKL and HKL at KL/HNO$_3$ ratio of 1/3 (Fig. 6-9) and 1/4 (Fig. 6-10) with various HNO$_3$ concentrations. As shown in both Figures, the HNO$_3$ treatment of SKL or HKL at KL/HNO$_3$ ratio of 1/3 or 1/4 produced DKL products with significantly higher content of carboxyl group. For example, the carboxylic content of both SKL and HKL (1 mmol/g) was interested to above 5 mmol/g for the DKL products obtained at KL/HNO$_3$ ratio of 1/3 or 1/4. Interestingly, the DKL products from SKL contain a higher content of phenolic groups. In contrast, the DKL products derived from HKL contain a reduced content of phenolic groups (e.g., the content of phenolic groups decreases from 2.526 mmol/g in the original HKL to 1.156 mmol/g in the DKL obtained with 35% HNO$_3$.
treatment of HKL at KL/HNO₃ ratio of 1/3 (Fig. 6-9), likely due to the oxidative ring opening reactions (Grushnikov et al., 1970).

**Figure 6-9** Contents of carboxylic and phenolic hydroxyl groups of the DKL products obtained from the HNO₃ treatment of SKL (A) and HKL (B) at KL/HNO₃ ratio of 1/3 with various HNO₃ concentrations.
Contents of carboxylic and phenolic hydroxyl groups of the DKL products obtained from the HNO$_3$ treatment of SKL (A) and HKL (B) at KL/HNO$_3$ ratio of 1/4 with various HNO$_3$ concentrations.

The above results suggest that the treatment of lignin with nitric acid leads to substantial increase of carboxylic group for both SKL and HKL lignins, which could be attributed to extensive oxidation especially at high concentration of HNO$_3$ (35%) and a long treatment time (84 h). These findings are consistent with previous studies (Ludwig et al., 1971; Chudakov et al., 1968). Under severe oxidation reaction conditions, lignin is degraded into lower molecular weight oligomers, fragments such as oxalic and acetic acids as well as CO$_2$. Furthermore, treatments with a higher KL/HNO$_3$ ratio produced depolymerized lignins with a high carboxylic group and lower molecular weight. The formation of carboxyl groups by oxidation of lignin with HNO$_3$ was likely attributed to the oxidation of quinones (the intermediates) that could lead to rupture of the ring (Grushnikov et al., 1970). Recently, Khabarov et al. (2016) reported a series of nitration experiments on sulfate lignin dissolved in an aqueous dioxane medium and concentrated nitric acid. They achieved nitrated lignin with a high content of nitro groups. Under severe oxidation conditions, the aromatic ring can be oxidized and opened by demethylation step followed by...
by oxidation to quinoid structures and muconic acid derivatives as illustrated in Scheme 2 (see Fig. 6-11).

![Scheme 2](image.png)

**Figure 6-11** Scheme 2. Ring opening mechanism in HNO₃ oxidation of lignin (Khabarov et al., 2016).

Nitrolignin contains considerable number of hydroxyl group (Ludwig et al., 1971), which might attribute to the cleavage β-aryl ether linkage and demethoxylation of the lignin during the treatment. These would likely improve the contents of aliphatic and phenolic hydroxyl groups. The increased phenolic hydroxyl group in the DKL products was confirmed with the depolymerized products from SKL (Fig. 6-9). In contrast, HNO₃ oxidation of HKL lignin reduced the phenolic hydroxyl group content in the DKL products (Figs. 6-9 and 6-10).

### 6.4.6 Py-GC/MS analysis

Table 6-3 summarizes the Py-GC/MS analysis results for the depolymerized kraft lignin products from HKL-1/4-35% or SKL-1/4-35%. This method provides fast verification of the structure of DKL products. It should be noted that no significant difference was observed between the SKL and HKL-derived de-polymerized products. As shown in Table 3, a great portion of the volatile fragments of the depolymerized lignin are aromatic substances of guaiacyl type. Carboxyl acids, phenolic functional groups are the main volatile compounds identified by Py-GC/MS. Furthermore, a considerable amount of aliphatic hydroxyl groups such as methacrylic anhydride were also detected in the DKL products, indicating aromatic ring rupture caused by extensive oxidation (Grushnikov et al., 1970). These functional groups are likely formed via the cleavage of β-aryl etheric bonds and demethoxylation of lignin (Zhao et al., 2014).
Moreover, nitration compounds such as 4-Nitroguaiacol, Phenol, 2,4-dinitro-6-methoxy and Benzene, 1-ethoxy-4-nitro were detected, suggesting that oxidation and nitration were simultaneously occurred during HNO₃ oxidation of lignin at room temperature.

Table 6-3. Py-GC/MS analysis results for the depolymerized kraft lignin products from HKL-1/4-35% or SKL-1/4-35% (Note: small peaks with an area less than 2 % of the total area were not included).

<table>
<thead>
<tr>
<th>RT (min)</th>
<th>Library/ID</th>
<th>Mₖₑ</th>
</tr>
</thead>
<tbody>
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<td>3.69</td>
<td>Furfural</td>
<td>96</td>
</tr>
<tr>
<td>8.39</td>
<td>Phenol, 2-methoxy-</td>
<td>124</td>
</tr>
<tr>
<td>14.99</td>
<td>Phenol, 2,6-dimethoxy-</td>
<td>154</td>
</tr>
<tr>
<td>15.93</td>
<td>Vanillin</td>
<td>152</td>
</tr>
<tr>
<td>16.31</td>
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<td>17.86</td>
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<td>17.93</td>
<td>4-Nitroguaiacol</td>
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<tr>
<td>18.21</td>
<td>3-Hydroxy-4-methoxybenzoic acid</td>
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<td>19.06</td>
<td>Metharbital</td>
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<td>Phenol, 2,4-dinitro-6-methoxy-</td>
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<td>Benzoic acid, 4-hydroxy-3,5-dimethoxy</td>
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<tr>
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<td>Aspidinol</td>
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<tr>
<td>26.22</td>
<td>1-Acetyl-2-amino-3-cyano-7-isopropyl-4-methylazulene</td>
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6.5 Conclusions

This work demonstrated a novel cost-effective and efficient process for kraft lignin depolymerization with concentrated HNO₃ at room temperature. This simple oxidative lignin de-polymerization provides simultaneous oxidation and nitration of kraft lignin to form DKL products with more than 90% yield and a relatively low molecular weight about 1300 Da for both SKL and HKL substrates at KL/HNO₃ ratio of (1/4) and HNO₃ concentration of 35%. Functionalized aromatic monomers, mainly with carboxylic acids and nitro groups were obtained. The obtained depolymerized lignin products were characterized by GPC-UV, FTIR, potentiometric titration, TGA/FTIR, Py-GC/MS and elemental analysis. The products show high solubility in water at low pH and low decomposition temperatures than the original kraft lignins. The novelties of this approach
may be summarized here: no heat, catalyst and product purification are needed, as well as that this approach can be readily scaled-up to an industrial-scale process.

6.6 References


Kee, M. L., 1968 The degradation of lignin with nitrous acid, thesis the degree of Doctor of Philosophy Department of Chemistry, MeGill University, Montreal, Canada, pp. 3-19.


Chapter 7

Conclusions and recommendations for further work

7.1 Conclusions

In this thesis, different lignin depolymerization techniques were verified and successfully proved. The results of kraft black liquor, kraft lignins (softwood and hardwood), and hydrolysis lignin represent an important step towards developing a cost-effective approach for valorization of lignin. The depolymerized products exhibited low molecular weight with high solubility in common organic solvents which indicates high reactivity than lignin control. Therefore, the products can be perfect candidate for many applications. A proprietary process has also been developed for efficient and cost effective depolymerization of HL under recoverable chemicals.

The summary of the detailed conclusions could be drawn from this research as follows:

1. In first part of this work, the effects of reaction temperature on the hydrolytic treatment of kraft black liquor (KBL) under catalytic (NaOH) and non-catalytic conditions were studied with both original KBL (lignin substrate concentration of 13 wt%) and diluted KBL (lignin substrate concentration of 9 wt.%). The DKL products were precipitated from treated black liquor by lowering the pH to 2 using sulphuric acid. The obtained DKL products were characterized by GPC-UV, FTIR, $^{31}$P NMR and elemental analysis. The research demonstrated effective depolymerization of kraft lignin in KBL at 250-300 °C with NaOH as a catalyst at a NaOH/lignin ratio of about 0.3 (w/w) using the diluted KBL. Particularly low molecular weight lignins were produced by treating kraft black liquor under the above conditions but in the presence of a capping agent (phenol) or a co-solvent (methanol). In the latter cases, the depolymerized lignin (DKL) products obtained exhibited an Mw of around 1000-2000 Da at a yield of about 30-45 % depending on the operating conditions. Compared with lignin depolymerization work reported in the literature, where technical lignin was used, direct treatment of black
liquor has many advantages as it would lead to a significant reduction in capital and operating costs associated with separation of lignin from black liquor.

2. In this work, we developed a novel, cost-effective approach to produce depolymerized hydrolysis lignin (DHL) using recoverable white liquor (WL) from the kraft recovery cycle. The weight-average molecular weight (Mw) of the lignin was significantly reduced from non-measurable levels to 2600 Dalton at 190 °C for 1h at a WL:HL ratio of 2:1 (w/w). Moreover, a significant increase in non-condensed phenolic hydroxyl and carboxylic acid group contents was observed with decreasing Mw. We found that effective hydrolysis lignin depolymerization can be achieved at WL/HL ratio ≥ 1:1 - below this ratio, minimal lignin depolymerization was observed. The approach developed could be significantly more cost-effective if integrated into kraft pulp mill operations where fresh WL can be utilized with the residual WL recovered using the existing chemical recovery system. Process scale-up was demonstrated using a 20-L circulating reactor, in which case, the Mw of the DHL produced after treatment at 170 °C for 2h was 2400 Dalton.

3. Lignin depolymerization and functionalization can be achieved by a simple environmentally friendly one pot approach. This investigation shed light on lignin oxidation and depolymerization by comprehensive oxidation. Highly concentrated hydrogen peroxide has been proved a very affective route to produce low molecular weight depolymerized lignin at room temperature.

The obtained depolymerized products were characterized by GPC-UV, FTIR, 31P NMR, TGA, Py-GC/MS and elemental analysis. The results showed effective depolymerization of SW and HW lignins at ambient temperature, and the products exhibited Mw around 1400 Da at KL/H2O2 ratio 1:1 with high carboxylic group content. Moreover, the products showed lower decomposition temperatures than both original untreated substrates. Py-GC/Ms results disclosed highly oxygenated fragments with functional groups such as carboxylic acids, esters, ketones, and aldehydes. The novelty of this concept is that no heat, no catalyst, and no purification or processing after the treatment would be needed.
4. We have found that concentrated nitric acid especially more than 30% is a powerful reagent on kraft lignin depolymerization at room temperature. This simple strategy provides a simultaneous oxidation and nitration on kraft lignin with relatively low molecular weight about 1300 Da for both SW and HW substrates at KL/HNO₃ ratio of (1/4) and HNO₃ concentration of 35%. Functionalized aromatic monomers, mainly with carboxylic acids and nitro groups mainly are obtained with more than 90% yield. The obtained depolymerized products were characterized by GPC-UV, FTIR, potentiometric titration, TGA, Py-GC/MS and elemental analysis. The products show high solubility in water at low pH and low decomposition temperatures than the original kraft lignin for both substrates, which means high potential for various applications. The novelty of this strategy is that no heat, catalyst, and purification or processing after the treatment would be needed. Furthermore, the approach can be scaled-up potentially to an industrial level.

7.2 Recommendations for further work

1- Further investigate the effect of mixing hydrodynamics on lignin depolymerization.

2- Perform direct depolymerization of the black liquor with white liquor at temperatures above 200 °C in a pilot scale reactor.

3- Conduct feasibility study for the hydrolysis and oxidation approaches for producing valuable chemicals and materials.

4- Further investigate the gas emissions during the treatment of the oxidation approaches and reactor design scale up.

5- Curry out more investigations on DHL as a flocculant or other applications.
Curriculum Vitae

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