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Investigations of Thermal Treatment of Softwood Kraft Lignin Under Fractional and Ablative Pyrolytic Conditions

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INVESTIGATIONS OF THERMAL TREATMENT OF SOFTWOOD KRAFT LIGNIN UNDER FRACTIONAL AND ABLATIVE PYROLYTIC CONDITIONS

A Thesis

Submitted to the Graduate Faculty of the Louisiana State University and Agricultural and Mechanical College in partial fulfillment of the requirements for the degree of Master of Science in Biological & Agricultural Engineering in

The Department of Biological & Agricultural Engineering

by

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B. Sc., Obafemi Awolowo University, Ile-Ife, Nigeria, 2014
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To my mom and dad
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ABSTRACT

Lignin is second to cellulose in abundance among polymers in nature. Research studies on the development of new products and material combinations in which lignin degradation/conversion products are involved are still in their infancy, because fundamental knowledge about its structure, reactivity, and material and polymer behavior, is still lacking.

The objective of this research study was to investigate the complex thermal deconstruction and mechanistic behavior of a type of technical lignin, known as Kraft lignin, under depolymerization and to develop operating conditions for parameters influencing resulting product yields and operation of pyrolysis reactors.

Softwood Kraft lignin (s-KL) and methanol-fractionated (ex-KL) samples were thermally depolymerized via fractional (stepwise) pyrolysis at temperatures from 175 °C to 700 °C. An isothermal STDS (system for thermal diagnostic studies) reactor with a modified reaction chamber was used to obtain the distribution and the yields of pyrolysis products in five groups - the major tar products; guaiacols, vanillins, phenols, syringols, and sulfur-containing compounds. Sulfur-containing compounds, as intrinsic contaminants (both adsorbed and covalently bound to KL matrices), were found to strongly inhibit the formation of the major pyrolysis products. The yields of the major products were inversely correlated to the release of sulfur-containing compounds, i.e. the lesser the content of sulfur in the KL matrix, the higher the yields of major products. The initial pretreatment of ex-KL by Soxhlet extraction in methanol caused the high yields and early release of tar components at lower temperatures from ex-KL pyrolysis. No sulfur-containing bio-oil liquid products were detected from pyrolysis of both lignins indicating that sulfur-containing products were in the gas phase. A mechanistic explanation for the absence of sulfur-containing bio-oil
products, and the inhibitory effect of sulfur-containing compounds, as well as the relatively high char content in depolymerization of both lignin substrates are presented.

Analytical techniques were subsequently used to compare the distribution of primary pyrolysis products from the fast pyrolysis of softwood Kraft lignin (s-KL) in the STDS and ablative IR CO$_2$ laser reactors. Lesser transfer times and higher abundance of products were noticed from the IR CO$_2$ laser ablative pyrolysis.
CHAPTER 1.
INTRODUCTION

1.1. INTRODUCTION.

Availability of energy is an essential requirement for daily living. From home heating and electricity to fuels for our automobiles and transportation, a steady and sustainable source of energy is critical in any modern society. Energy can be classified based on provenance into renewables and non-renewables. The major renewable sources of energy include solar, wind, water (hydro), and biomass. Non-renewable energy comes primarily from coal, nuclear, petroleum, and natural gas. In 2015, the world’s total energy demand was ~ 542 quadrillion British thermal units (Btu) (EIA 2017). Of this amount, renewable energy sources provide only ~ 75 quadrillion Btu or 13 percent, whereas oil, coal, and natural gas supply almost 82 percent or ~ 444 quadrillion Btu (EIA 2017). Coal, petroleum, and natural gases are often collectively referred to as fossil fuels. Although fossil fuels currently serve most of the world’s energy needs (BP 2017), the use of fossil fuels as an energy source comes at the risk of various consequences (Johansson 2013, Krane 2017, Jewell, McCollum et al. 2018). Burning fossil fuels produces carbon dioxide and other deleterious gases such as carbon monoxide, nitrogen oxides and sulphur oxides, as well as ash (Hayhurst and Lawrence 1992, Heede 2014, Graven 2015, Ioan and Amelitta 2015, Heede and Oreskes 2016, Shan, Guan et al. 2018).

In fact, combustion of these fossil fuels is the greatest source of the greenhouse gases responsible for global warming (Hansen, Sato et al. 2000, Crutzen, Mosier et al. 2007). Global warming is particularly noticed in warmer climates in the Artic and Antarctica Polar Regions, thus causing ice melting (Vaughan and Doake 1996, Oppenheimer 1998), increase in sea levels, and ultimately altering the composition of neighboring sea water (Hughes 2000, Karl and Trenberth 2003). Rising sea levels, in turn, hamper many beneficial human activities including fishing,
settlement, and land cultivation (Schneider, Easterling et al. 2000, Mimura 2013, Obia, Archibong et al. 2015, Islam and Wong 2017). More so, prices of crude oil and natural gas have been unstable due to several factors including increasing demands from a burgeoning world population, uneven global distribution of fossil fuel reserves, and the resulting economic and political tensions among different nations on the planet (Stéphane Dées 2008, van Beers 2013, Rentschler 2016, Jonas and Glen 2018). Crude oil and coal mining operations (as fossil fuel sources) have distorted ecosystems and the natural environment through oil spills and oil toxicity diseases (Teal and Howarth 1984, Mei and Yin 2009, Pennings, McCall et al. 2014, Langangen, Olsen et al. 2017).

Energy from nuclear plants is the second largest source next to fossil fuels (Pioro and Duffey 2015, Zou, Zhao et al. 2016). Some concerns stemming from use of nuclear energy are safety issues due to storage and handling of radioactive materials and the proper disposal of nuclear wastes (Alice Napoleon 2008, Christodouleas, Forrest et al. 2011, Wheatley, Sovacool et al. 2016). Nuclear wastes take thousands of years to decay and only few countries have the wherewithal to appropriately reprocess the debris. Typical renewable energy sources include, but are not limited to, wood biomass, alternative biomass fuels (such as ethanol and biodiesel), waste energy, hydropower, geothermal, wind and solar. Hydroelectric energy requires large water bodies, high starting costs, and causes severe environmental havoc to aquatic life (Pimentel, Herz et al. 2002, Kaunda, Kimambo et al. 2012). In 2011, renewable energy production in the United States surpassed energy production from nuclear power for the first time in a decade, by contributing over 2.245 quadrillion BTU of energy, representing 11.7 percent of total US energy versus 2.125 quadrillion BTU for nuclear power (EIA 2016).

Geothermal power plant installations engender land instability, have the potential to lead to man-made natural disasters such as earthquakes (Frick, Regenspurg et al. 2011), and require
huge starting costs to power heating and cooling systems (Orbis 2017). Solar and wind energy sources, though abundant, are intermittent and susceptible to variations in time of year, weather conditions, and location (Azarpour, Suhaimi et al. 2013). While their cost is decreasing, finding reliable methods for their storage still pose significant challenges (Lakatos, Hevessy et al. 2011). Despite the afore-mentioned drawbacks of these energy sources, they are still chiefly being used to power homes, businesses and economies around the world. This is due to the absence of viable renewable energy sources that could compete with them on costs and environmental safety. Thus, there is the need to produce energy from sources that are relatively available, cheap, sustainable, and safe for the environment.

The need to harness lignocellulosic biomass to efficiently produce cost-competitive renewable fuels has become critical over the past decade due to rising global energy demands and the need to bolster energy security in various economies (Hoffert, Caldeira et al. 2002). The US Department of Energy’s Office of Energy Efficiency and Renewable Energy (EERE) has set a year 2022-target to develop and integrate biomass-derived technologies that are cost-competitive with fossil fuels and can co-produce renewable hydrocarbon fuels (Reed 2012, Energy 2016, EPA 2017). To meet this goal, over 16 billion gallons of fuels would be needed from biofuel production facilities (EPA 2017). If achieved, this target would help expedite efforts in ensuring a more secure and sustainable energy future by reducing U.S.’s dependence on petroleum-based fuels, creating new jobs, and helping to improve general quality of life (EERE 2016). In line with this critical need, low-value biomasses must be harnessed to create industrial fuels and chemicals as well as value-added products at high rates of efficiency with high quantity yields, low process waste, and at relatively low costs.
Developing novel energy solutions from lignocellulosic biomass by converting biomass into clean fuels, energy, and chemicals will play a significant role and be critical to success in achieving this goal (Ragauskas, Williams et al. 2006, Anwar, Gulfraz et al. 2014, Balan 2014, Kang, Appels et al. 2014, Sorek, Yeats et al. 2014, Ghosh, Dasgupta et al. 2015, Luque and Triantafyllidis 2016, Alonso, Hakim et al. 2017, Ge, Dababneh et al. 2017). To this end, several efforts are underway to develop valuable products and material combinations in which cellulose, hemicelluloses, lignin or their degradation/conversion products serve as quality feedstock (Jung, Kim et al. 2015, Kim and Han 2016). Pyrolysis is believed to be one of the most economical ways to valorize biomass for liquid fuels (Maschio, Koufopanos et al. 1992, Czernik and Bridgwater 2004, Vasalos, Lappas et al. 2016). Clean fuel production methods that utilize the thermochemical conversion of biomass has an edge, in that they can potentially position biomass from lignin as a source of liquid fuel starting with most organic materials (Zhang, Xu et al. 2010, Bhaskar and Pandey 2015). Energy from biomass was the largest source of total renewable energy in the US, and the third-largest renewable source of electrical power in the US, after hydropower and wind. Of 10.7 GW of generated renewable energy capacity, 7.0 GW was sourced from forest product industry and agricultural industry residues, and 3.7 GW came from municipal solid waste (Bain, Denholm et al. 2012).

Biomass is waste material obtained from living organisms such as plants and grown trees to produce heat or generate electricity. These plants absorb carbon dioxide during their growth stages in similar quantities to those which are later released when they are burnt or converted, thus making them more environmentally friendly compared to fossil fuels. With biomass, there is a relatively short carbon recycle period of grown biomass (several years or decades) as opposed to the millions of years it took to turn carbon into fossil fuels. Energy from biomass can be used for
any of the three common energy needs: transportation, electricity and heating/cooling. The efficiency of biomass sources for each need increases from transportation to cooling. While biomass pellets for heating can harness up to 90% of total energy produced, bio-electricity plants have efficiencies comparable to coal plants, and biofuels from crops and algae have even lesser efficiencies.

Lignocellulosic biomass, a primary source of bio-oils, is a renewable energy resource potentially useful for producing fuels, chemicals, and converted into value-added products across several industries (Anex, Aden et al. 2010). Lignin is the most abundant natural aromatic polymer on earth. It is formed in the cell wall after deposition of the polysaccharides; cellulose and hemicelluloses (Xu, Khachatryan et al. 2017). It is found in all vascular plants and makes up to 15 – 40% of dry matter from woody plants. Lignin supports the cell walls, modulates fluid flow and guides against the enzymatic degradation of other plant parts (Datta, Kelkar et al. 2017). As a feedstock, it is generally collected from pulp and paper mills as a waste material in form of black liquor, a complex natural polymer primarily resulting from oxidative coupling of three phenyl propane monomers (a benzene ring with a tail of three carbons) differing in their degree of methoxylation: 4-coumaryl, coniferyl, and synapyl alcohols (Amthor 2003, Moon†, Shin et al. 2011, Abdelaziz, Brink et al. 2016) (Figure 1.1). It is generally believed that the biosynthesis of lignin occurs via the polymerization of these three main phenylpropane units also called monolignols (Ralph 1999). Structural blocks in lignin are bonded by either ether linkages (C-O-C) or carbon-carbon bonds (C-C), with the major inter-unit linkage is of the β-O-4 kind (Xu Chunbao 2017).

Lignin has become a main source of aromatic chemicals and biofuels following the conversion successes achieved in ethanol bio refineries that utilize the cellulose and hemicellulose
As the nature’s most abundant aromatic hydrocarbon, lignin is considered as a promising renewable alternative source to produce high-value products including materials, fuels and aromatic chemicals currently produced by the petroleum industry (Abdelaziz, Brink et al. 2016, Wu, Dutta et al. 2017). However, lignin-carbohydrate networks are formed in the cell wall via chemical linkages such as ethers and esters between lignin and the polysaccharide constituents, thus making the direct separation of individual polymers difficult (Mikame and Funaoka 2006, Aminzadeh, Zhang et al. 2017). The structure of lignin in wood has been discussed in several review articles (Freudenberg 1932, Brown, Falkehag et al. 1967, Rencoret, Gutiérrez et al. 2011, Santos, Capanema et al. 2012, Hu, Pan et al. 2014) and based on this knowledge, numerous studies with lignin model compounds have been performed to gain an understanding of the chemistry behind its structural composition (Phillips 1934, McCarthy and Islam 1999, Huang, Liu et al. 2013, Crestini, Lange et al. 2017).

![Figure 1.1. Main monolignols responsible for lignin biosynthesis; lignin structure (Rauber, Dier Tobias et al. 2018).](image)

The precise structure of lignin is still unknown. However, advances in spectroscopy and studies in investigating deconstruction products have shed more light onto the structural properties
of lignin. Although, the primary linkage in softwood lignin has been found to be the β-O-4 linkage (~ 45-50%), other subunits of lignin that have been discovered, including dibenzodioxocins (Karhunen, Mikkola et al. 1999), isochroman (Ralph 1999), and spiro-dienone (Zhang and Gellerstedt 2001), still make up less than 10% of the entire lignin structure (Chakar and Ragauskas 2004).

The industrial chemical alteration of lignin is typically done using the kraft pulping process. The goal of chemical pulping is to isolate cellulosic fibers from one another by removing enough lignin, to produce pulp to be used in making paper and similar materials. Thus, a major by-product obtained in large quantities during the chemical pulping of wood is the industrial (or technical) lignin. In a standard kraft cooking process, wood is treated with white liquor – an aqueous solution of sodium hydroxide (NaOH) and sodium sulfide (Na₂S) – in a digester (Zhu, Westman et al. 2014, Pineda and Lee 2016). The liquor chemically dissolves the lignin that binds the cellulose fibers together to form a liquid stream known as weak black liquor. The black liquor is washed away from the pulp and is sent to the kraft recovery system, where the pulping chemicals are recycled for future use and the dissolved organic compounds are used as fuel to provide steam and energy for the process. The resulting lignin is known as Kraft lignin.

During this delignification process, structural changes such as cleavage of α-O-4 and β-O-4 linkages occur thus resulting in lower molecular weight lignin, different from the starting lignin (Koda, Koda et al. 2005). The recovery of lignin introduces sulfur (in the form of sulfuric acid) into the industrial recovery process (Gosselink, Abächerli et al. 2004, Košiková and Gregorová 2005, Azadi, Inderwildi et al. 2013, Gellerstedt 2015). The usual odor in a kraft mill is as a result of the emission of unwanted impurities in form of high content of residual sodium salts (Tan, MacFarlane et al. 2009) and reduced sulfur compounds, mostly methane thiol (CH₄S), hydrogen
sulfide (H₂S), dimethyl sulfide [(CH₃)₂S], and dimethyl disulfide [(CH₃)₂S₂], which are present in the lignin derived from the Kraft process. Softwood Kraft Lignin (s-KL), being a type of technical lignin, is a promising feedstock with potential applications in a variety of large-scale industrial operations emphasizing green chemical and sustainable material production (Brodin, Sjöholm et al. 2009). Its intricate and evasive structure however significantly hampers this positive outlook. More so, based on the Kraft pulping process from which s-KL is produced, this poorly understood structure stems from the intrinsic heterogeneity of natural Kraft lignin and the convoluted reaction mechanisms of the applied delignification process (Yang and Liu 2005, Pineda and Lee 2016).

Thus, product yields significantly differ from the native lignin present in the starting reactants. Despite the excessive abundance of s-KL and many research efforts devoted to understanding its detailed, contemporary structure, characteristics and valorization process and structural elucidation, little is known as regarding the detailed structure of softwood Kraft lignin (Crestini, Lange et al. 2017). Technical lignins differ from one another based on the species and geographical source, extraction method used, and structural aromatic components (Liitiä, Maunu et al. 2003, Constant, Wienk et al. 2016). S-KL, being a technical lignin, therefore needs to be studied given this heterogeneity among this biomass sub-class. Due to its aromatic structure, Kraft lignin can be an attractive source of aromatic compounds and serve as an enduring starting material in oil & gas industry applications. A detailed structural investigation and understanding of S-KL chemistry is, thus, of critical importance if value-added products are to be produced on a sustainable and cost-friendly scale.

The pulp and paper industry produces an estimated 70 million tons of lignin from pulping processes annually. Of this amount, less than 2 percent (1.4 million tons) is recovered and used as
a low-value resource as dispersing or binding agents and the rest is used to generate low-value internal energy in mills (Orbis 2017). Thus, this nature’s most abundant resource is grossly underutilized. Given the development and interest in operating lignocellulosic bio refineries for production of biofuels and useful chemicals, effective solutions must be made available to convert this waste into energy and specialty chemicals. In fact, such solutions must be achieved to meet the target set by the U.S. Energy Security and Independence Act of 2007 mandating the production of 79 billion liters of second generation biofuels annually by 2022 (EISA 2007). To advance the utilization of lignin in new applications or products, better knowledge is required on the sourcing, the separation process, and their impact on the structural and chemical characteristics of the obtained materials. Since total lignin availability in the biosphere well exceeds 300 billion tons and increases by around 20 billion tons each year, it remains a critical challenge to commercially apply Kraft lignin into the production of materials for industrial fuel, energy, and chemicals (Hu, Zhang et al. 2018).

Over 55 million metric tons of Softwood kraft lignin (S-KL) is produced worldwide annually (Gellerstedt, Tomani et al. 2012). Whereas hardwood lignins yield guaiacyl- and syringyl-type compounds as major products, softwood lignins mostly contain guaiacyl-type products (Lin, Sui et al. 2015). However, the only structure for softwood kraft lignin that we have is that of Marton, suggested in 1971 (Erdtman 1972). It is based on the effects of kraft pulping methods and wet chemical characterization techniques on lignin model compounds.

Two of such lignin-to-energy approaches are: direct combustion and pyrolysis. Of these two, pyrolysis has attracted a lot of scholarship (Balat 2008, Liu, Wang et al. 2014, Kan, Strezov et al. 2016, Dhyani and Bhaskar 2017, Wang, Dai et al. 2017). Pyrolysis is the thermochemical conversion of organic materials at elevated temperatures in an oxygen-free environment to produce
solid (char), liquid (tar), and gas products (Chen, Duan et al. 2008). It is the most promising method used to obtain desired gas, liquid, and solid (char) products from biomass in an oxygen-free atmosphere. Pyrolysis converts biomass into condensed lower molecular weight bio-oil, vapors as gaseous products (Hanif, Capareda et al. 2016), and often heat (Figure 2); and thus provides potential for transforming low-value materials into resourceful bio-fuels and valuable industrial chemicals. Total yields from pyrolysis take into account the decomposition of the raw material (primary reaction) and the reactions undergone by primary volatiles (secondary or side reactions). Some pyrolysis methods that have been used in the past include: fast, catalytic fast, intermediate, slow, and vacuum (Westerhof, Brilman et al. 2012, Czajczyńska, Anguilano et al. 2017). Different types of reactors that have been developed include fixed bed, fluidized bed, tubular and pyroformed reactors. The heating rates, temperature and residence times of the volatiles in the reactor are the critical parameters for secondary reactions to occur (Ranzi, Debiagi et al. 2017, Thompson, Ciesielski et al. 2017). The sufficiency of a particular pyrolysis method using a named reactor depends on the choice of input biomass and the applied process conditions. More research studies have focused on investigating the quantity, quality and experimental conditions for product yields and selectivity of lignin-sourced biomass pyrolysis (Leng, Wang et al. 2013, Xianjun, Zongkang et al. 2015, Hanif, Capareda et al. 2016).

Fast pyrolysis, a process involving the rapid thermal decomposition of biomass into liquid fuels and chemicals in the absence of oxygen, has been used to investigate the chemical structure and product distribution of several lignin-derived biomass. Fast pyrolysis however has demerits including coking, waste of high-molecular weight products, low-quality bio oils (containing a lot of water), high quantity of char, and the complicated process of post-reaction separation of the reaction products (Serio, Chen et al. 2000, Dayana, Abnisa et al. 2016).
In fractional pyrolysis, the same biomass sample is continuously heated at increasing temperature intervals in a reactor bed, until no new products are formed. Product yields are affected by the bed temperature, residence times of the volatiles, and the extent of secondary reactions undergone by the volatile products (known as the secondary char effect).

Most literature on the thermal deconstruction of kraft lignin focus on its conventional pyrolysis while studies of stepwise or fractional pyrolysis of kraft lignin remain scarce. Several studies involving GC coupled with micropyrolyzers (Choi and Meier 2013) and TGA coupled with GC (Zhang, Resende et al. 2012) have been done. In fractional pyrolysis, a single biomass sample is pyrolyzed at successive progressive temperatures for the same or different time to aid the systematic devolatilization of thermal degradation products whereas in conventional pyrolysis, a biomass sample is ramp-heated and isothermally heated at specific pyrolysis temperature, whereby each pyrolysis temperature run starts from a fresh biomass material alongside products formed during the ramp heating and isothermal steps with the primary goal of maximizing product yield (de Wild, Uil et al. 2009, Bennadji, Khachatryan et al. 2018). Bio-oil obtained from conventional fast pyrolysis is typically acidic, contains high oxygenate concentrations, and costs more to treat.
before commercial applications due to its composition of products with varying functional groups including phenols, esters, dehydrated carbohydrates, alcohols, aldehydes, furans, and acids (Yaman 2004, Fatih Demirbas 2009). However, since fractional pyrolysis operates under relatively mild conditions to fractionate products during biomass depolymerization, its resulting product mix can be more stable and less susceptible to undesired secondary reactions, thus providing a cost-effective approach to produce high-quality oil and valuable chemicals (Westerhof, Brilman et al. 2011, Westerhof, Brilman et al. 2012, Lyu, Wu et al. 2015).

An equally promising approach to reducing impacts of secondary reactions while increasing bio-oil yields is the ablative pyrolysis method. Using lasers as a heat source for exciting substrate molecules during pyrolysis of organic materials has been investigated in recent years (Chen, Duan et al. 2008, Matthias, Stephan et al. 2014). Many studies of energy transfer and deposition, and the resulting chemical reactions are now commonplace. However, the use of irradiated light from lasers in the parametric range of normal "thermal" chemical reactions has not attracted similar attention. One peculiar application where infrared lasers could prove extremely useful is in the pyrolysis of organic polymers such as lignocellulosic biomass where the traditional heating by a hot-walled vessel is inefficient due to side reactions (Caballero, Font et al. 1996), whereas the use of shock-tube techniques is made difficult by low substrate volatility (Prins, Lindén et al. 2009). This technique, called the laser-powered homogeneous pyrolysis (LPHP), allows rate measurements over a wide temperature range in short reaction times to minimize the deleterious effects of secondary reactions (McMillen, Lewis et al. 1982).

Since secondary tar-forming reactions abound in conventional pyrolysis due to the transport-limiting steps in the pyrolysis system (Zhang, Yang et al. 2012) and longer residence times (Peters and Bruch 2003), a more suitable pyrolysis method would provide varying
temperature profile in the pyrolysis reactor with the highest near the cell axis and about room temperature around the cell walls. Due to the sharp temperature drop from the border to the cell center of the pyrolysis reactor, the ablative pyrolysis may have a significant effects on amounts and quality of product yields (Russell 1990, Mantashyan 1998). Thus, laser-induced ablative pyrolysis approach could be used to thermally degrade and convert lignocellulosic biomass into bio oils and other light hydrocarbons with minimal secondary effects at higher yield and selectivity of products. This way, ablative pyrolysis technique can be effectively exploited to generate more high-quality (or upgraded) bio-oil in a "wall-less" reactor. Apart from the relatively low cost of using CO$_2$ lasers, the CO$_2$ laser ablation process offers faster gas absorption rates, photochemical heat transfer, and high wavelength bands (9.4 – 10.6 µmeters) thus making it suitable for Kraft lignin, as compared to UV lasers with lower wavelengths (Inayoshi, Hori et al. 1996, Tolstopyatov 2005).

Laser ablation of aromatic polymers such as Kraft lignin requires more deliberate effort than that typically seen in inorganic samples. This is due, in part, to the thermochemical changes caused by the irradiation of the laser beam on the organic polymer. The initial and limiting step in laser ablation is the conversion of light energy from the laser beam to the internal energy of the target sample. Although different lasers have been used for similar studies, few have been done using IR CO$_2$ lasers. IR CO$_2$ industrial lasers are relatively easier to use, powerful, and commonly used. Apart from these and the relatively low cost of using an IR CO$_2$ laser, its higher radiation wavelength bands (9.4 to 10.6 µm) and faster gas absorption rates make it suitable for S-KL in comparison to a UV laser.

Although various pyrolysis technologies for converting kraft lignin have been introduced, significant gaps in knowledge still exist in regards to a more acceptable structure of softwood kraft
lignin. Particularly, the role of unwanted sulfur-containing compounds and the high percentage of sodium salts from the kraft pulping process (Yang, Yan et al. 2007, Kumar 2009) on the thermal deconstruction of kraft lignin is still relatively unknown. Also, the complexity and heterogeneity of the kraft lignin structure as well as paucity of processing methods involving minimal secondary reactions for kraft lignin pyrolysis have been a major hindrance to gaining significant mechanistic understanding of kraft lignin pyrolysis (Milne, Chum et al. 1992, Gosselink, Abächerli et al. 2004, Crestini, Lange et al. 2017). Given the increasing attraction towards the valorization of the naturally abundant kraft lignin into renewable fuels and chemicals, detailed mechanistic understanding of the chemical subunits of kraft lignin is critical in order to aid in its selective industrial-scale conversion.

1.2. OBJECTIVES.

Given the highly non-uniform and obscure structure of s-KL, the two key objectives of this research project are as follows:

- **Investigate the impact of sulfur-containing compounds on softwood kraft lignin pyrolysis yields:** Due to the heterogeneous and polydisperse nature of s-KL, it is very important to obtain the highest optimizable pyrolysis yields. This research study aims to investigate the impact of unwanted sulfur-based compounds (collected with s-KL during the kraft pulping process) on the yield quantity and quality from the fractional pyrolysis of two KL types. Knowledge of sulfur content levels and resulting product group yields for various s-KL types would help inform suitable s-KL combinations for maximum fuel and chemical production.

- **Investigate the product distribution arising from the primary reactions during s-KL ablative pyrolysis with IR CO$_2$ laser:** Because secondary reactions affect total yield
quantity and bio-oil quality of biomass, the need to understand the distribution of products based on various ablative pyrolysis profiles cannot be overstressed. This study investigates the effect of feedstock chemistry (IR CO$_2$ laser power, s-KL pellet concentration, and carrier gas flow rates) on the ensuing chemical speciation.

The results will provide useful insights for developing pyrolysis models to predict yields of specific and desired chemical products from s-KL.
CHAPTER 2.
SULFUR CONTAMINATIONS INHIBIT DEPOLYMERIZATION OF KRAFT LIGNIN

2.1. INTRODUCTION

The need to harness lignocellulosic biomass to produce cost-competitive renewable fuels has become increasingly critical over the past decade due to rising global energy demands and the need to bolster energy security across nations. Pyrolysis, the rapid thermochemical decomposition process that can be used to convert biomass into liquid fuels, synthesis gas and chemicals in the absence of oxygen, has been used to investigate the chemical structure and product distribution of several lignin-derived biomass. Softwood Kraft Lignin (s-KL), a type of technical lignin, is a promising feedstock with potential applications in a variety of large-scale industrial operations that emphasize green chemical and sustainable material production (Brodin, Sjöholm et al. 2009). Technical lignins differ from one another based on the species and geographical source, extraction method used, and structural aromatic components (Liitiä, Maunu et al. 2003, Constant, Wienk et al. 2016).

Technical or industrial Kraft lignin is a by-product produced in large amounts during the chemical or Kraft pulping of wood (Mansouri and Salvadó 2006). In Kraft pulping, the fractions that are soluble in aqueous alkali represent more than 90% of the lignin in wood and are known as black liquor. During this process, structural changes such as cleavage of α-O-4 and β-O-4 linkages occur, resulting in lower-molecular weight lignin, which is different from the starting lignin (Koda, Koda et al. 2005). The resulting lignin is known as Kraft lignin (KL). The presence of sulfur-based compounds in the lignin derived via the Kraft process is significant due to the use of sulfuric acid as an acidifying agent for black liquor (Vishtal and Kraslawski 2011). While pulp mills use Kraft
lignin mainly as an energy source through various thermal conversion systems, investigative studies are currently being done to convert KL into various bio-based fuels and industrial chemicals such as biopolyols and biophenols (Dessbesell, Yuan et al. 2018). In order to enhance the bio-oil properties of KL, several methods including fast pyrolysis with additives (Ben and Ragauskas 2011), fractional precipitation (Ståhl, Ershova et al. 2015), NMR characterization (Crestini, Lange et al. 2017, Rönnols, Jacobs et al. 2017), among other methods, have been investigated. These processes often produce bio oil yield at efficiency ~ 40% with increased char concentrations (Caballero, Font et al. 1997).

However, not much attention has been paid to the effect of impurities on KL pyrolysis, such as sulfur-based intrinsic compounds (sulfur-containing compounds) present in lignin derived from the Kraft process either as free molecules (free sulfur, sulfides, sulfites, sulfones, sulfates, disulfides, polysulfides, thiols, etc.) adsorbed on KL lattice or covalently bound moieties linked to the KL macromolecule (Svensson 2008, Tomani, Axegård et al. 2011, Ståhl, Ershova et al. 2015, Evdokimov, Kurzin et al. 2018, Han, Sophonrat et al. 2018). The sulfur content in KL however hampers its industrial potential (Evdokimov, Kurzin et al. 2018). We thus present below a literature synopsis of the pyrolysis of KL with various free and/or bound sulfur content to illustrate the effects of sulfur containing contaminants on the depolymerization of KL.

The pyrolysis of softwood KL dates back to the early 1970s (Freudenberg 1932, Erdtman 1972, McCarthy and Islam 1999). Caballero et al. (Caballero, Font et al. 1997) studied the primary reactions from the pyrolysis of powdered Kraft lignin (1.7 % sulfur content) in a Pyroprobe-1000 tubular secondary reactor set-up at 450 °C – 900 °C. Results showed that decomposition of lignin occurs at a wider temperature range than those of cellulose and hemicelluloses, and that lignin products obtained at lower temperatures are those likely to come from side groups of the complex
3D aromatic lignin polymer. Gradients in particle temperatures, volatile-solid reactions, and cracking or char formation were also noticed due to the large-sized KL particles from the effects of sample compression and compacting. However, products obtained by Caballero et al. (Caballero, Font et al. 1997) differ substantially from those reported lately by Brodin et al. (Brodin, Sjöholm et al. 2010). Sudden occurrence of products was noticed throughout the entire 200 °C – 900 °C interval in their study of the step-wise analytical pyrolysis of pure pine/spirce softwood Kraft lignin (2-8 mg), although most products were formed at the 500 °C – 600 °C range and none were detected beyond 700°C. For instance, guaiacol, acetoguaiacone, and 4-ethyl guaiacol were major products observed at 200 °C, but not detected at 300 °C; 4-propylguaiacol, 4-vinyl guaiacol and 4-methyl guaiacol were detected at 400 °C; 4-methyl, 4-ethyl, and 4-vinyl guaiacol at 500 °C; 4-methyl, 4-ethyl guaiacol and guaiacol (again) at 600 °C, while 2-methyl phenol, 4-methyl phenol, and toluene were significant products observed at 700 °C. With pre-oxidized KL, guaiacol was observed at higher temperatures (~600°C), and no syringols were seen at any pyrolysis temperature. The lignin end-groups represented by model compounds such as coniferyl (sinapyl) alcohols and conifer aldehydes were also absent across all temperatures examined. Further analysis showed the presence of CO₂ (from carboxylic groups) and methyl thiol and SO₂ (from putative presence of organically-bound sulfur in Kraft lignins), but only at the higher temperatures (above 600 °C) (Brodin, Sjöholm et al. 2010).

Caballero et al. (Caballero, Font et al. 1996) also studied the volatile yields from KL (1mg, with 1.7 % sulfur content) pyrolysis using a Pyroprobe-1000 modified with a semi-batch flow reactor at 500-900 °C. Results showed 33.99% as the maximum tar yield and aromatic hydrocarbons as the most thermally stable products, followed by unsaturated and short-chained hydrocarbons. Nowakowski et al. (Nowakowski, Bridgwater et al. 2010) compared the results
from fast pyrolysis of different lignin types (sulfur-free and sulfur-containing) from several international studies. The highly-purified ALM (Asian Lignin Manufacturing Ltd.) lignin exhibited a much wider range of decomposition compared to the non-high-purity ETEK lignin (SEKAB E-Technology Corp., Sweden) from TGA and DTA analyses.

The pyrolysis of the sulfur-free lignin in a micro-oven pyrolyzer-GC/MS yielded higher guaiacols, phenols, carbohydrate (cellulose and hemicellulose) degradation products or sugars such as levoglucosan and 2,3-anhydro-D-mannosan, and hydrocarbons compared to the sulfur-containing lignin. Instead, the sulfur-containing lignin yielded higher sugars (~60.0 % in peak area) due to its relatively impure form, while the sulfur-free lignin produced only ~5.2 % of those compounds. In addition, the sulfur-containing lignin produced no syringols, while the sulfur-free lignin yielded ~33.7 % of syringols, thus suggesting that the yield of syringols was influenced by the extent to which sulfur was present in the lignins. Nowakowski et al. (Nowakowski, Bridgwater et al. 2010) found that the excessive cellulose also had similar effects of reducing bio-oil yield while making it hard for the lignin to be processed in the fast pyrolysis reactors. Also, the softwood-derived lignins showed absence of syringols across all temperatures, whereas the pyrolysis beyond 600 °C yielded larger proportion of volatiles (Nowakowski, Bridgwater et al. 2010) as compared to biomass pyrolysis at 500 °C.

Zhang et al. (Zhang, Resende et al. 2012) used pyrolysis GC-MS and TGA/FTIR techniques to study the effects of lignin source on the fast and conventional pyrolysis products of synthetic Kraft lignin low in sulfonates, with properties similar to those of Kraft lignin derived from wood, from 200 °C to 1000 °C. From FTIR data, they inferred that the Kraft lignin does not contain any carbonyl functional groups. Using GC-MS, they found eight major products – in descending order by peak area percentile – dimethyl-disulfide (15.2 %), guaiacol (15 %), 4-
vinylguaiacol (3.3%), phenol (2.8%), 4-methyl guaiacol (2.6%), vanillin (2.4%), acetic acid (2.4%), and 4-methyl phenol (2%) – all composing ~46% of the total peak area. Their TG analyses showed that less than 54% of the sample was lost with char residue and ash remnants, while most weight loss up to 200 °C was due to water with no release of volatiles. The weight loss between 200 °C-500 °C was ~30% with minimal evolution of aromatics with the first major lignin decomposition suggested to occur at a single temperature of 332°C. Furthermore, CO and CO₂ were the major products formed beyond 700°C.

Investigative studies focusing on the effect of co-existing impurities in Kraft lignin such as sulfur-containing species in form of free sulfur, sulfides, sulfites, sulfones, sulfates, disulfides, polysulfides, thiols, etc. on pyrolysis process of KL are scarce or inconclusive (Ludwig and Sarkanen 1971, Erdtman 1972, Ståhl, Ershova et al. 2015, Evdokimov, Kurzin et al. 2018, Han, Sophonrat et al. 2018). The nature of the sulfur groups has been well described in a number of publications (Field, Drummond et al. 1958, Ludwig and Sarkanen 1971, Tomani, Axégård et al. 2011), thus leading to the general belief that sulfur is present in lignin mostly as organically bound sulfur, sulfate ions, elemental sulfur, and adsorbed polysulfide forms (Svensson 2008, Evdokimov, Kurzin et al. 2018). About half the amount of bound sulfur has been shown to be in form of disulfide, R₂S₂ (oxidized mercaptan groups) and the other half was attached to the carbon atom(s) (thiirane structures – sulfur attached to two carbon atoms) (Rydholm 1985, Svensson 2008, Evdokimov, Kurzin et al. 2018). The relative distribution of the sulphur content in the studied softwood lignin was reported as follows (Svensson 2008): about 29% as inorganic sulphur, about 1% as elemental sulphur, and approximately 70% as organically bound sulphur. Additionally, MeSH as well as (Me)₂S are released as by-products of “kraft pulping” in pulp mills and remain

Since knowledge of the effects of temperature on product yields can aid in understanding the nebulous heterogeneous structure of Kraft lignin, this study investigates, for the first time in detail, the fractional (step-wise) pyrolysis of non-treated, softwood Kraft lignin (s-KL) versus treated, extracted by ethanol, Kraft lignin (ex-KL) in temperature range of 175 °C – 700 °C. An isothermal STDS (System for Thermal Diagnostic Studies) reactor, which has been successfully implemented for the pyrolysis processes of a number of organics (Rubey and Grant 1988, Asatryan, Bennadji et al. 2017), biomass components, cellulose and lignin (Kibet, Khachatryan et al. 2012, Bennadji, Khachatryan et al. 2018), was used for the depolymerization experiments of s- and ex-KLs.

This manuscript illustrates the significant effect of sulfur-containing compounds, as contaminants, on the pyrolysis data of the initial s-KL and, particularly, on the yield of bio-oil generation. We assume the sulfur-containing compounds (either adsorbed or covalently bound to the Kraft lignin macromolecule) can participate in secondary reactions in both phases namely on solid surface of the initial KL, as well as in the gas phase, drastically affecting on the yields of bio-oil. A mechanistic explanation of the role of sulfur contaminants on product distribution as well as char formation from s-KL pyrolysis is also presented.

2.2. MATERIALS AND METHODS

2.2.1. Starting materials

The s-KL alkaline lignin (pH = 9.0) was supplied from TCI America (Portland, OR) as a black powder. The particle size of the alkaline lignin used was < 125 µm. The sulfate content as an ignition residue was 23.6%, methoxyl group content – 11.9%, and water – 5.5% (Certificate of Analysis). The s-KL was employed for pyrolysis experiments as received. A fraction derived by
Soxhlet extraction of s-KL by methanol {KL solubility in methanol ~ 6.1g/kg (Melro, Alves et al. 2018)} was used to obtain the hydrophobic portion (Norgren and Edlund 2001) referred to here as the extracted KL (ex-KL).

For the determination of sulphur content in the lignin samples, wet digestion followed by inductively coupled plasma (ICP) analysis was used. The Softwood Kraft lignin (s-KL) and extracted Kraft lignin (ex-KL) used contained 3.61% (w) and 2.91% (w) sulfur respectively, as determined by ICP-MS analysis.

The structural characteristics of both initial (feed) and pyrolyzed (in form of char) softwood and extracted Kraft lignins were examined by taking FT-IR spectra recorded from 4000 cm\(^{-1}\) to 400 cm\(^{-1}\) at a resolution of 4 cm\(^{-1}\) in reflectance mode using the Bruker Tensor 27 FT-IR Spectrometer (Bruker Optics, Billerica, MA) and using the OPUS 7.2 Data Collection program for data processing.

XPS analysis of initial and pyrolyzed biomass samples was performed on an ESCA 2SR X-ray Photoelectron Spectroscope (Scienta Omicron, Denver, CO, USA) equipped with monochromated Al K\(\alpha\) X-ray source (15 kV, 450 W, vacuum < 4.6 x 10\(^{-9}\) mbar) to determine the quantitative elemental compositions and the bonding states of atoms in the biomass samples. Survey and high-resolution scans of individual elements were recorded and binding energies for the high-resolution spectra were calibrated by setting C-C peak at 284.8 eV in post-data processing using Casa XPS processing software.

2.2.1. Preparation of extracted Kraft lignin (ex-KL)

The extracted Kraft lignin (ex-KL) was prepared in the following manner: about 30 g of KL was placed in a Soxhlet extraction thimble unit connected to a round bottom flask containing 100 ml of methanol (technical grade, Thermo Fisher Scientific, Morris, NJ). The alkaline lignin
was extracted for over 24 h to obtain the hydrophobic alkaline lignin fraction, after which the solvent was evaporated from the sample with a Rotavapor R-100 rotary evaporator (Buchi Corp., New Castle, DE). The solid product was air dried and further dried under high vacuum at 40 °C for 48 h. In all, about 3 g of highly hydrophobic lignin was extracted and was kept in a desiccator for experiments. The particle size of the extracted Kraft lignin was < 150 µm. An additional sulfur-free lignin sample referred to as Deep Eutectic Solvent-KL (DES-KL) was tested for comparison. The sulfur-free lignin was obtained using the procedure described elsewhere (Muley, Mobley et al. 2019).

2.2.1.2. Fractional pyrolysis procedure

The fractional pyrolysis of a biomass sample is a protocol that involves a continuous pyrolysis of the sample, i.e. the same sample is continually heated at each pyrolysis temperature, until no significant products are formed (Iatridis and Gavalas 1979, Agblevor and Besler-Guran 2002, Agblevor, Beis et al. 2010, Kibet, Khachatryan et al. 2012, Kibet, Khachatryan et al. 2015, Bennadji, Khachatryan et al. 2018).

2.2.2. Experimental setup

The decomposition peculiarities of softwood and modified Kraft lignins were performed in a system for thermal diagnostic studies (STDS) reactor (Kibet, Khachatryan et al. 2012, Bennadji, Khachatryan et al. 2018) (Figure S1 in Appendix). The STDS consists of the reactor compartment, the temperature control console, sample injection port, a cryogenic trap, and a detection system comprising of a GC–MS as shown in Supplementary Information, Figure S1. The STDS, via its in-line system, allows the quantitative transport of organic materials from a reactor furnace through a transfer line at 280 °C to a GC injection port where products are cryogenically trapped at -60 °C. The STDS with modified reaction chamber consists of a vertical movable sample
holder with a basket at the end, a quartz pyrolysis reactor (7 mm ID x 110 mm long) and a 30 mm-central section located in the isothermal zone of the furnace.

The lignin sample in the deactivated quartz basket (o.d.= 4 mm, length = 8mm, sample mass ~ 8mg at thickness of 2-3 mm) was purged by ultra-high purity N₂ gas for 3 minutes at room temperature in a cold zone, outside of the heated section of the reactor. The basket then inserted rapidly into the isothermal zone of the preheated reactor at specified temperature to be pyrolysed for 3 minutes. A typical residence time of 0.2 s was maintained via flow rate adjustment to reduce homogeneous gas-phase reactions, aid rapid removal of reaction products and ensure uniformity between temperature runs. The pyrolysis gas was varied such that the residence time was held constant for every temperature change. Three thermocouples were placed at three locations of the quartz tubular reactor to measure established temperatures during pyrolysis.

After each run, the same solid lignin residue was moved back to the cold zone for 3 min, cooled to room temperature by flow of N₂ gas in readiness for pyrolysis at the next temperature, starting at 175 ºC in 25 ºC (or 50 ºC at higher temperatures) increments until a final temperature at which product formation is negligible. Upon the completion of each pyrolysis run, the mass loss by weight was determined with an analytical balance (accuracy of ± 10⁻⁴ mg).

2.2.3. Characterization of lignin samples and pyrolysis products by GC-MS

The mass (or peak area) percentage yields, retention times, and other peak properties of evolved organic volatiles were determined by GC-MS analysis. The pyrolysis products from the injection port passed into an in-line GC-MS system (Agilent 6890N gas chromatograph equipped with a 5973N mass selective detector-MSD). The pyrolysis volatile products initially were trapped and condensed with cryogenic nitrogen (-60 ºC) at the head of capillary column (Agilent J&W DB-5ms Ultra Inert GC Column, 30 m x 0.25 mm x 0.25 µm). After each pyrolysis experiment
products were resolved by chromatographic separation using the following temperature program: from -60 °C to 180 °C at 4 °C /min and 1 min hold time at 180 °C, and then ramped at 10 °C /min to a final temperature of 300 °C and held for 5 min. The mass spectra were operated in EI mode at 70 eV and scanned from 10 to 650 m/z at 2.5 scans/s frequency.

The progress of data acquisition and lignin product analysis was monitored using Mass Hunter Workstation software (version B.07.02). The chromatographic peaks were identified based on Wiley and NIST 2005 mass spectral libraries alongside retention times of standard mixtures. All reactions were performed at least in duplicates (commonly in triplicates) and average product yields were determined. The reproducibility of the experiments was within 2-5 % variation for the mass loss profiles and yields of lignin volatiles. Some characteristic GC-MS chromatograms from the pyrolysis of s- and ex-KLs are presented in Supplementary Information (Figure S2-S3).

2.2.4. X-ray photoelectron spectroscopy (XPS) analysis.

XPS analysis of initial and pyrolyzed biomass samples was performed on an ESCA 2SR X-ray Photoelectron Spectroscope (Scienta Omicron, Denver, CO, USA) equipped with monochromated Al Kα X-ray source (15 kV, 450 W, vacuum < 4.6 x 10^{-9} mbar) to determine the quantitative elemental compositions and the bonding states of atoms in the biomass samples. Survey and high-resolution scans of individual elements were recorded and binding energies for the high-resolution spectra were calibrated by setting C-C peak at 284.8 eV in post-data processing using Casa XPS processing software.
2.3. RESULTS AND DISCUSSION

2.3.1. Profiles of mass loss for s-KL and ex-KL

Fractional pyrolysis of two Kraft lignins was carried out in a vertical semi-batch reactor with residence time of 0.2 s at temperatures from 175 °C to 700 °C as described above. The fractional pyrolysis of DES-KL was performed to aid comparison with the two Kraft lignins using their decomposition profiles (see Supplementary Information).

Figure 2.1. Thermal decomposition profiles and their first order derivatives (dashed lines) of softwood Kraft lignin (s-KL) and extracted Kraft lignin (ex-KL); the samples were not dried before pyrolysis.

The pattern of weight losses for lignins are depicted in Figure 2.1, alongside the first derivative of weight loss of the lignins vs. temperature (dW'/dt). It is common for lignin samples to have initial decrease in weight due to water removal (Yang, Yan et al. 2007, Brebu, Cazacu et al. 2011) starting at lower temperatures. Smooth mass loss of s-KL was observed until 300 °C, while an accelerated degradation was detected from 300 °C to 350 °C with maximal rate at ~ 310
°C (Figure 2.1). No appreciable changes in the rates of lignin degradation were noticed at temperatures beyond 425°C for s-KL (Figure 2.1).

As seen from the first order derivatives (dashed lines in Figure 2.1), the initial region of loss of moisture and removal of light-weight volatiles from s-KL pyrolysis at 200 °C is followed by the second region, devolatilization, at 225 °C. Most of the devolatilization took place in the second region due to the cleavage of weak bonds in the constituent components of the s-KL polymer and the formation of stronger bonds to replace the broken bonds (Roque-Diaz, Villas et al. 1985, Faravelli, Frassoldati et al. 2010, Cheng, Winter et al. 2012). On the derivative curves, the positions of the peaks show the temperatures at which maximum rate of weight loss occurred. The peaks (shown by a noticeable change in slope of the thermal decomposition profiles) can be seen at 300 °C and 350 °C for s-KL, 300 °C and 340 °C for ex-KL, and 275 °C and 350 °C for DES-KL (Appendix). The third decomposition region, starting from ~ 425 °C for both s-KL and ex-KL, shows a much lesser rate of weight loss than the second stage. It was observed that s-KL decomposes slowly, ex-KL decomposes rapidly from 175 °C to 200 °C, and DES-KL decomposes more rapidly with decomposition still occurring at 500 °C, further than either s-KL or ex-KL. This is likely due to the absence of sulfur in DES-KL which promotes more sample depolymerization at higher temperatures (~500 °C).

The pattern for ex-KL pyrolysis (brown solid rectangles) generally follows the same trend as for s-KL, however, the pyrolysis starts at lower temperature with a high rate, followed by a smoother region from 225 to 300 °C and with maximal rate at ~ 325 (335) °C, Figure 2.1. Beyond 425 °C, both lignins (s-KL and ex-KL) pyrolysis ends up at high content of the char residue namely 47% and 43% for ex-KL and s-KL in decreasing percentages respectively, all at pyrolysis temperature of 700 °C.
2.3.2. Temperature dependence of the yields of volatiles from pyrolysis of s-KL and ex-KL

The pyrolysis of Kraft lignin yields three major groups of products: a residue (char), volatile products (tar) and gases (water, CO, CO₂ and other light gases, including sulfur-based compounds). A representative temperature-distribution of the quantified yields of major product i.e. guaiacol and its derivatives is presented in Figure 2.2. A characteristic GC-MS track for tar volatiles is represented in Figure S2 – S3. The yields of major grouped products detected from pyrolysis of s-KL in descending order of GC-MS peak area percentages, for instance at 300 °C, were; guaiacol (30.69 %), vanillin (10.63 %), acids & aldehydes (4.97 %), phenolics (1.59 %), and syringols (1.26 %).

![Figure 2.2](image)

Figure 2.2. The yields of grouped guaiacol and guaiacol derivatives (guaiacol; 6-methyl guaiacol; 4-ethyl guaiacol) from fractional pyrolysis of s-KL (blue solid line) and ex-KL (brown solid line). The dashed lines are cumulative yields of guaiacol derivatives calculated from experimental data for both lignins.

High content of total sulfur-containing compounds (50.86 %) in gaseous form such as dimethyl sulfide (CH₃)₂S, dimethyl disulfide (CH₃SSCH₃), methane thiol (CH₃SH), and sulfur
dioxide SO₂ was detected. The molecular structures and formulas of all detected tar compounds are summarized in Table S1.

The evolution of guaiacols in s-KL pyrolysis started at 250 °C, reaching its highest peak at 300-315 °C and steadily decreased to negligible yields thereafter. A shift of the yields of guaiacol products toward low temperatures and dramatic increase in the yields of guaiacols at 250 °C was observed from pyrolysis of ex-KL, Figure 2.2 (brown solid line); the evolution of guaiacols started at ~200 °C, reached its maximum peak at 250 °C, and steadily declined to negligible amounts beyond 350 °C.

It is currently unclear the cause for the drastic change in the yields of guaiacol and its derivatives at such low temperatures far from the maximal rate of decomposition at ~325 °C from pyrolysis of ex-KL (Figure 2.1).

Detection of the high yields of the major product – guaiacol at low temperatures was also reported in literature from pyrolysis of technical softwood Kraft lignin (Brodin, Sjöholm et al. 2010). One likely cause of this trend could be that some guaiacol fractions may have intrinsic character as part of Kraft lignin manufacturing (Koda, Koda et al. 2005, Brodin, Sjöholm et al. 2010). In fact, Soxhlet extraction of s-KL with methanol to yield ex-KL leads to the release of guaiacol, given that it has been initially captured in the lattice of the Kraft lignin. Some other important products, vanillin and syringols also show similar behaviors during pyrolysis of ex-KL. For instance, the high yields of vanillin were already detected at 250 °C (Figure S3). The yields of phenolics were far less significant for extracted lignin with only a minor peak at 315 °C (not shown). A summary of the yields of total tar components (guaiacols + vanillin + phenolics + syringols) from fractional pyrolysis of the two lignin substrates (solid lines), and the cumulative yields of the total tar (dashed lines) are provided in Figure 2.3.
The early release of the major tar components from pyrolysis of fractionated ex-KL (brown lines) corresponds to the early pyrolysis profile of the ex-KL, Figure 2.1, brown solid circles. The yields of total tar from s-KL pyrolysis (~2 %, w) are much less than the total tar from ex-KL samples (~ 15%, w) (Figure 2.3), thus buttressing the significant observation of a late release of tar components from s-KL pyrolysis (blue solid and dashed lines, Figure 2.3) in comparison with the analogous data from ex-KL pyrolysis. It is intriguing whether early detection of tar components and their high yields from pyrolysis of ex-KL depends on the behavior of sulfur-containing compounds detected experimentally or if the pretreatment of s-KL

![Figure 2.3. The yields of total tar (guaiacols + vanillin + phenolics+ syringols) from fractional pyrolysis of s-KL (blue solid line) and ex-KL (brown solid line). The dashed lines are cumulative yields of the tar calculated from experimental data for both lignins.](image-url)
makes a significant difference.

![Graph showing peak intensities of sulfur-containing compounds](image)

**Figure 2.4.** Peak intensities of sulfur-containing compounds (dimethyl sulfide, dimethyl disulfide, methane thiol, sulfur dioxide) obtained as a function of temperature from the fractional pyrolysis of s-KL and ex-KL.

### 2.3.3 Temperature dependence of the yields of sulfur-containing compounds from pyrolysis of s-KL and ex-KL.

The early release of sulfur-containing compounds (dimethyl sulfide (CH$_3$)$_2$S, dimethyl disulfide CH$_3$SSCH$_3$, methane thiol CH$_3$SH, sulfur dioxide SO$_2$) was pronounced in the ex-KL pyrolysis more than for the s- KL (Figure 2.4). For extracted fraction of Kraft lignin, a consistent increase in yields of sulfur-compounds was noticed starting from 175 °C up till the maximum peak at 345 °C followed by a steady decline. For s-KL, the yields of sulfur-containing compounds were considerably smaller with significant yields starting at 300 °C, then a maximum peak at 315 °C, and a steady decline afterwards.

The maximum rate of depolymerization of s-KL (Figure 2.1) reaches at ~ 300(310) °C which matches with the maximum amounts of total sulfur-containing compounds released between
~ 300-315 °C into gas phase. Similarly, the maximum amounts of sulfur-containing compounds in the gas phase released from 315 to 345 °C matches with the maximum rate of pyrolysis of ex-KL at ~ 325 °C (Figure 2.1). In fact, as the yields of released sulfur-containing compounds reach a maximum in the gas phase, the trend of pyrolysis rate also accelerated for both lignins.

Dramatically different behavior was observed in accumulation of tar compounds from both lignins pyrolysis. Indeed, the decomposition of ex-KL pyrolysis between 175 °C and 250 °C occurred via the release of large amounts of guaiacol (Figure 2.2) and vanillin (Figure S3) in comparison with the analogous data from s-KL pyrolysis. However, not significant cumulative amounts of sulfur-containing compounds were released at this low temperature region (Figure 2.5) where the general trend of the cumulative yields of sulfur-containing compounds from pyrolysis of both KLS can be compared; whereas, the total amount of sulfur-containing compounds is higher from ex-KL pyrolysis at high temperatures by factor of 1.5, which is in consonance with the XPS data, Table 2.1.

More solid residue % from pyrolysis of ex-KL (47%) vs. s-KL (40%) at 700 °C (Figure 2.1) can be also explained based on atomic concentration data from Table 1. The thermal stability of lignins is reduced with higher sulfur contents; the greater weight loss in lignosulfonate samples containing higher sulfite groups has been shown in publications (Ház, Jaslonsky et al. 2013, Pang, Zhang et al. 2017). Consequently, the ex-KL exhibits relatively low thermal stability because of increased sulfur content (S atomic concentration 4.07%, Table 2.1) and hence more active depolymerization profile, Figure 2.1.
As the sulfur content decreases drastically in the pyrolyzed sample (Figure 2.4) the residue becomes more stable (due to less sulfur containing in pyrolyzed sample, 0.74 %, Table 1) and as a result, more residue yield is detected from pyrolysis of ex-KL at higher temperatures. Different behavior was observed with the pyrolysis of s-KL – less release of sulfur-containing compounds into gas phase, high content of sulfur in residue (S atomic concentration 3.95%) and hence, decreased yields of residue (40%) due to its instability.

Table 2.1. Analysis of XPS patterns (atomic concentration) of initial and pyrolyzed s-KL and ex-KL samples (details in supporting information).

<table>
<thead>
<tr>
<th>Sample</th>
<th>C (%)</th>
<th>O (%)</th>
<th>S (%)</th>
<th>Na (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial s-KL</td>
<td>61.70</td>
<td>27.88</td>
<td>2.21</td>
<td>8.22</td>
</tr>
<tr>
<td>Pyrolyzed s-KL</td>
<td>27.65</td>
<td>42.24</td>
<td>3.95</td>
<td>26.16</td>
</tr>
<tr>
<td>Initial ex-KL</td>
<td>50.07</td>
<td>33.03</td>
<td>4.07</td>
<td>12.83</td>
</tr>
<tr>
<td>Pyrolyzed ex-KL</td>
<td>44.99</td>
<td>36.42</td>
<td>0.74</td>
<td>17.86</td>
</tr>
</tbody>
</table>

Nevertheless, an alternative explanation could also be the fact that the long-term treatment of the s-KL by methanol (overnight Soxhlet extraction) disturbed the structural properties of s-KL.

Figure 2.5. Cumulative average yields of sulfur-containing compounds (dimethyl sulfide, dimethyl disulfide, methane thiol, sulfur dioxide) from pyrolysis of s-KL (blue dashed line) and ex-KL (brown dashed line).
in a way that the ex-KL fraction was more prone to depolymerization at low temperatures, Figure 2.1, 3. This phenomenon (initial pretreatment) is not without precedent in literature, for instance the initial treatment of lignin increases bio-oil yields via pre-torrefaction (Waters, Janupala et al. 2017), hydrothermal treatment in subcritical water (Islam, Taki et al. 2018), formic acid (Løhre, Halleraker et al. 2017), and ultrasound pretreatment (Karnjanakom, Guan et al. 2015).

To validate this hypothesis, FTIR analyses of both s-KL and ex-KL samples have been performed along with corresponding residue (char) examination, Figs. 2.6 (a) and (b). The frequencies and nature of the bands of the functional groups of the Kraft lignins are presented in Table S2. The initial s- and ex- Kraft lignins showed more complex spectra compared to those of the pyrolyzed samples.

![Figure 2.6a. FT-IR spectra of initial (red) and pyrolyzed (blue) softwood Kraft lignin fractions.](image)
Figure 2.6b. FT-IR spectra of initial (green) and pyrolyzed (black) extracted Kraft lignin fractions.

The absorption band observed at 3342(3) cm\(^{-1}\) (O-H stretching in phenolic and aliphatic structures) as well as at 2935 cm\(^{-1}\); 2970 cm\(^{-1}\) (C-H stretching of methyl, methylene, Table S2) was more pronounced in the initial ex-KL compared to the s-KL. Also, well resolved spectrum was detected from ex-KL in the characteristic for lignins region from 1640 cm\(^{-1}\) (aromatic skeletal vibrations) to 1033 cm\(^{-1}\) (aromatic C-H deformation) and below. Most probably the pretreatment of s-KL as well as less sulfur content in the initial ex-KL (2.91%) favors early removal of sulfur compounds in the first stages of pyrolysis as well as accelerated pyrolysis of ex-KL and hence, release of large amounts of tar components.

The sulfur content has direct relation on stability and reactivity on lignin pyrolysis; the greater weight loss in lignosulfonate samples containing higher sulfite groups has been shown in publications [35, 36]. As the sulfur content decreases drastically in the pyrolyzed sample, especially for ex-KL (Figure 2.6, the total amount of sulfur-containing compounds in the gas phase is higher from ex-KL pyrolysis by factor of 1.5 at high temperatures), the residue becomes much
stable, Figure 2.2. As a result, more residue yield is detected from pyrolysis of ex-KL at higher temperatures (47% at 700 °C, Figure 2.2) due to expected less sulfur content which was also shown by XPS analysis of the char (Figure S4) from ex-KL (sulfur atomic concentration, 0.74 %, Table S3). On the other hand, high initial content of sulfur in s-KL (3.61% (w)) resulted in lesser release of sulfur-containing compounds in the gas phase, and high content of sulfur in the residue (atomic concentration of sulfur = 3.95%, Table S3) revealed decreased yields of residue (40% at 700°C) due to the instability of chars at high temperatures.

Note that sulfur bonding in both lignins was not conclusively established based on FTIR analysis (Figure 2.6 a, b, Table S2). The characteristic bonds containing sulfur are assigned mostly below 1400 cm⁻¹ which are difficult to analyze due to the complex bands from various modes of vibration (Abdelaziz and Hulteberg 2017). The XPS analysis has qualitatively shown existence of sulfur for initial lignins as well as corresponding chars, FigureS4; the surface atomic concentrations of elements are summarized in Table S3.

It is also important to compare the chars from s-KL and ex-KL pyrolysis, Figure 2.6 (a, blue line) and (b, black line), respectively. The FT-IR spectra of pyrolyzed Kraft lignins show that almost all the functional groups in both lignins have lower intensity due to thermal decomposition. More aromaticity (at 1442 cm⁻¹, aromatic skeletal vibration) has been seen for the char from pyrolysis of s-KL at concomitant appearance of surface carbonyl group at 1727 cm⁻¹, Figure 2.6 a. While the char from ex-KL pyrolysis significantly stayed intact to the initial lignin structure.

Therefore, the high yields and early detection of tar from ex-KL pyrolysis most probably is related to the pretreatment of s-KL (which causes also increased content of the sulfur in the initial sample, Table 1 and hence, instability). The low yields and late release of tar compounds from s-KL pyrolysis (Figure 2.3) may have direct relationship with the sulfur-containing
compounds adsorbed or linked to the lignin macromolecule. Importantly, the temperatures of maximal yields of tar compounds from s-KL pyrolysis (~ 300 °C, Figure 2.3) match to the maximum yields of released sulfur-containing compounds at 300 °C-315 °C (Figure 2.4) as well as with maximum rate of depolymerization of s-KL at 300 (310) °C, Figure 2.1.

2.3.3.1 Inhibitive effects of sulfur-containing compounds on depolymerization of KLs: A mechanistic explanation

Based on previous section results, we can assume that the depolymerization of KL samples, besides the pretreatment effect of the solvents, is activated at certain temperatures when the release of sulfur-containing compounds is effective. The sulfur-containing compounds that are adsorbed on (or linked to) the matrix of KL inhibit the process of depolymerization, and thus delay the release of tar components. We also note that the adsorbed sulfur-containing compounds block the active reaction sites. This is due to the fact that the early removal of sulfur from s-KL (and more effectively from ex-KL) pyrolysis at lower temperatures (175 °C - 250 °C, Figure 2.4 and 2.5) can be attributed to the sulfur compounds adsorbed on KL lattice (Bardet, Gellerstedt et al. 1984, Dondi, Zeffiro et al. 2014). It remains to be investigated whether these adsorbed sulfur-containing compounds affect the depolymerization rate of s-KL. This hypothesis is illustrated in Figure 2.7 via possible transformations of the one of the model compounds of lignin, cinnamyl alcohol, to phenolic compounds by attacking of H atoms to the Cα=Cβ double bond. Recently, our collaborators reported a comprehensive potential energy surface analysis of the p-CMA and p-CMA + H - atom systems using various DFT and ab initio protocols to examine the possible roles of the concerted molecular elimination and free-radical mechanisms in the formation of major products (Asatryan, Bennadji et al. 2017). The calculations particularly suggested a set of the chemically activated radical channels relevant to the low temperature product formation under pyrolysis conditions (Figure 2.6, upper two channels).
The coordination (simple adsorption) of thiol-like compounds to the double bond moieties, Figure 2.7, may deactivate all processes involving the transformations of the side chains typical for lignin pyrolysis both at low as well as high temperatures (Akazawa, Kojima et al. 2015, Asatryan, Bennadji et al. 2017).

Sulfur-containing compounds are well-known to play deactivating roles in heterogeneous catalysis (Argyle and Bartholomew 2015). There is limited information on the suppressing/inhibiting effect of the sulfur-compounds on formation of such carcinogenic chemicals as dioxins (Pandelova M, Stanev I et al. 2009, Wu HL, Lu SY et al. 2012, Fujimori T, Nishimoto Y et al. 2014), however the mechanism of suppression is unknown. Recent studies have indicated that formation of metal sulfates coincides with PCDD/F inhibition (Fujimori T, Nishimoto Y et al. 2014). A detailed understanding of the inhibition mechanism is beyond the
scope of this work. We note only that our preliminary data support the hypotheses provided in ref. (Feld-Cook EE, Bovenkamp-Langlois L et al. 2017) concerning the possible suppression resulted from the blocking of the active reactive centers by different agents such as sulfides, SO$_2$, or sulfur containing organic compounds.

Therefore, the sulfur-containing compounds in KL constitute detrimental impurities and reducing the sulfur content in KL will favorably improve the yields of valuable products and chemicals. Lignins with a lower sulfur content could be a more useful feedstock to produce a variety of value-added products such as those reported in literature (Caballero, Font et al. 1997, Košíková and Gregorová 2005, Evdokimov, Kurzin et al. 2018).

The sulfur-centered radicals, when released in gas phase, could also cause a carrier change in the radical-chain depolymerization of the Kraft lignins (Figure 2.4 and 2.5). The sulfur-containing compounds in the gas phase could dramatically change concentration of the active pool radicals such as H and OH (responsible for radical-chain depolymerization of lignin) as scavengers through reaction (1):

$$H (OH) + RSH \rightarrow RS^* + H_2 (H_2O)$$

The S-H bonds in alkane-thiols, CH$_3$SH and CH$_3$CH$_2$SH are known to be weaker than the corresponding C–H bonds (87.5 and 87.6 kcal/mol versus ca. 94.2 kcal/mol, respectively) (Gunturu A. 2011, Asatryan R. October 2006). In the case of methyl thiol, it has been shown experimentally and theoretically that the dominant pathway for the reaction of H atoms with CH$_3$SH is the formation of methylthiyl radical (Kerr, Alecu et al. 2015), reaction (1a):

$$H + CH_3SH \rightarrow CH_3S^* + H_2$$

We note that the key role of the OH(H) radicals in pyrolysis of lignin and model compounds has been actively discussed in literature and advocated also in recent publications
Newly formed sulfur centered radicals \( \text{RS}^\bullet \) (reaction 1, chain “carrier change”) are more passive, and therefore exert a negative influence on the further depolymerization of KL. This could provide a rationale for the lower rates of the pyrolysis of KLs as the concentration of sulfur-containing compounds increases in the gas phase (Figure 2.1 and 2.5).

The thiyl radicals may also form from the dissociation of relatively weak persulfide –S-S-bond in intrinsic persulfides \((\text{R}_2\text{S}_2)\) via reaction (2) (reported bond energy is less than 74 kcal/mol) (Benson 1978, Vandeputte, Reyniers et al. 2010):

\[
\text{R}_2\text{S}_2 \rightarrow 2 \text{RS}^\bullet
\]  

(2)

Reaction 2 is one of the main initiation reactions of the decomposition of \((\text{CH}_3)_2\text{S}_2\) (formation of \(\text{RS}_2^\bullet\) is also considered in the gas phase (Vandeputte, Reyniers et al. 2010).

The activity of persulfides \((\text{R}_2\text{S}_2)\) in the metabolism and mechanisms by which sulfur atoms are incorporated into biomolecules in biosynthetic reactions have been extensively discussed (Ollagnier-de-Choudens, Lascoux et al. 2003). Another possible source for the formation of thiyl radicals involving phenoxy radicals \((\text{PhO}^\bullet)\) (see Reaction 3 below) is the reactivity of \(\text{PhO}^\bullet\) radicals towards intracellular macromolecules (ascorbate, thiols, RSH, etc.) and membrane lipids which is more pronounced and have been discussed in literature (Foti, Ingold et al. 1994, Stoyanovsky, Goldman et al. 1995). A thiyl radical \((\text{RS}^\bullet)\) potentially can be generated in biological environments, (Stoyanovsky, Goldman et al. 1995) as in reaction 3:

\[
\text{PhO}^\bullet + \text{RSH} \rightarrow \text{PhOH} + \text{RS}^\bullet
\]  

(3)

The formation of oxygen centered, phenoxy type \(\text{PhO}^\bullet\) radicals during lignin pyrolysis has been recently confirmed in a number of publications (Kibet, Khachatryan et al. 2012, Bährle,
A reaction pathway similar to that of reaction 3 could serve as an alternative route to remove more reactive PhO• radicals in process of lignin pyrolysis by replacing them with less active thiyl radicals, RS•. All above mentioned channels for formation of thiyl radicals in the gas phase are potential sources to depress the concentration of OH(H) as well as PhO• pool radicals and hence, the rate of radical-chain decomposition pathways of lignin.

As regards the condensation reactions of sulfur-centered radicals, we note that whereas numerous reaction pathways for formation of thiyl radicals exist (reactions 1-3), no sulfur-containing biofuel compounds (likely to form during further reactions of thiyl radicals) were detected in either the present work or a recently published study (Han, Sophonrat et al. 2018). Thus, we can infer that thiyl radicals are much more passive and that instead of insertion and addition reactions (to aromatic rings, unsaturated bonds etc. via the formation of sulfur-containing compounds), the self-condensation reaction of RS• (reaction 4) is dominant:

\[
2\text{CH}_3\text{S}^\bullet \rightarrow [(\text{CH}_3\text{S}^\bullet)_2] \rightarrow \text{CH}_3\text{-S-S-CH}_3
\]  (4)

Upon comparison with the reaction by participation of analogue CH\text{3O}• radicals in reaction (5) with reaction (4);

\[
2\text{CH}_3\text{O}^\bullet \rightarrow [(\text{CH}_3\text{O}^\bullet)_2] \rightarrow 2\text{CH}_2\text{O} + 2\text{H}
\]  (5)

one can see the highly significant advantage of self-condensation of CH\text{3S}• over that of CH\text{3O}• by comparing the corresponding rate constants of reactions 4 and 5 (NIST 1998), with the ratio greater than 10, thus illustrating high dimerization capability of thiyl radicals:

\[
k_4/k_5 = [4.0 \times 10^{-11} \text{ cm}^3/\text{molecule.sec}] / [3.0 \times 10^{-12} \text{ cm}^3/\text{molecule.sec}] > 10
\]
Similarly, the rate constant of the addition reaction of CH$_3$S• to unsaturated hydrocarbons (e.g. ethylene) is in the order of $2.0 \times 10^{-15}$ cm$^3$/molecule.sec, which is much slower than that for the self-condensation in reaction (4). These phenomena could explain the absence of sulfurized bio-oil products during pyrolysis of s-KL.

Nevertheless, abstraction or addition reactions by participation of sulfur-centered radicals may occur according their rate constants, as evident in the formation of covalently linked S atoms in lignin macromolecule, for instance formation of thiirane, epo-sulfide bonds, (addition of sulfur to unsaturated olefinic bond in the side chain of lignin) or organically bound sulfur thiol (-SH) (Jiang, Nowakowski et al. 2010, Evdokimov, Kurzin et al. 2018). We note that the addition reactions of thiyl radicals to olefinic bonds depends on the environment of the double bond. For instance, the rate constants for addition of thiyl radical to propene is one order of magnitude higher ($1.0 \times 10^{-14}$ cm$^3$/molecule.sec) than that with ethene ($2.0 \times 10^{-15}$ cm$^3$/molecule.sec) when one hydrogen in ethene is replaced by methyl group producing propene. These reactions while having minor occurrence in the gas phase cannot compete, however, with the condensation reactions of sulfur-centered radicals (reaction 4).

The addition reactions rate constants are much higher in case of free sulfur atom (So) – the rate constant of reaction 6 is significantly higher, in order of $10^{-12}$ cm$^3$/molecule.sec (NIST 1998). This reaction may occur especially during the pulping process of black liquor. We note that during pulping processes, the ionic reactions are more preferable at elevated temperatures, 150°C-170 °C (Li, Sun et al. 2011), leading to the formation of thiirane structure of the lignin:

$$S + H_2C=CH-R \rightarrow H_2C (S) CH-R \text{ (like epoxide)}$$

(6)

The insertion reaction of elemental sulfur (ground state), an insertion phenomenon of sulfur into C-H bond (formation of organically bound sulfur (-SH)) with the rate constant in order of $10^{-1}$
$^{14}\text{cm}^3/\text{molecule.sec}$ (Eberhard and Klaus 1970), can be considered minor in comparison with the insertion into much weaker -C-S- bond in $(\text{CH}_3)_2\text{S}$ (or $(\text{CH}_3)_2\text{S}_2$), Reaction 7 ($k_7 = 3.43 \times 10^{-10}$ cm$^3$/molecule.sec) (Green, Lown et al. 1984):

$$\text{S} + \text{CH}_3\text{-S-CH}_3 \rightarrow \text{CH}_3\text{-S-S-CH}_3 \quad (7)$$

Further insertion of S ether in C-S or –S-S- bonds in $(\text{CH}_3)_2\text{S}_2$ molecule can lead to the formation of CH$_3$-S-S-S-CH$_3$ detected in sulfur-products of pyrolysis of KL (Sáiz-Jiménez and De Leeuw 1984, Ohra-aho, Tenkanen et al. 2005, Mu, Ben et al. 2013).

Finally, if we assume formation of sulfur-energized atoms in the gas phase during pyrolysis of KL, the dimerization termolecular reaction (8) by formation of S$_2$ can be one of the preferable pathways with high reaction rate constant, $k_8 = 1.18 \times 10^{-29}$ cm$^6$/molecule$^2$.sec (NIST 1998):

$$\text{S} + \text{S} + \text{M} \rightarrow \text{S}_2 + \text{M} \quad (8)$$

Therefore, the absence of sulfurized bio-oil products during pyrolysis of s-KL is most likely, since the self-condensation reactions of S-centered radicals (including sulfur atoms) are dominant over addition/insertion/abstraction reactions towards the formation of bio-oil compounds.

2.3.3.2. Char formation

The high content of char produced from pyrolysis of KL, reaching up to 50 % or more (Sharma, Wooten et al. 2004, Beis, Mukkamala et al. 2010, Ben and Ragauskas 2011, Brazil, Costa et al. 2018, Lazaridis, Fotopoulos et al. 2018) is another interesting phenomenon to examine. The lowest residue content from pyrolysis of other types of lignins have been reported; for instance, char from hydrolytic lignin pyrolysis at high temperatures reaches up to 28-30 % (Kibet, Khachatryan et al. 2012, Barekati-Goudarzi, Boldor et al. 2017), 26-33 % from Klason lignin
In general, a reasonable explanation for the char formation from pyrolysis of lignin might be that the methide intermediate structures formed from the pyrolysis of lignin (or lignin model compounds) are easily polymerized via charring process (Asatryan, Bennadji et al. 2017). However, the methylation of phenolic hydroxyl groups, which suppresses the formation of methide structures, lowers the yield of the char (Kim, Dutta et al. 2017). Similarly, the pretreatment of lignin phenolic hydroxyl, carboxyl and other functional groups by calcium hydroxide leads to less agglomeration during pyrolysis (Zhou, Brown et al. 2015).

Most probably, the mechanisms of charring processes are similar for all lignins including KL. However, KL differs from others because of its high content of sulfur as mentioned above, either as free impurities (So; S₂; S₈), as sulfur-containing compounds namely methyl thiols, dimethyl persulfides etc. (Evdokimov, Kurzin et al. 2018, Messmer, Guerrini et al. 2018), or as covalently linked atoms to the polymer chain (Han, Sophonrat et al. 2018). Since sulfur-containing compounds suppress the free-radical fast oxidation reactions of KL macromolecules especially by lowering the concentration of OH/H, this phenomenon can be the main source of suspending further depolymerization of KLs and hence high content of unreacted lignin.

On the other hand, the radical - chain re-polymerization reactions can be also initiated by participation of, for instance, methylthiy radicals CH₃S• formed in reaction 1. While the most favorable reaction of thiyl radicals is dimerization, as mentioned above, thiyl radicals to some extent can initiate re-polymerization reactions either in the gas phase or on the surface. This scenario may lead to new charring processes, while minor, among the schemes discussed for sulfur free lignins (Cho, Chu et al. 2012, Asatryan, Bennadji et al. 2017, Kim, Dutta et al. 2017).
Thus, due to the deactivation of depolymerization processes by sulfur-containing compounds as initial, non-converted as well as newly formed KL macromolecules (after re-polymerization) may remain on the char, thus increasing the residue content upon pyrolysis. Naturally, some amount of sulfur should be incorporated in the char content. Indeed, large amounts of sulfur were detected in the char reported in some publications (Sharma, Wooten et al. 2004, Beis, Mukkamala et al. 2010, Zhang, Resende et al. 2012) as well as shown in the present work (Table 2.1).

2.4. CONCLUSION

Various studies have researched the effect of temperature on pyrolysis of general wood and lignin feed stocks. There is, however, a scarcity of literature data focused on characterizing the product distribution from fractional pyrolysis of KL below 500 °C and the role of sulfur impurities on the overall thermal decomposition. Fractional pyrolysis of two types of softwood Kraft lignin (s-KL) and extracted Kraft lignin (ex-KL) at 175 °C - 700 °C was investigated in an STDS (System for Thermal Diagnostic Studies) reactor.

Product distributions and analyses were performed based on major chemical tar groups observed – guaiacols, vanillin, phenolics, syringols, as well as sulfur-containing compounds. Products yields from ex-KL pyrolysis drastically differed from that of s-KL pyrolysis; early formation of tar at temperatures below 300 °C was observed which was attributed to the initial pretreatment of the lignin (overnight Soxhlet extraction in methanol). The yields of sulfur-containing products constantly increased with temperature culminating in the maximal release of them at ~ 315°C for pyrolysis of s-KL and ~ 345°C for ex-KL. The sulfur content has dramatically significant effects on production of oil compounds from both, especially s-KL pyrolysis; the tar yields increased significantly alongside the removal of sulfur-containing light gases. A
mechanistic explanation of inhibitive effect of sulfur-containing compounds on formation of tar as well as char production was developed.
CHAPTER 3.
THERMAL TREATMENT OF SOFTWOOD KRAFT LIGNIN UNDER FRACTIONAL AND ABLATIVE PYROLYTIC CONDITIONS

3.1. INTRODUCTION

Attenuation of global fossil energy reserves, increasing need to combat global warming, fluctuating crude oil prices, and heavy reliance on foreign fuels have influenced the need for economically viable and energy-efficient alternative energy sources (Kothari, Tyagi et al. 2010, Zhou, Lou et al. 2010, Dutta, Daverey et al. 2014, Díaz-Abad, Millán et al. 2019, Huang, Xia et al. 2019, Xia, Pan et al. 2019). Although there are several renewable energy sources (solar, wind, hydroelectric, geothermal, hydrogen), plant biomass is the only present renewable source suitable for the production of solid, liquid and gaseous transportation fuels (Huber, Iborra et al. 2006, Anex, Aden et al. 2010, Ionel and Cioabla 2010, Ozturk 2016, Kumar, Varkolu et al. 2019, Wyman, Cai et al. 2019). However, significant bottlenecks exist in converting plant biomass into renewable fuels, as the starting material has to be readily abundant, not suitable as food, environmentally benign, cheap to produce, and the products need to conform to stated ASTM standards (Muley and Boldor 2013, Sindhu, Binod et al. 2019).

Biomass-derived lignin is a natural resource that satisfies all aforementioned criteria. It is nature’s most abundant aromatic biomacromolecule, comprised of three monolignols monomers (p-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol) (Gellerstedt, Tomani et al. 2012), and it is co-produced during biomass fractionation and pulp processing (Gellerstedt 2015). In a typical lignocellulosic biomass, lignin holds the lignocellulose matrix together by occupying the spaces between cellulose and hemicellulose (Figure S1). Different types of lignins exist based on the biomass source (softwood, hardwood, annuals, etc.) and on the isolation process used (kraft pulping, ethanol organosolv pretreatment, ionic liquids, etc.) (Gopalakrishnan, Ceylan et al. 2013,
Tian, Chandra et al. 2017). Lignin recovered from the kraft pulping of pinewood (softwood), referred to as softwood Kraft lignin (s-KL), is a most appealing biomass-sourced lignin to study because; (1) it has potential to be easily available, given kraft pulping is the dominant chemical pulping process and that softwood is the primary lignocellulosic material in the northern hemisphere (Chakar and Ragauskas 2004, Alekhina, Ershova et al. 2015); (2) it can crosslink more readily than hardwood lignin, given it consists of guaiacylic monomers as compared to syringylic monomers in its hardwood counterpart (Norberg, Nordström et al. 2013); (3) it is highly reactive compared to hardwood lignins, and is uniform across wood species due to the structural similarity in monolignol (its guaiacyl-propane units) (Liu, Jiang et al. 2015).

Despite the potential of s-KL however, the intrinsic heterogeneity and non-hydrolyzable cross-linked property of native lignin (Wang, Ruan et al. 2015), complex isolation chemistries and structure of s-KL, imprecise distribution of its molecular weight, high reactivity of its decomposition intermediates (Deuss, Scott et al. 2015), and unwanted sulfur-based and carbohydrates impurities from the isolation process, preclude the use of s-KL in valuable fuel and chemical applications (Alekhina, Ershova et al. 2015, Crestini, Lange et al. 2017). Specifically, detailed understanding of the discrete chemicals structure, physicochemical features and thermal properties of s-KL must be established if the development of high-value chemicals, materials, and technologies based on s-KL feedstock is to be achieved (Chakar and Ragauskas 2004, Norberg, Nordström et al. 2013, Ragauskas, Beckham et al. 2014).

The pyrolysis of softwood Kraft lignin, an irreversible process of chemically decomposing this aromatic biopolymer at elevated temperatures in the absence of oxygen, shows great promise for converting s-KL lignin into fuels, materials, and suitable industrial precursors (Chakar and Ragauskas 2004). Pyrolysis processes are differentiated by the temperatures and vapor residence
times of the lignin biomass. For optimum liquid biofuel production, moderate temperatures and shorter vapor residence times are generally required (Bridgwater 2012, Jahirul, Rasul et al. 2012).

Any unconventional approaches that may improve biofuel yields and product selectivity are highly desirable. A better alternative to above conventional methods of pyrolysis could be the infrared CO₂ laser pellet ablation (IR LPA) technique (Meier and Faix 1999, Bridgwater 2012, Bridgwater 2018). Laser ablation is a subtractive technique used to rapidly heat and remove thin fractions from the surface of a material, solid (or sometimes liquid) body, by irradiating it with an intense continuous wave (CW) or pulsed beam from a laser source (Dowding 2010, Mattox 2010, Serra, Duocastella et al. 2010, Zhang and Guan 2014).

At lower laser flux, the material evaporates or sublimes upon the absorption of laser energy, whereas at higher flux, the material is typically converted to plasma. With the IR LPA approach, low power (a few watts) from IR CO₂ laser is focused on circular s-KL pellets positioned in the LPA reactor under a fast flow of the carrier gas N₂ through the reactor, to rapidly desorb products from the pellet surface, minimizing unwanted secondary reactions and interactions of released products with the hot surface of pellets.

Generally, the effect of laser irradiation on organic polymers has been studied in the past (Srinivasan and Braren 1989, Sumiyoshi, Ninomiya et al. 1994, Juha, Bittner et al. 2005, Mukarakate, Scheer et al. 2011). Among the latest efforts to break down kraft lignin into distinct aromatics is the laser pellet ablation technique, which has been substantially studied over the past decade, in most cases with UV lasers (Srinivasan and Braren 1989, Kelley, Arnaud et al. 1994). In ablation, laser energy is transformed into the internal energy of the material (Khachatryan, Xu et al. 2016). However, scarce attention has been given to similar processes in the IR spectral range, especially with CO₂ lasers. An advantage of this method is that small particle size of biomass is
not necessary for ablative pyrolysis, unlike other fast pyrolysis methods. The CO\textsubscript{2} continuous laser beam pyrolyzes the lignin particles in an ablation reactor under homogeneous conditions, followed by a swift quenching and momentum transport (diffusion) of various products out of the “hot zone” to avoid unwanted further secondary reactions (degradation, cleavage, or condensation) (Khachatryan, Barekati-Goudarzi et al. 2018).

The IR LPA technique offers several benefits over other techniques since: (1) it provides efficient photochemical heat transfer mechanism and higher wavelength bands (9.4 – 10.6 µm) as compared to UV lasers with photophysical heat transfer processes and lower wavelengths (0.2 µm), thus increasing the penetration depth of the laser beam; (2) pyrolysis reactions are rapidly quenched from the hot to the cold zone across the reactor, thus reducing condensation or other secondary reactions; (3) CO\textsubscript{2} lasers are cheaper relative to other industrial lasers.

Recently, softwood Kraft lignin (s-KL) and methanol-fractionated extracted Kraft lignin (ex-KL) samples were thermally depolymerized via fractional (stepwise) pyrolysis at temperatures from 175 °C to 700 °C (Daniel, Khachatryan et al. 2019). An isothermal STDS (System for Thermal Diagnostic Studies) reactor with a modified reaction chamber was used to obtain the distribution and the yields of pyrolysis products; it was found that the sulfur-containing compounds, as intrinsic contaminants (both adsorbed and covalently bound to KL matrixes), were found to strongly inhibit formation of the pyrolysis products. Decreasing of sulfur content from 3.61% (s-KL) to 2.91% (ex-KL – after Soxhlet extraction of s-KL in methanol) had dramatic effect on products distribution; the yields of the major products (guaiacols, vanillins, phenols, syringols) were dependent on the release of sulfur-containing compounds, i.e. the lesser the content of sulfur in the KL matrix, the higher the yields of major pyrolysis products. A mechanistic explanation for the absence of sulfur-containing bio-oil products and the inhibitory effect of sulfur-containing
compounds, as well as the relatively high char content in depolymerization of both lignin substrates were developed. To further establish the intriguing character of S-contaminants on bio-oil production from s-KL pyrolysis a dramatically different reactor – ablative pyrolysis of s-KL under IR CO₂ laser irradiation has been explored.

In this present work, we studied the thermal behavior of softwood Kraft lignin from ablative fast pyrolysis with respect to its product distribution under minimal secondary reaction conditions. The effects of N₂ carrier gas flow rates, IR CO₂ laser powers, and optical chopper frequencies on specific product species (e.g. guaiacols, vanillins, phenolics, syringols, and sulfur-containing compounds) were also investigated.

In this present work, the results from both conventional, fractional pyrolysis (batch reactor) and ablative pyrolysis (CO₂ laser-powered pellet ablation reactor – LPPA) of s-KL are compared to investigate the yields and distribution profiles of released pyrolysis products, especially the extent to which sulfur contained in the s-KL influences on depolymerization reaction from both reactors. This knowledge will aid better understanding of how the product composition of softwood Kraft lignin varies during the ablative fast pyrolysis by IR CO₂ laser with the broader aim of producing cost-effective bio oils, various energy materials and commodity chemicals.

3.2. MATERIALS AND METHODS

3.2.1. Materials

The s-KL alkaline lignin used in this study (s-KL, Indulin, pH 9.0) was supplied from TCI America (Portland, OR) as a black powder, with methoxyl group and water contents of 11.9% and 5.5%, respectively. The total sulfur content was not indicated from manufacturer, but the sulfate content as an ignition residue was 23.6% (Certificate of Analysis). The s-KL was used for pyrolysis experiments as received. For 100% content s-KL pellets, a few mg of s-KL (~320 mg) was placed
in an agate mortar and ground to disperse any sign of crystallinity. The ground mixture was tightly packed and pressed in a 15mm-diameter dry pressing die set (Across International, Livingston, NJ, USA). The die set was further pressed using a hydraulic press at 300 psi to obtain firmly pressed 15 mm diameter s-KL pellets. For other concentrations of s-KL (0.1%, 10%, 50%, etc.) and FT-IR transmission analysis, KBr was added to the s-KL powder and ground to a fine mixture to make thin and transparent KBr:s-KL pellets suitable for FTIR analysis.

3.2.2. FT-IR and SEM imaging measurements of Softwood Kraft lignin/KBr mixtures

FTIR spectra were obtained from lignin pellets treated with KBr. A Bruker Tensor 27 FT-IR spectrometer was used to obtain mid-infrared spectra of lignin pellets inserted in KBr real crystal cards placed in a Salt Plate/IR card/Pellet holder while spectroscopic data was viewed and analyzed using Bruker’s OPUS (Optical User Software) Data Collection Program.

Scanning electron microscopy (SEM) was used to study the anatomical degradation and structural changes in the surface structure of softwood Kraft lignin (s-KL) after ablative treatment at high resolution. All scanning electron micrographs were performed using a FEI Quanta 400 FEG instrument (Hillsboro, OR, USA) under high vacuum with an Everhart-Thornley detector and a solid-state backscatter detector.

Fresh and ablated s-KL pellets were mounted on aluminum stubs using carbon tape and coated with 20 nm platinum sputter (Sputter Emitech / K550 model) using a Cressington model 203 (Watford, England) sputter coater for 8 mins to prevent charging. This was longer than the standard 4 mins due to the higher water content in the fresh and ablated s-KL pellets. Imaging was performed at beam accelerating voltages from 12.5 to 25 kV and working distance of ~ 38 mm. Over 40 images from eight randomly selected regions on characteristics samples of both fresh and
ablated SW KL samples were acquired to ensure reproducibility of the results; from these groups, characteristic images were chosen at both 500 x and 2,000 x magnifications.

3.2.3. **IR LPA reactor: Technique and experimental set-up**

Fast ablative pyrolysis experiments were carried out in a cylindrical quartz pyrolysis tube IR reactor holding Kraft lignin/KBr pellets (diameter = 15 mm) with lignin of various compositions (Figure 3.1). Typically, the s-KL pellet (~ 300 mg, 15 mm diameter) was placed on a glass holder in the center of the pyrolysis tube. Pure N₂ gas with flow rate of 250 mL/min was used as a carrier gas to convey and rapidly desorb ablated products from the pellet surface through the reactor chamber. Laser power (0.5W – 4W) provided by an IR CO₂ laser (Synrad Firestar v40 CO₂ laser, FSV40KWD, Mukilteo, WA) was aimed at the pellet surface, intermittently obstructed by an optical chopper system (Thorlabs Inc., Newton, NJ). The optical chopper (4 Hz – 10 kHz) was used to modulate light from the continuous laser beam using its high-precision chopper blades. The optical chopper reduces the intensity from the laser power source at various chopper frequencies.

The ablated products pass through the reactor chamber into an impinger immersed in either ice water (0 °C) or dry ice / ethanol mixtures (-78 °C) for condensation of products. Upon ablative pyrolysis, the reaction system was additionally flashed by N₂ gas to complete further transport of released products adsorbed on reactor walls. The condensates were also recovered by washing the reactor with dichloromethane followed by evaporation under reduced pressure in preparation for characterization and chemical analysis.
3.2.4. Conventional batch reactor – Fractional pyrolysis

The fractional pyrolysis of a s-KL sample is a protocol that involves the continuous pyrolysis of the sample, i.e. the same sample is continually heated at each pyrolysis temperature, until no significant products are formed (Iatridis and Gavalas 1979, Agblevor and Besler-Guran 2002, Agblevor, Beis et al. 2010, Kibet, Khachatryan et al. 2012, Kibet, Khachatryan et al. 2015, Bennadji, Khachatryan et al. 2018). The decomposition peculiarities of softwood Kraft lignins were performed in a system for thermal diagnostic studies (STDS) reactor (Kibet, Khachatryan et al. 2012, Bennadji, Khachatryan et al. 2018). The STDS consists of the reactor compartment, the temperature control console, sample injection port, a cryogenic trap, and a detection system comprising of a GC–MS. The STDS, via its in-line system, allows the quantitative transport of organic materials from a reactor furnace through a transfer line at 280 °C to a GC injection port where products are cryogenically trapped at -60 °C. The STDS with modified reaction chamber consists of a vertical movable sample holder with a basket at the end, a quartz pyrolysis reactor (7 mm ID x 110 mm long) and a 30 mm-central section located in the isothermal zone of the furnace.
The lignin sample in the deactivated quartz basket (o.d.= 4 mm, length = 8mm, sample mass ~ 8mg at thickness of 2-3 mm) was purged by ultra-high purity N₂ gas for 3 minutes at room temperature in a cold zone, outside of the heated section of the reactor. The basket was then inserted rapidly into the isothermal zone of the preheated reactor at specified temperature to be pyrolyzed for 3 minutes. A typical gas residence time of 0.2 s was maintained via flow rate adjustment to reduce homogeneous gas-phase reactions, aid rapid removal of reaction products and ensure uniformity between temperature runs. The pyrolysis gas was varied such that the residence time was held constant for every temperature change.

3.2.5. GC-MS analysis

Product composition of pyrolysis products (in form of vaporized liquid samples) were studied via gas chromatography−mass spectroscopy (GCMS) using a Varian 1200 series system with a DB5 capillary column and Wiley 6N library, and the area under the peaks were integrated for product composition. The mass (or peak area) percentage yields, retention times, and other peak properties of evolved organic volatiles were determined by GC-MS analysis (Agilent 6890N gas chromatograph equipped with a 5973N mass selective detector-MSD). The pyrolysis volatile products from fractional pyrolysis initially were trapped and condensed with cryogenic nitrogen (-60 °C) at the head of capillary column (Agilent J&W DB-5ms Ultra Inert GC Column, 30 m x 0.25 mm x 0.25 µm). After each pyrolysis experiment products were resolved by chromatographic separation using the following temperature program: from -60 °C to 180 °C at 4 °C /min and 1 min hold time at 180 °C, and then ramped at 10 °C /min to a final temperature of 300 °C and held for 5 min. The mass spectra were operated in EI mode at 70 eV and scanned from 10 to 650 m/z at 2.5 scans/s frequency.

Pyrolysis products from ablative pyrolysis were collected from the sampling port (Figure 3.1) in DCM solution kept at ice water (or dry ice) temperature. The condensed samples were
analyzed on GC-MS after hand injection (1 μl). The yield for each product group was normalized to the final mass of the condensed residue after ablation and vaporization to reduce batch-to-batch variation.

Data collection and processing from both reactors were performed using Enhanced Data Analysis and Agilent MassHunter Qualitative Analysis B.07.00. The yield for each product group was normalized to the final mass of the condensed residue after ablation to reduce batch-to-batch variation. The chromatographic peaks were identified according to NIST 2005 and Wiley libraries and retention time of known mixtures. All reactions were performed in triplicates, and the product yields were averaged. The reproducibility of the experiments was within 2–5% variation with respect to the rate of mass loss and to the yields of most of the ablation products.

3.2.6 EPR measurements

The paramagnetic activity of the samples after pyrolysis both in fractional as well as in ablative pyrolysis mode were analyzed by EPR spectroscopy. The EPR spectra were recorded on a Bruker EMX-20/2.7 EPR spectrometer (Bruker Instruments, Billerica MA) with dual cavities, X-band (100 kHz) and microwave frequency at 9.516 GHz. The typical parameters were: sweep width = 200 G, EPR microwave power from 0.5 mW to 64 mW, modulation amplitude ≤ 4 G, and time constant and sweep time in most cases were 10.24 ms and 167.77 s, respectively.

The dimensionless magnetic moment of a radical, g-factor, (a characteristic value which measures how the magnetic environment of unpaired electrons differ from that of a free, gas-phase electron, g = 2.0023) was calculated using Bruker’s WINEPR program, a comprehensive line of software, allowing control of the EPR spectrometer, data-acquisition, automation routines, tuning and calibration on a Windows-based PC (Eaton, Eaton et al. 2010). The exact g-values for key spectra were determined by comparison with a 2, 2-diphenyl-1-picrylhydrazyl (DPPH) standard.
3.3. RESULTS AND DISCUSSION

3.3.1. Comparison of Fractional and Ablative Pyrolysis of s-KL in both batch and LPPA reactors

The softwood Kraft lignin (s-KL) was thermally depolymerized via fractional (step-wise) pyrolysis at temperatures from 175 °C to 700 °C in STDS reactor (Figure S1), and reported elsewhere (Daniel, Khachatryan et al. 2019). It was shown that the sulfur content had dramatic effect on products distribution; the yields of the major products (guaiacols, vanillins, phenols, syringols) were dependent on the release of sulfur-containing compounds, i.e. the lesser the content of sulfur in the KL matrix, the higher the yields of major pyrolysis products. The left-hand side presents the quartz basket loaded with ~ 7-8 mg s-KL at thickness of ~ 3mm and placed inside the pyrolysis reactor. The flow rate of the N₂ carrier gas is in the range from 120 to 50 mL/min in entire temperature region to keep the residence time = 0.2 sec fixed in the post basket zone. The transfer time through the lignin layer at flow rates indicated above was about 4-8 ms, Figure 3.2.

It is highly probable that as the bio-oil components form, they can also be decomposed on the surface through secondary tar reactions (STR). To minimize the contact of bio-oil compounds with the surface, the ablation approach can thus be an alternative to remove rapidly the products from the black spot (volcano-shaped, Figure 3.2, right hand side) due to the quick flow of the carrier gas over the surface. The flow rates can even be higher, as higher flow rates present no significant difficulty for sampling, Figure 3.1.

The flashing residence time over the volcano constitutes less than 1 ms at carrier gas flow rates from 300 mL/min to 750 mL/min, thereby significantly minimizing the occurrence of STRs. The rate of STR decreases also dramatically after post-ablation zone (Figure 3.1) because the LPPA reactor was operated at room temperature.
Figure 3.2. Vertical with open button quartz reactor for fractional pyrolysis (left-hand side). The right-hand side represents a pellet from pure s-KL located in the IR LPPA reactor (Fig. 1). The black spot volcano shape forms after laser irradiation (the beam diameter = 2.5mm).

The advantages of LPPA of s-KL vs. conventional pyrolysis can be seen by comparing the product distribution from their GC-MS analysis, Figure 3.3 (ablative pyrolysis) and Figure 3.4 (fractional pyrolysis). Higher abundance of products from ablative pyrolysis of s-KL was observed. Instead of 13 products from fractional pyrolysis (Figure 3.4), about 31 products were detected from ablative pyrolysis. The products from the ablative pyrolysis (Figure 3.3) of softwood Kraft lignin can be classified into three categories: a) methoxy phenols – guaiacols, 4-vinyl guaiacol, 4-ethyl guaiacol, b) phenolics – phenol, vanillin, creosols; syringols - and c) aromatics – benzene, 1,2-dimethoxy. Guaiacol was the predominant product of s-KL ablative pyrolysis, followed by vanillin. Among the phenolics, phenols were the lowest, whereas benzene, 1,2-dimethoxy had the lowest yield across all categories at all flow rates investigated.
Figure 3.3. Characteristic GC-MS chromatogram from laser ablation of softwood Kraft lignin. Parameters include: 7% laser power, 100 Hz optical chopper frequency, 100% s-KL composition; X and Z distances on translation stage: 10 mm and 17 mm respectively, 5 min experiment time.

Table 3.1. Characteristic product distribution from laser ablation of Kraft lignin.

<table>
<thead>
<tr>
<th>S/N</th>
<th>RT (min)</th>
<th>Compound</th>
</tr>
</thead>
<tbody>
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<td>1</td>
<td>4.596</td>
<td>Toluene</td>
</tr>
<tr>
<td>2</td>
<td>4.684</td>
<td>Thiophene, 3-methyl- (sulfur-containing)</td>
</tr>
<tr>
<td>3</td>
<td>5.982</td>
<td>2-Cyclopenten-1-one</td>
</tr>
<tr>
<td>4</td>
<td>7.273</td>
<td>2,4-Dimethylfuran</td>
</tr>
<tr>
<td>5</td>
<td>7.376</td>
<td>Butanoic acid, 4-hydroxy-</td>
</tr>
<tr>
<td>6</td>
<td>7.465</td>
<td>Anisole</td>
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<td>19</td>
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<td>3,4-dimethoxytoluene</td>
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<td>11.927</td>
<td>Benzaldehyde, 4-methoxy-</td>
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<td>21</td>
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<td>31</td>
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Figure 3.4. Characteristic GC-MS chromatogram from fractional pyrolysis of s-KL at 300°C in batch (STDS) reactor.

Table 3.2. Characteristic product distribution from fractional pyrolysis of Kraft lignin.

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<td>13</td>
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Also, by moving the translation stage in the IR LPPA set up towards the laser beam, similar product distributions were observed from two different spots on the s-KL pellet, Figures 3.5. (a) and (b), thus confirming the reproducibility of the IR LPPA approach.
Figure 3.5 (a) and (b). Similar product distributions obtained by GC-MS from ablation of a single s-KL pellet at two different ablation spots.
Table 3.3. Similar characteristic product distributions from laser ablation of different spots on a s-KL pellet.

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<td>Homovanillic acid</td>
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</table>

3.3.2. FTIR analysis and SEM imaging: Effect of IR CO\(_2\) laser ablative pyrolysis on s-KL pellets

FTIR results showed a marked difference in the transmittance levels of different compositions of s-KL pellets mixed with KBr (Figure 3.6). The pellet with the lower s-KL composition (0.1%) showed a stronger transmittance compared to that with higher s-KL composition (1%). The heat source from the laser altered the surface texture of the s- Kraft lignin pellets by reducing the lignin content, hence the reason for the more spaces in between droplets compared to the fresh or non-treated Kraft lignin pellets (Bocchini, Galletti et al. 1996). Figure 3.7 shows the range of droplet sizes and coverage density that can be observed by SEM imaging of surfaces of fresh and ablated s-KL pellets. It was noticed that fresh pellets exhibited droplets of a more irregular shape compared to smoother and more spherical shapes in ablated pellets (Figure 3.7a).

Larger spheres of different shapes and sizes were formed on the surface of the ablated pellets (Figure 3.7b). Coalesced particles with round or elliptical shapes were also noticed on the
surface, which is likely indicative of the lignin and/or hemicellulose content in the structure of s-KL. The ablated lignin pellet showed droplets of more globular structures due to heating effects from the IR laser. The ablated KL particles were found to be small, almost spherical in shape, which is likely due to the effect of the laser energy on the surface, so that the particles take a thermodynamically more stable form (spherical) due to surface tension as the surface area of the pellet surface in contact with the irradiation (Fierro, Torné-Fernández et al. 2006).

As the pellet is being laser irradiated, hot molten lignin is formed, which is then vaporized and later cooled to form spherical droplets. A more detailed observation reveals that the surface of the KL particles is very rough. Also, loss of pith or porous formation on lignin pellet surfaces, and exposure of fiber strips were noticed for the pellets ablated at higher amounts of IR laser powers. Particularly, morphological anomalies were more pronounced at increased laser powers (7% laser power vs. 5%) likely caused by the removal of lignin from the pellet surface during ablation.

Figure 3.6. FTIR spectra showing variations between 0.1% and 1% composition of s-KL in KBr pellet mixture.

Fresh s-KL pellets (Figure 3.7a) displayed a compact morphology, while the treated samples (Figure 3.7b) showed increased exposure of spherical droplets and a more disoriented
morphology. As shown in Figure 3.8 (top and bottom), however, the surface morphology at higher flow rates (≥ 750 mL/min) were rougher than that at lower flow rates (≤ 450 mL/min). This observation can be alluded to the fact that higher flow rate increases heat transfer at micro scale and dissipates the heat over a large area/volume thus increasing the amount of lignin being pyrolyzed.

3.3.3. EPR Examination: Sulfur-centered radicals

The sulfur containing products regularly detected from fractional pyrolysis of s-KL (dimethyl sulfide, dimethyl disulfide, methane thiol, sulfur dioxide) were not observed from the ablative pyrolysis of s-KL. However, an EPR examination of the deposit from the walls of the LPPA reactor showed surprisingly trace amounts of a new type of radicals tentatively assigned as sulfur-centered radicals, Figure 3.9. Along with organic radical at \( g = 2.0030 \), a new type of radical(s) at \( g_1 = 2.0630; g_2 = 2.0250 \) and \( g_3 = 2.002 \) were detected. These parameters are close to the ones calculated for sulfur-centered radicals, particularly for disulfide type radicals; for instance for methyl disulfide radical – \( \text{CH}_3-\text{SS} \) with \( g_1 = 2.0630; g_2 = 2.0280 \) and \( g_3 = 2.002 \) (Engström, Vahtras et al. 2000). Several EPR peaks were not identified; different candidates calculated in above reference could be responsible for the peaks assigned shown with asterisks in Figure 3.9.
Figure 3.7. SEM imaging showing surface textures of 100% sKL pellets before and after ablative pyrolysis (250 X; 500 X; 2000 X magnification).

It is also worthy of note that both the detected and the organic radicals \((g = 2.0030, \text{Figure 3.7})\) were stable and detectable over a few weeks in ambient conditions. Note that similar types of radicals (Figure 3.9, green line) were not detected from fractional pyrolysis, Figure 3.10; the char was subjected to EPR analysis and a broad EPR line was detected at very low \(g\) value = 2.0024 which is typical for deoxygenated char/soot from combustion/pyrolysis processes. Since the char after s-KL pyrolysis has high sulfur content (Daniel, Khachatryan et al. 2019), the broadening of the EPR line can be as a result of spin-orbital interaction between the free electron and sulfur. Note that after decreasing the sulfur content in the initial lignin, and consequently in the char, the \(\Delta H_{p-p}\) (Figure 3.10) drops down from 22.5 G to ~ 6G, results not shown).
Figure 3.8. SEM imaging showing effects of flow rates (TOP: 450 mL/min; BOTTOM: 750 mL/min) on surface textures of 100% sKL pellets before and after ablative pyrolysis (250 X; 500 X; 2000 X magnification).

The phenomenon of non-detection of sulfur compounds from ablative pyrolysis can be reasonable, if the IR absorbance bands of a few sulfur compounds are compared (Figure 3.9); all sulfur containing compounds have strong absorption at CO$_2$ laser wavelength of 10.6 μm (944 cm$^{-1}$). Most probably, these compounds decompose on the pellet surface as the laser beam first ablates the pellet. Additionally, the abundant sulfur compound physiosorbed on the surface of KL was reported as disulfide type molecules (Daniel, Khachatryan et al. 2019). The IR absorption spectra for major sulfur-containing compounds detected from the fractional pyrolysis of s-KL were,
however, not detected from the ablative pyrolysis of s-KL pellets (Figure 3.11).

![Figure 3.9. A comparison of EPR spectra of the initial s-KL (red line) and the deposit in LPPA reactor after ablative pyrolysis of s-KL pellet, green line.](image)

Thus, more bio-oil compounds were detected from the ablative pyrolysis of s-KL due to the absence of sulfur compounds as well as the number of benefits of ablative pyrolysis over fractional pyrolysis as presented above.
Figure 3.10. A comparison of EPR spectra of the initial s-KL (red line) and the residue/char after fractional pyrolysis of s-KL, green line.

<table>
<thead>
<tr>
<th></th>
<th>g value</th>
<th>dHp-p, G</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial s-KL</td>
<td>2.0044</td>
<td>6.4</td>
</tr>
<tr>
<td>Char</td>
<td>2.0024</td>
<td>22.5</td>
</tr>
</tbody>
</table>

Figure 3.11. The IR absorption spectra for major sulfur-containing compounds detected from fractional pyrolysis of s-KL which were, however, not detected from ablative pyrolysis of s-KL pellets.
3.4. CONCLUSION

Infrared laser ablation has been successfully applied to study the distribution of products in softwood Kraft Lignin (KL). Distribution of products from ablation of pure s-KL pellets were different from those obtained for the conventional pyrolysis of s-KL without additives; guaiacol, vanillin, and phenol products at high abundance were detected in comparison with conventional, fractional pyrolysis of s-KL. It was concluded that sulfur-containing products were decomposed on the surface before release into gas phase due to absorbance of laser energy at 10.6 μm; as it has been seen in fractional pyrolysis experiments, sulfur containing products were inhibitors for s-KL pyrolysis. Sulfur containing products underwent decomposition in IR laser ablation, as no major sulfur-containing products were detected among bio-oil compounds. Also, trace amounts of sulfur-centered stable radicals were detected from the deposits on the walls of the LPPA reactor, as an indicator of the formation of persistent sulfur-centered radicals, probably due to some repolymerization reactions of sulfur-centered radicals. Upon reducing the content of KL in the pellet mix, product yields surprisingly decreased non proportionally. Guaiacol and vanillin were the major products of the laser ablation of pellets containing KL less than 20% by composition.

Although SEM technique has been proven to characterize surface structures of samples, it was noticed that surface morphology of s-KL highly depends on s-KL pellet preparation and laser experimental conditions. A general trend was established indicating that during the ablative treatment of s-KL pellets, s-KL converts to glassy stage most probably by melting and some globules were formed at exposure of minimal laser power.
CHAPTER 4.
SUMMARY AND FUTURE WORK

4.1 Summary of research contributions

The thermal deconstruction of lignocellulosic biomass via destructive distillation of biorenewable resources, also known as pyrolysis, is an irreversible thermal conversion process for biomass at elevated temperatures in an inert atmosphere. Pyrolysis has been successfully used to produce industrial ethylene, coke, and other chemicals from petroleum and coal. This research focused on improving pyrolytic capabilities for the conversion of high-potential biomass such as softwood Kraft lignin into syngas (hydrogen and carbon monoxide) and other wide range of useful liquid chemical products. Below is a summary of the major technical results from this study:

- **Effects of sulfur content on the yields of liquid products from pyrolysis of softwood Kraft lignin:** Product distributions from fractional pyrolysis of two types of softwood Kraft lignin (s-KL) and extracted Kraft lignin (ex-KL) at 175 °C - 700 °C showed major chemical tar groups observed – guaiacols, vanillin, phenolics, syringols, as well as sulfur-containing compounds. The yields of sulfur-containing products constantly increased with temperature, and has dramatically significant effects on production of oil compounds from both, especially s-KL pyrolysis.

- **Design of IR CO$_2$ laser irradiation experimental conditions for optimal peak yields of ablative pyrolysis products:** In the LPPA reactor, sulfur-containing products were decomposed on the surface before release into gas phase, since no major sulfur containing products were detected among bio-oil compounds. Also, little amounts of sulfur-centered stable radicals detected in the wall of the LPPA reactor is indicative of the formation of
persistent sulfur-centered radicals likely caused by some repolymerization reactions of the sulfur-centered radicals.

- **Evaluative comparison of thermal treatment of softwood Kraft lignin under fractional and ablative pyrolytic conditions:** The IR LPPA approach was found to yield more desired products and yields due to the ability to significantly reduce secondary tar reactions due to rapid gas flow rates, constant residence times in the reactor, and the absence of wool layer in the ablation reactor, and the room temperature condition at which the IR laser pyrolysis was carried out as compared to the higher temperatures at which the fractional pyrolysis study was done.

4.2. **Recommendations for future work**

Thermal deconstruction through fractional pyrolysis (batch reactor) and ablative pyrolysis (CO\textsubscript{2} laser-powered pellet ablation reactor – LPPA) of s-KL have been studied in this work. Recommendations for future work include a detailed analysis of sulfur-containing compounds specifically of sulfur dioxide (SO\textsubscript{2}), hydrogen sulfide (H\textsubscript{2}S), and organic sulfur; mass losses due to heat and mass transfer from ablative pyrolysis by LPPA with the goal of achieving an overall balance via established methods and calibrated standards; studying the effect of decreasing the composition of Kraft lignin on the yields of guaiacol and vanillin, as a non-proportional drop in yields was observed as the composition was reduced from 100 % to 0.1 %; extensive identification of radicals seen from EPR analysis and spin trapping; and vacuum pyrolysis of Kraft lignins with the aim of examining the resulting paramagnetic radicals.
APPENDIX. Supplementary information for Chapter 2.

Figure S1. Schematic diagram of the STDS (system for thermal diagnostic studies) for pyrolysis of biomass (lignin, cellulose etc.).

Figure S2. Thermal decomposition profiles and their first order derivatives (dashed lines) of softwood Kraft lignin (s-KL), extracted Kraft lignin (ex-KL) and DES-KL; the samples were not dried before pyrolysis.
Figure S3a. Product distribution from fractional pyrolysis of s-KL at 250°C.

1. Phenol, 2-methoxy (C\textsubscript{7}H\textsubscript{8}O\textsubscript{2}); 2. vanillin (C\textsubscript{8}H\textsubscript{8}O\textsubscript{3}); 3. phenol, 2,4-bis(1,1-dimethylethyl) (C\textsubscript{14}H\textsubscript{22}O); 4. tetradecanoic acid (C\textsubscript{14}H\textsubscript{26}O\textsubscript{2}); 5. pentadecanoic acid (C\textsubscript{15}H\textsubscript{30}O\textsubscript{2}).

Figure S3b. Product distribution from fractional pyrolysis of s-KL at 300°C.

Figure S3c. Product distribution from fractional pyrolysis of s-KL at 315⁰C.

Figure S4a. Product distribution from fractional pyrolysis of ex-KL at 250ºC.

1. Dimethyl disulfide; 2. phenol; 3. phenol, 2-methoxy; 4. phenol, 4-ethyl-2-methoxy; 5. 2-methoxy, 4-vinylphenol; 6. syringol; 7. vanillin; 8. vanillic acid, methyl ester; 9. benzene acetic acid, 4-hydroxy-3-methoxy-; 10. homovanillyl alcohol; 11. homovanillic acid; 12. tetradecanoic acid; 13. Pentadecanoic acid.

Figure S4b. Product distribution from fractional pyrolysis of ex-KL at 300ºC.

Figure S4c. Product distribution from fractional pyrolysis of ex-KL at 345ºC.

<table>
<thead>
<tr>
<th>RT, min</th>
<th>Compound Name</th>
<th>Formula</th>
<th>Chemical Structure</th>
<th>MW</th>
</tr>
</thead>
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<tr>
<td>4.566</td>
<td>Creosol</td>
<td>C₈H₁₀O₂</td>
<td><img src="image" alt="Chemical Structure" /></td>
<td>138.164</td>
</tr>
<tr>
<td>5.818</td>
<td>Acetic acid, methyl ester (or methyl acetate)</td>
<td>C₃H₆O₂</td>
<td><img src="image" alt="Chemical Structure" /></td>
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<tr>
<td>6.56</td>
<td>Toluene</td>
<td>C₇H₈</td>
<td><img src="image" alt="Chemical Structure" /></td>
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<td>7.801</td>
<td>Benzene</td>
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<td>78.112</td>
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<td>12.699</td>
<td>p-Cymene</td>
<td>C₁₀H₁₄</td>
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<td>134.218</td>
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<td>12.699</td>
<td>m-Cymene</td>
<td>C₁₀H₁₄</td>
<td><img src="image" alt="Chemical Structure" /></td>
<td>134.218</td>
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<td>Guaiacol</td>
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<td>Veratrol</td>
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<td>14.544</td>
<td>2-Methoxy-6-Methylphenol</td>
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</table>

(Table cont’d)
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<thead>
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<th>RT, min</th>
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<th>Formula</th>
<th>Chemical Structure</th>
<th>MW</th>
</tr>
</thead>
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<td>14.737</td>
<td>p-Cresol</td>
<td>C₇H₈O</td>
<td><img src="image" alt="C7H8O Structure" /></td>
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<tr>
<td>15.172</td>
<td>3,4-Dimethoxytoluene (or homoveratrol)</td>
<td>C₉H₁₂O₂</td>
<td><img src="image" alt="C9H12O2 Structure" /></td>
<td>152.190</td>
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<td>15.640</td>
<td>4-Ethylguaiacol</td>
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<td><img src="image" alt="C9H12O2 Structure" /></td>
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<td>15.970</td>
<td>1,4-Dimethoxy-2,5-dimethylbenzene</td>
<td>C₁₀H₁₄O₂</td>
<td><img src="image" alt="C10H14O2 Structure" /></td>
<td>166.217</td>
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<td>15.989</td>
<td>2-Methoxy-4-vinylphenol</td>
<td>C₉H₁₀O₂</td>
<td><img src="image" alt="C9H10O2 Structure" /></td>
<td>150.174</td>
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<td>16.328</td>
<td>Syringol</td>
<td>C₈H₁₀O₃</td>
<td><img src="image" alt="C8H10O3 Structure" /></td>
<td>154.163</td>
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<td>16.385</td>
<td>Benzene methanol, alpha-ethyl-4-methoxy-(or 1-(4-Methoxyphenyl)-1-propanol)</td>
<td>C₁₀H₁₄O₂</td>
<td><img src="image" alt="C10H14O2 Structure" /></td>
<td>166.217</td>
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<td>16.677</td>
<td>Vanillin</td>
<td>C₈H₈O₃</td>
<td><img src="image" alt="C8H8O3 Structure" /></td>
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<td>17.003</td>
<td>Isovanillin</td>
<td>C₈H₈O₃</td>
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<td>152.147</td>
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(Table cont’d)
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<tr>
<th>RT, min</th>
<th><strong>Compound Name</strong></th>
<th><strong>Formula</strong></th>
<th><strong>Chemical Structure</strong></th>
<th>MW</th>
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<td>17.016</td>
<td>Isoeugenol</td>
<td>C_{10}H_{12}O_{2}</td>
<td><img src="image1" alt="Chemical Structure" /></td>
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<td>17.194</td>
<td>Benzaldehyde, 3,4-dimethoxy- (or vetraldehyde)</td>
<td>C_{9}H_{10}O_{3}</td>
<td><img src="image2" alt="Chemical Structure" /></td>
<td>166.174</td>
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<tr>
<td>17.278</td>
<td>Methyl eugenol</td>
<td>C_{11}H_{14}O_{2}</td>
<td><img src="image3" alt="Chemical Structure" /></td>
<td>178.228</td>
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<td>17.749</td>
<td>Acetophenone</td>
<td>C_{8}H_{8}O</td>
<td><img src="image4" alt="Chemical Structure" /></td>
<td>120.148</td>
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</tbody>
</table>

Chemical structures from [www.ChemSpider.com](http://www.ChemSpider.com); RT = Retention Time; MW = Molecular Weight.

Table S2. FT-IR spectral assignment of major peaks for softwood and extracted Kraft lignins.

<table>
<thead>
<tr>
<th>Wave number (cm⁻¹)</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>600</td>
<td>Sulfur bonds</td>
</tr>
<tr>
<td>628, 635</td>
<td>Broad band of C-S bond</td>
</tr>
<tr>
<td>672</td>
<td>C-S vibration of sulfonic group</td>
</tr>
<tr>
<td>724, 779, 813, 816, 900</td>
<td>S-OR esters</td>
</tr>
<tr>
<td>853, 854</td>
<td>Aromatic C-H bending</td>
</tr>
<tr>
<td>1033</td>
<td>Aromatic C-H deformation and C-H out-of-plane vibrations</td>
</tr>
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</table>

(Table cont’d)
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<tr>
<th>Wave number (cm(^{-1}))</th>
<th>Assignment</th>
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</thead>
<tbody>
<tr>
<td>1127</td>
<td>Aromatic C-H in-plane deformation in guaiacyl rings</td>
</tr>
<tr>
<td>1157</td>
<td>C-O stretch in ester groups</td>
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<tr>
<td>1207, 1210</td>
<td>C-O stretch in syringol rings</td>
</tr>
<tr>
<td>1262</td>
<td>C-O of guaiacyl rings</td>
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<tr>
<td>1379</td>
<td>C-H stretch in methyl groups</td>
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<tr>
<td>1416</td>
<td>Vibration of aromatic rings of lignin</td>
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<tr>
<td>1442, 1462, 1640, 1667</td>
<td>Aromatic skeletal vibrations</td>
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<td>1510, 1512</td>
<td>Benzene rings stretching for softwood lignin</td>
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<td>1586</td>
<td>Aromatic ring of lignin plus C=O stretching</td>
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<td>1727</td>
<td>Unconjugated C=O</td>
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<td>2840</td>
<td>Symmetric C-H stretching in -CH(_2)- and tertiary C-H groups</td>
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<td>2935, 2970</td>
<td>C-H stretching of methyl or methylene group chains</td>
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<tr>
<td>3342, 3343</td>
<td>OH stretching in phenolic and aliphatic structures</td>
</tr>
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</table>
X-ray photoelectron spectroscopy (XPS) analysis

XPS analysis of untreated and pyrolyzed biomass samples was performed on an ESCA 2SR X-ray Photoelectron Spectroscope (Scienata Omicron, Denver, CO, USA) equipped with mono-chromated Al Kα X-ray source (15 kV, 450 W, vacuum < 4.6 x 10^{-9} mbar) to determine the quantitative elemental compositions and the bonding states of atoms in the pyrolyzed biomass samples. Survey and high-resolution scans of individual elements were recorded and binding energies for the high-resolution spectra were calibrated by setting C-C peak at 284.8 eV in post-data processing using Casa XPS processing software.

Table S3. Analysis of XPS patterns of initial and pyrolyzed s-KL and ex-KL samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>C (%)</th>
<th>O (%)</th>
<th>S (%)</th>
<th>Na (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial s-KL</td>
<td>61.70</td>
<td>27.88</td>
<td>2.21</td>
<td>8.22</td>
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<tr>
<td>Pyrolyzed s-KL</td>
<td>27.65</td>
<td>42.24</td>
<td>3.95</td>
<td>26.16</td>
</tr>
<tr>
<td>Initial ex-KL</td>
<td>50.07</td>
<td>33.03</td>
<td>4.07</td>
<td>12.83</td>
</tr>
<tr>
<td>Pyrolyzed ex-KL</td>
<td>44.99</td>
<td>36.42</td>
<td>0.74</td>
<td>17.86</td>
</tr>
</tbody>
</table>

X-ray photoelectron spectroscopy (XPS) analysis of the initial and pyrolyzed softwood (s-KL) and extracted (ex-KL) Kraft lignin biomass samples are presented in Figure 2. The quantitative elemental compositions of initial and pyrolyzed softwood Kraft lignin (s-KL) and extracted Kraft lignin (ex-KL) samples are listed in Table 1. It shows that the chemical content (in % of signal) originating from various elements. The chemical content of C decreased, whereas chemical contents of O, S and Na increased in initial samples of s-KL compared to ex-KL, due to the Soxhlet extraction of s-KL by methanol. Upon fractional pyrolysis, the chemical content of C significantly decreased in s-KL but mildly so in ex-KL, whereas chemical contents of O and Na increased in initial compared to pyrolyzed samples for both s-KL and ex-KL. The chemical content of sulfur (S) in pyrolyzed s-KL was higher than that in the initial s-KL sample, whereas the trend
is the reverse in the case of ex-KL: sulfur content in pyrolyzed ex-KL was lower than that in the initial ex-KL sample. It can thus be inferred that after fractional pyrolysis, s-KL had more O, S, and Na and less C, whereas ex-KL had more O, Na and less C, S.

Figure S4 presents the XPS results of (s-KL) and extracted Kraft lignin (ex-KL) samples.

![Figure S4. XPS patterns of initial and pyrolyzed softwood Kraft lignin (s-KL) and extracted Kraft lignin (ex-KL) samples.](image)

Analysis of the XPS spectra of s-KL and ex-KL show peaks C 1s at binding energy close to 285 eV and peak O 1s at binding energy close to 534 eV. Meanwhile, the spectra show peaks S 2p at binding energy 169 eV, with large quantity of oxygen (the O 1s peak at binding energy of 534 eV). Lesser ex-KL (3 g of 30 g or ~10%) was extracted from the starting s-KL, hence composition analysis from XPS which showed high of % of sulfur in ex-KL (4.07%), which is almost twice that in s-KL (2.21%) which is consistent with the extraction results based on overall
mass balance. Also, pyrolyzed s-KL and ex-KL biomass samples had higher intensities than the initial biomass.
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VITA

Dideolu J. Daniel was born in Ibadan, Nigeria. He received his Bachelor of Science degree in Agricultural & Environmental Engineering with honors from Obafemi Awolowo University of Nigeria in December 2014. In the Spring of 2017, he started his Master of Science program in Biological & Agricultural Engineering under the supervision of Dr. Dorin Boldor at Louisiana State University.