

UNIVERSIDADE FEDERAL DE VIÇOSA

IARA FONTES DEMUNER

**MODIFICAÇÕES NA LIGNINA KRAFT DE EUCALIPTO E PRODUÇÃO DE
LIGNOSULFONATOS**

**VIÇOSA - MINAS GERAIS
2021**

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Tese apresentada à Universidade Federal de Viçosa, como parte das exigências do Programa de Pós-Graduação em Ciência Florestal, para obtenção do título de *Doctor Scientiae*.

Orientador: Cláudio Mudadu Silva

Coorientadores: Fernando José Borges Gomes

Ana Márcia M. L. Carvalho

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RESUMO

DEMUNER, Iara Demuner, D.Sc., Universidade Federal de Viçosa, março de 2021. **Modificações na lignina kraft de eucalipto e produção de lignosulfonatos.** Orientador: Cláudio Mudadu Silva. Coorientadores: Fernando José Borges Gomes e Ana Márcia Macêdo Ladeira Carvalho.

A lignina é o segundo polímero natural mais abundante do mundo, após a celulose. Como subproduto da indústria de celulose e papel, aproximadamente 50 milhões de toneladas de lignina são produzidas anualmente em todo o mundo. A combinação de um mercado em crescimento e os potenciais ganhos econômicos relacionados à biorrefinaria da lignina kraft, aumenta o interesse em pesquisas para avaliar seu amplo espectro de aplicações. Esse estudo teve como objetivo realizar uma revisão completa da estrutura da lignina, processos de extração, modificação química da lignina kraft e possíveis aplicações de seu alto valor agregado. Após o processo de desconstrução da madeira pelo processo kraft, a lignina se caracteriza como um polímero altamente complexo e de baixa reatividade. O presente estudo avaliou o efeito do tratamento térmico do licor na reatividade da lignina kraft extraída. O licor negro foi tratado termicamente nas temperaturas de 175, 200 e 225 °C e em tempos de reação de 30, 90 e 150 minutos. As ligninas do licor original e dos licores termicamente tratados foram extraídas e caracterizadas quanto à sua composição química, análise final, poder calorífico e Py-GC-MS para avaliar as modificações causadas pelo tratamento térmico. O tratamento térmico promoveu desmetilação e desmetoxilação na lignina kraft de eucalipto. Observou-se também redução da relação S/G das ligninas tratadas termicamente e aumento do teor de catecol e metoxicatecol no tratamento de 225 °C e 150 minutos em relação à referência. A lignina kraft de eucalipto, isolada termicamente do licor tratado, foi considerada mais reativa do que a lignina original. Como atualmente a produção de lignosulfonatos se limita ao processo sulfito, a produção de lignosulfonatos a partir da lignina kraft mostra-se uma abordagem promissora, sendo também objetivo desse trabalho a produção de lignosulfonatos através de sulfonação ácida e sulfometilação de lignina kraft de eucalipto. Para o processo de sulfometilação, foram avaliadas três temperaturas (100, 130 e 160 °C) e três razões molares de hidroximetilsulfonato de sódio lignina (0,8; 1,2 e 1,6). Para o processo de sulfonação ácida, foram avaliadas as temperaturas de 80, 100 e 120 °C e a razão molar H₂SO₄/lignina de 10, 20 e 30. A sulfonação ácida não foi eficiente para a produção de lignosulfonatos a partir da lignina kraft, no entanto, o lignosulfonato produzido pelo processo

de sulfometilação (160 °C e razão molar de 1,6) apresentou teor de enxofre (5,23%) semelhante ao encontrado para o lignosulfonato comercial (5,28%). Além disso, foi confirmado a inserção de grupos sulfonatos na lignina kraft por meio da análise de FTIR e também devido a elevada solubilidade em água. Ficou evidenciado que o tratamento térmico do licor negro residual é uma forma de modificação química da lignina kraft, com a geração de novos sítios ativos de reação e grupos catecol em sua estrutura. Além disso, a lignina kraft pode ser utilizada para produção de lignosulfonatos pelo processo de sulfometilação.

Palavras-chave: Lignina kraft. Modificação química. Reatividade. Sulfonação.

ABSTRACT

DEMUNER, Iara Demuner, D.Sc., Universidade Federal de Viçosa, March, 2021. **Modifications in eucalyptus kraft lignin and lignosulfonates production.** Advisor: Cláudio Mudadu Silva. Co-advisors: Fernando José Borges Gomes and Ana Márcia Macêdo Ladeira Carvalho.

Lignin is the second most abundant natural polymer after cellulose. As a by-product of the pulp industry, approximately 50 million tons of lignin are produced worldwide annually. The combination of a growing market and potential economic gains related to lignin kraft biorefinery increases the interest in assessing its broad spectrum of applications. This study carried out a complete review of lignin structure, extraction processes, chemical modification of kraft lignin and its possible high added value applications. The black liquor was heat-treated at temperatures of 175, 200 and 225°C and reaction times of 30, 90 and 150 minutes. The lignins from the original liquor and the heat-treated liquors were extracted and characterized by their chemical composition, elemental analysis, heating value and Py-GC-MS to evaluate the changes caused by the thermal treatment. The thermal treatment promoted demethylation and demethoxylation on the eucalypt kraft lignin. A reduction in the lignin S/G ratio of heat-treated lignins and an increase in the catechol and methoxycatechol content in the treatment of 225°C and 150 minutes period were also observed when compared to the reference. The eucalypt kraft lignin isolated from the heat-treated liquor was considered more reactive than the original lignin. Once the production of lignosulfonates is currently limited to the sulfite process, the production of lignosulfonates from kraft lignin turns a promising approach. Another aim of this work was to produce lignosulfonates through acid sulfonation and sulfomethylation of kraft lignin. During sulfomethylation process, three temperatures (100, 130 and 160 °C) and three molar ratios of sodium hydroxymethylsulfonate/lignin (0.8; 1.2 and 1.6) were evaluated. For acid sulfonation process, the temperatures of 80, 100 and 120 °C and molar ratio H₂SO₄/lignin of 10, 20 and 30 were evaluated. Acid sulfonation was not efficient for the production of lignosulfonates from kraft lignin, however, the lignosulfonate produced by the sulfomethylation process (160 °C and molar ratio of 1.6) showed a sulfur content (5.23%) similar to that found in commercial lignosulfonate (5.28%). In addition, it was confirmed the insertion of sulfonate groups in kraft lignin through FTIR analysis and also due to the high-water solubility. It was evidenced that the heat treatment of the residual black liquor is a form of chemical modification of lignin kraft, with the generation of new active

reaction sites and catechol groups in its structure. In addition, kraft lignin can be used to produce lignosulfonates by the sulfomethylation process.

Keywords: Kraft lignin. Chemical modification. Reactivity. Sulfonation.

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INTRODUÇÃO GERAL

O Brasil é segundo maior produtor mundial de polpa celulósica, com o uso intenso da madeira de eucalipto como matéria prima. Segundo a Indústria Brasileira de Árvores, 20.953 milhões de toneladas de polpa celulósica foram produzidas no país em 2020, com o aumento de 6,4% comparado ao ano anterior (IBÁ, 2021).

Atualmente, 98-99% das polpas celulósicas produzidas no mundo são gerados pelo processo kraft, o qual converte a madeira em polpa celulósica usando uma solução de sulfeto de sódio (Na_2S) e hidróxido de sódio (NaOH) a uma temperatura de 155-175 °C. Esse processo visa a hidrólise e solubilização da lignina e a obtenção da polpa celulósica. Essa polpa consiste, basicamente, de celulose e hemiceluloses e é amplamente utilizada para produção de diversos papéis, como embalagens, *tissue* e impressão e escrita.

Para produção de polpa para dissolução, pode ser adotado um pré tratamento antes do processo kraft, para remoção de hemiceluloses, ou a polpação sulfito. As polpas solúveis têm como característica o elevado teor de alfa-celulose e são utilizadas para produção de derivados de celulose através de derivatizações específicas para cada produto (Longue Júnior et al., 2015).

Como licor residual do processo kraft, o licor negro é caracterizado pela presença de componentes orgânicos e inorgânicos que foram removidos da madeira. O material orgânico consiste na lignina e em carboidratos, sobretudo hemiceluloses, que foram solubilizadas durante o processo de polpação. O licor é enviado para o ciclo de recuperação química para regeneração dos reagentes inorgânicos utilizados na polpação e geração de energia para o processo através de sua queima. Além disso, a queima do licor negro oriundo do processo de polpação é uma estratégia importante para redução de efluentes gerados na fábrica kraft (Tran e Vakkilainen, 2008).

No conceito de biorrefinaria, utilizar uma parte da lignina presente no licor para conversão de produtos de alto valor agregado é economicamente mais racional do que utilizá-la totalmente como combustível nas fábricas kraft (Macfarlane et al., 2009). Além da potencial geração de produtos de alto valor agregado a partir da lignina extraída do licor negro, a remoção de parte da lignina do licor negro kraft diminui a carga de sólidos para a caldeira de recuperação. Como consequência, um maior volume de licor negro pode ser queimado na caldeira e a produção de polpa celulósica pode ser aumentada.

A biorrefinaria de produtos naturais é uma abordagem promissora para promover o uso mais amplo da lignina, sendo baseada na integração de conversão de biomassa, processos

e equipamentos para produzir combustíveis, energia e produtos químicos. No entanto, para os processos de biorrefinaria ainda é necessário implantar estratégias para gerenciar a lignina e seus subprodutos, o que torna-se essencial para estabelecer a viabilidade econômica dos processos (Galkin e Samec, 2016; Tian et al., 2017; Huang et al., 2018).

Devido à grande complexidade química da lignina e de sua baixa reatividade e solubilidade, faz-se necessários estudos para ampliar os usos da lignina kraft em uma biorrefinaria e potencializar a sua conversão em produtos de maior valor agregado. Além disso, a lignina tem uma estrutura química heterogênea e de alta polidispersividade (Park et al., 2018), o que pode levar a propriedades indesejáveis, impactando as suas aplicações em novos produtos (Naseem et al., 2016; Roopan, 2017). Alternativas para aumentar a reatividade da lignina podem ser adotadas para potencializar a geração de novos produtos, através da modificação química do licor negro ou da lignina extraída.

As possíveis aplicações da lignina kraft englobam a produção de lignosulfonatos, carbonos técnicos, fibras de carbono, combustíveis de transporte, bioplásticos e adesivos, sendo importante avaliar e obter informações sobre as características que a lignina deve apresentar para cada uso específico.

A produção de lignosulfonatos a partir da lignina kraft é promissora porque atualmente a produção de lignosulfonatos se limita ao processo sulfito, o qual representa 1-2% da produção mundial de polpa celulósica (Konduri e Fatehi, 2015; He e Fatehi, 2015). Os lignosulfonatos provenientes do processo sulfito são utilizados como dispersantes, surfactantes, rações animais, pesticidas, aditivos para perfuração de petróleo, estabilizadores em suspensões coloidais e como plastificantes em misturas de concreto (Fatehi e Ni, 2011; Madad et al., 2011; Vishtal e Kraslawski, 2011; Zhou et al., 2013), e acredita-se que essas aplicações também poderão ser aplicadas aos lignosulfonatos produzidos a partir da lignina kraft.

A geração de lignosulfonatos consiste no processo de sulfonação da lignina kraft, podendo ser realizado através dos métodos de sulfonação ácida ou por sulfometilação. A sulfonação ácida consiste no tratamento da lignina com ácido sulfúrico em altas temperaturas (Compere et al., 2005) e a sulfometilação consiste no tratamento da lignina purificada com sulfito de sódio ou bissulfito de sódio, na presença de um aldeído (formaldeído), ocorrendo uma hidroximetilação através da adição de formaldeído e sulfonação através da utilização de sulfito de sódio (Yu et al., 2013).

A produção de lignosulfonatos a partir de lignina kraft através de reações de sulfonação e sulfometilação dão origem a uma ampla gama de ligninas com diferentes graus

de sulfonação, pesos moleculares e grupos funcionais. Embora a lignina kraft seja completamente solúvel em condições alcalinas, a baixa solubilidade em pH neutro apresenta uma barreira à sua aplicação em sistemas aquosos (Helander et al., 2013). Devido à presença de grupos sulfônicos, os lignosulfonatos são anionicamente carregados e solúveis em água (Aro e Fatehi, 2017), melhorando as propriedades de solubilidade e densidade de carga da lignina kraft.

Para a ampliação do conceito de biorrefinaria nas indústrias kraft, ainda é necessário realizar adequações do processo, como a avaliação da matéria prima utilizada no processo de polpação, o processo de isolamento da lignina kraft do licor negro, modificações estruturais na lignina isolada, otimizações de processos de conversão química e qualidade do produto final. Além disso, a avaliação ambiental dos resíduos e efluentes gerados no processo de conversão química da lignina kraft também devem ser estudados e otimizados.

Na produção de lignosulfonatos pelos processos de sulfonação ácida e sulfometilação, os licores ácido e alcalino gerados podem ser queimados na caldeira de recuperação, juntamente com o licor negro. A grande vantagem da queima desses efluentes é a recirculação de compostos de enxofre e sódio e o aumento do percentual de recuperação de sulfeto de sódio e hidróxido de sódio utilizados na polpação kraft. Assim como o efluente do processo LignoBoost, esses efluentes podem retornar ao ciclo na etapa de evaporação.

O presente estudo foi dividido em três capítulos: i) Capítulo 1 no qual é apresentado uma revisão completa da estrutura da lignina, processos de extração, modificação química da lignina kraft e possíveis aplicações de alto valor agregado dessa lignina; ii) Capítulo 2 no qual é avaliado o efeito do tratamento térmico do licor negro na reatividade da lignina kraft de eucalipto; iii) Capítulo 3 no qual é avaliado a produção de lignosulfonatos a partir da lignina kraft de eucalipto.

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CAPÍTULO 1

BIOREFINERY REVIEW: WIDE-REACHING PRODUCTS THROUGH KRAFT LIGNIN

ABSTRACT

This review details the structure of lignin and curates information on the characteristics that this polymer must have for each specific use. Lignin is a by-product of the pulp and paper industry and the second most abundant biopolymer after cellulose. Approximately 50 million tons of lignin are produced worldwide annually, of which 98% to 99% is incinerated to produce steam, process energy. Just 1% to 2% of the lignin, derived from the sulfite pulp industry, is used in chemical conversion to produce lignosulfonates. Biorefining is a promising approach to promote the wider use of kraft lignin. However, using kraft lignin to produce high value-added products is a great challenge, due to its complex structure, low reactivity, and low solubility, which are factors that limit the lignin's large-scale use in biorefineries. Recent studies show that kraft lignin can be used as lignosulfonates and dispersants, technical carbons, transportation fuels, bioplastics, and adhesives, but some technological hurdles must be overcome and several industrial tests must be developed to make these uses viable.

Keywords: Lignin, biorefinery, kraft, chemical modification, applications

1. INTRODUCTION

Lignocellulosic biomass (wood and non-wood) is the most abundant renewable material in the world, and its three main components are cellulose, hemicellulose, and lignin. The potential scarcity and increase in the price of fossil fuels, as well as increasing environmental restrictions, makes biomass an important source of renewable energy (Garcia-Maraver *et al.* 2015). Besides cellulose and hemicellulose, lignin is recognizable as a potential raw material to produce various products.

Lignin is found in large quantities in the cell wall of wood as a highly branched and amorphous biomacromolecule, and it can be diverse in composition, depending on the vegetal source (Sjöström 1993). It is an aromatic polymer with phenolic hydroxyl groups and is the main organic component present in black liquor of the kraft process (Zhu *et al.* 2014).

As a by-product of the pulp and paper industry, approximately 50 million tons of lignin are produced annually worldwide, of which 98% to 99% of the industrial lignin is incinerated to produce steam and energy, while 1% to 2%, derived from the sulfite pulp industry, is used in chemical conversion to produce lignosulfonates (Mohan *et al.* 2006; Gellerstedt *et al.* 2012; Inwood 2014; Norgren and Edlund 2014). Despite the fact that lignin becomes more valuable after its conversion into chemicals (Macfarlane *et al.* 2009), its application as a source of chemicals remains limited, and most of the kraft lignin in black liquor is combusted as a fuel as well as a reductant of sulfate in sulfur recycling.

The kraft and sulfite processes can effectively solubilize and extract lignin from the lignocellulosic biomass, and they are used all over the world. The kraft process is predominant in the pulp and paper sector, giving rise to sizeable amounts of lignin that could potentially yield high value-added products (Ouyang *et al.* 2009).

The lignocellulose biorefinery concept, based on the chemical separation of the major components (cellulose, hemicelluloses, and lignin) and their further individual processing, is an interesting approach to maximize the added value of the final products (Vila *et al.* 2016). The pulp industries have specific uses for lignin by-products. For example, the kraft pulp industry uses lignin as a fuel feedstock, while in the sulfite industry the lignin is sold to produce lignosulfonates, after a minor chemical treatment. Nevertheless, it is necessary for biorefinery processes to implement strategies to manage lignin and its by-products, which is essential for establishing the economic viability of the processes (Galkin and Samec 2016; Tian *et al.* 2017; Huang *et al.* 2018).

In this context, the biorefining of natural raw materials is a promising approach to

promote the wider use of lignin. Such biorefining is based on the integration of biomass conversion, processes, and equipment to produce fuels, energy, and chemicals. In the last few years, the lignocellulosic biorefineries have focused on the valorization of cellulose and hemicellulose, the alleged sugar-based platform, whereas lignin was generally considered to be a low-value residue (Cherubini 2010; FitzPatrick *et al.* 2010; Doherty *et al.* 2011). Particularly in the case of the kraft pulp industry, removing part of the lignin from black liquor decreases the heat load to the recovery boiler. Therefore, more black liquor can be combusted in the boiler, and the pulp production can be increased if no other bottlenecks exist. In addition, high value-added products can potentially be obtained from the extracted lignin.

The conversion of lignin into valuable products is a way of unleashing its potential. However, according to Vishtal and Kraslawski (2011), the lignin's complex structure, low reactivity, and solubility are the main factors limiting its large-scale use in biorefineries. Additionally, lignin has a heterogeneous chemical structure and high polydispersity, which can lead to undesirable properties, impacting its applications in new products (Naseem *et al.* 2016; Roopan 2017; Park *et al.* 2018).

The use of kraft lignin to produce high-added-value products is a challenge due to the low yield, high costs, the validation of the new products by the performance testing, and the challenges involved in the integration of biorefinery (Wang *et al.* 2019). However, the combination of a growing market and the potential economic gains related to lignin biorefinery increases the interest in research to evaluate its large spectrum of applications. Kraft lignin can be used as lignosulfonates and dispersants, technical carbons (*e.g.*, carbon fibers), transportation fuels, bioplastics, adhesives, *etc.*

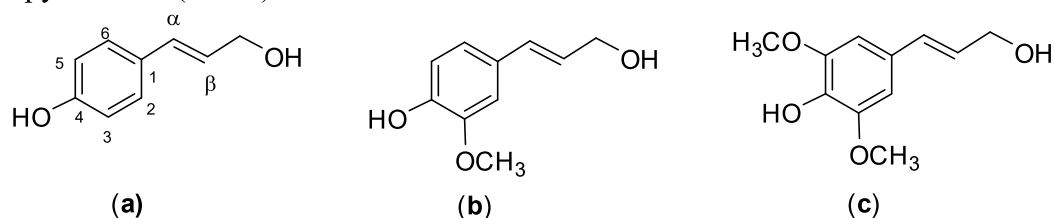
2. LIGNIN BIOSYNTHESIS AND STRUCTURE

Lignin is a natural macromolecule that is biosynthesized from a phenylpropanoid monomer structure, highly amorphous and branched with variable compositions depending on the plant source. In hardwood, lignin makes up 16% to 24% of the composition and 25% to 31% in softwood (Sjöström 1993; Klemm *et al.* 2002). In the cell wall, the lignin is chemically bound to carbohydrates by covalent bonds (benzyl esters, benzyl ethers, and phenyl glycosides), forming a structure of excellent resistance and durability (Smook 2002). The chemical structure of lignin is complex and can be described by the average empirical formula ($C_9H_{10}O_2(OCH_3)_n$), which is based on the phenylpropanoid unit (Kun and Pukánszky

2017).

Like most aromatic constituents of plants, the shikimic acid pathway related to carbohydrates and aromatic amino acids metabolism forms the lignin precursors, which provides the aromatic amino acid phenylalanine, a key step in the lignols biosynthesis (Cesarino *et al.* 2012; Liu 2012). In the course of the reaction, three hydroxycinnamyl alcohols (monolignols) are formed: *p*-coumaryl, coniferyl, and sinapyl, originating the lignins 4-hydroxyl phenyl (H), guaiacyl (G), and syringyl (S), respectively (Figure 1). Their structure differ only regarding the methoxyl groups and its degree of substitution in the aromatic ring.

Figure 1: Monolignol species. (a) *p*-coumaryl alcohol (H unit), (b) coniferyl alcohol (G unit), (c) sinapyl alcohol (S unit).



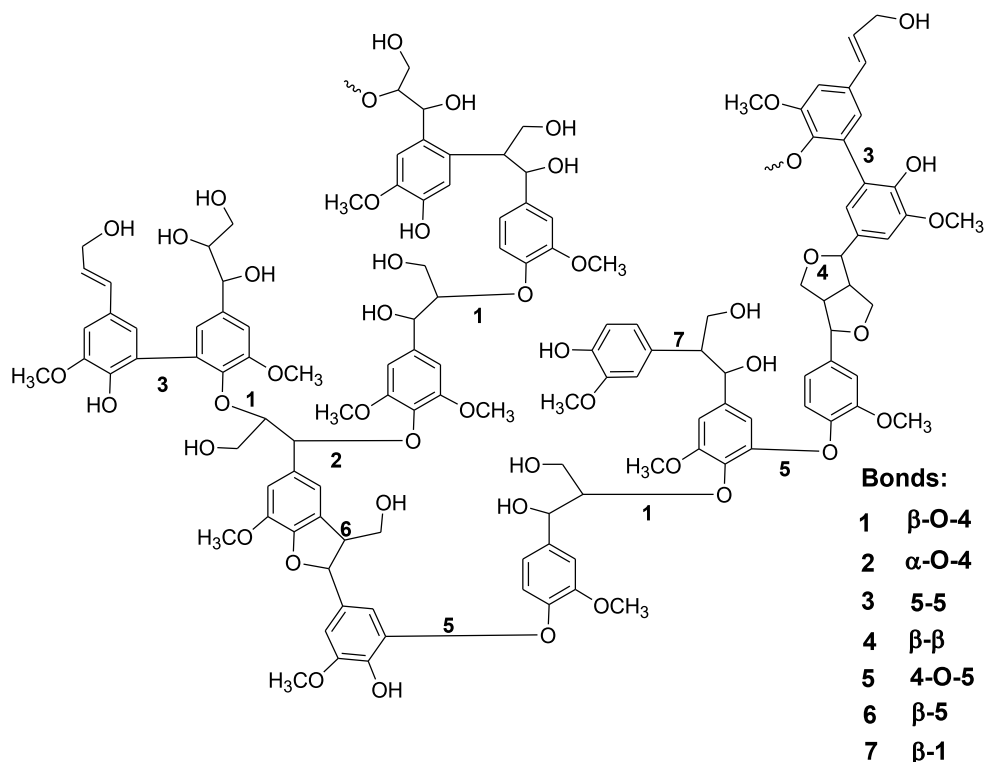
Source: Author

The lignin structure is formed through polymerization by enzymatic oxidation of these three monolignols. The radical sites are initiated by enzymes (*e.g.*, peroxidases or laccases), and the radical-radical combination between lignin monomers leads to the formation of the polymer (Davin *et al.* 2008; Vanholme *et al.* 2010). An important variety of inter-unit linkages is known, with the β -O-4 ether bonds indicating the most important and frequent type of connection between the lignin units in softwoods and hardwoods, representing approximately 50% and 60% of the bonds, respectively (Mašura 1982; Sjöström 1993; Chakar and Ragauskas 2004). In addition, other types of ether bonds (α -O-4, 4-O-5) are found in lignin with C-C covalent bonds (β - β , β -5, β -1, 5-5) (Figure 2).

The lignin macromolecule carries multiple functional groups, which are responsible for its reactivity: hydroxyl (either phenolic or aliphatic), methoxyl, carboxyl, carbonyl, benzyl alcohol, hydrolysable ether linkages, and condensed units in C2, C5, and C6 (Sjöström 1993; Brunow *et al.* 1998; Wang *et al.* 2017). The chemical reactivity and branching degree of lignin is dependent on the ratio of the three monolignols (Boerjan *et al.* 2003; Nanayakkara *et al.* 2009). The different proportions of the monomers in lignin have a high range of variation depending on the type of plant material (*e.g.*, softwood, hardwood, and grasses) and the diversity in inter-unit linkages, resulting in a molecule with a high degree of complexity and

heterogeneity (Norgren and Edlund 2014).

Figure 2: Main linkages in a softwood lignin.



Source: Figure adapted from Windeisen and Wegener (2012)

In softwoods, the G unit is dominant, while hardwood lignin normally contains both S and G units. In grasses, all 3 types of units are found, but the amount of H structures is less remarkable than the others (Gellerstedt and Henriksson 2008; Wang *et al.* 2009). The H/G/S ratio is 0:5/95:100/0 in softwood, 0:4/25:50/46:75 in hardwood, and 2-6/38:68/28:60 in grasses (Pinto *et al.* 2005; Notley and Norgren 2009; Del Río *et al.* 2012; Djajadi *et al.* 2018). Del Río *et al.* (2015) showed that the lignin from sugarcane bagasse is rich in syringyl units (H/G/S molar ratio of 2/38/60), the lignin from sugarcane straw is rich in guaiacyl units (4/68/28), and that both are different in their abundances of the unit linkages.

The G unit has no methoxyl groups linked on the C5 of the aromatic ring, leading to a greater possibility of C-C bonds in this position (Sjöström 1993). Therefore, softwood lignin is more condensed than hardwood lignin, and it is less reactive during kraft processes. According to Norgren and Edlund (2014), the lignin isolation from native sources is accomplished by the cleavage of bonds between different lignin monomers, resulting in the

chemical modification and formation of fragments of different sizes, with C-C bonds proving more difficult to be broken.

3. LIGNIN INDUSTRIAL EXTRACTION PROCESS

The pulp industry is the main commercial source of lignin, which is considered a potential by-product of adding value within the concept of biorefinery (Thakur *et al.* 2014; Jiang *et al.* 2018). The pulping processes are used to separate the lignocellulosic biomass components. The main processes are kraft, sulfite, soda, and organosolv (not commercial). These lignin extraction processes occur in acid and alkaline media or organic solvents, where lignin is progressively broken into low molecular weight fragments, resulting in changes in its physical-chemical properties (Doherty *et al.* 2011).

The various processes cause significant degradation and change the structure of the native lignins with a reduction in the amounts of aliphatic OH groups, β -O-4, and β - β bonds. Additionally, it is possible to observe an increase in the quantities of phenolic hydroxyl groups, carboxylic acids, and carbonyl groups, and in the degree of condensation, due to the formation and/or accumulation of condensed lignin structures (Capanema and Balakshin 2015). Therefore, the structure of the technical lignins is typically dependent on the extraction method and the raw material of origin (softwood, hardwood, or grasses) (Berlin and Balakshin 2014; Capanema and Balakshin 2014).

Currently, the sulfite process is responsible for the generation of lignosulfonates, but the kraft process is the most widespread and dominant worldwide. For these reasons, these two processes are detailed below.

3.1 Sulfite Process

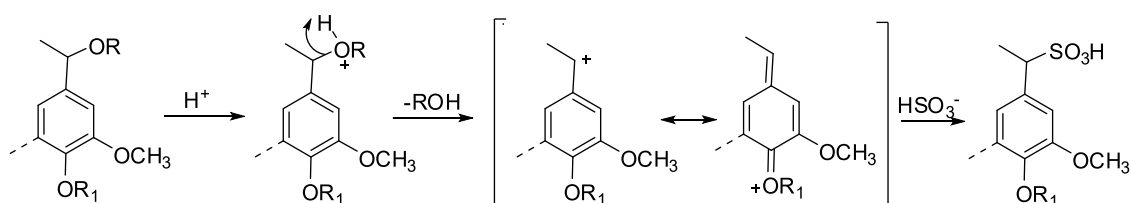
Regarding pulp production, the sulfite process is quantitatively less noticeable when compared to kraft process, but it is the most important in terms of marketable lignin, *e.g.* lignosulfonates with an annual production of approximately 1.8 million tons (Aro and Fatehi 2017).

Traditionally, lignosulfonates are obtained as by-products of sulfite cooking. The wood delignification is carried out by SO_2 and HSO_3^- (acid sulfite), HSO_3^- (bisulfite), or HSO_3^- and SO_3^{2-} (neutral sulfite), usually in the presence of a cation, such as sodium, calcium, magnesium, or ammonium, noting that the solubility of each specific sulfite salt is dependent on pH (Fan and Zhan 2008; Calvo-Flores and Dobado 2010).

The pulping reactions are generally conducted between 140 °C and 160 °C, and the process pH is between 1.0 and 2.0 (acid sulfite), 3.0 and 5.0 (bisulfite), and 6.0 and 7.0 (neutral sulfite). The proportions of sulfite, bisulfite, and sulfur dioxide depend on the pH of the reaction medium, and this affects the path of lignin degradation (Sjöström 1993; Smook 2002).

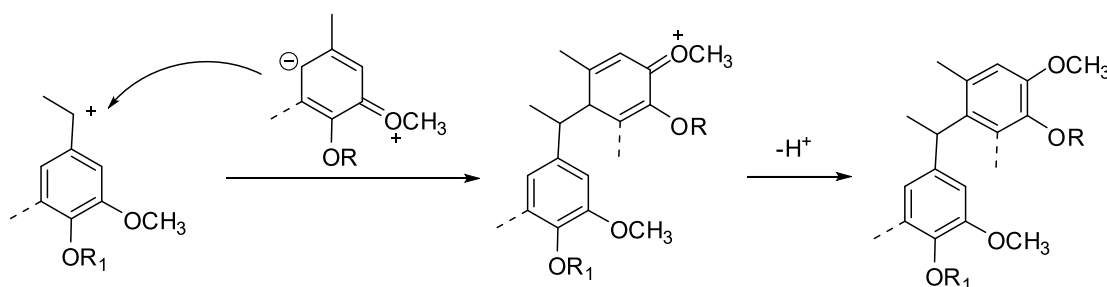
In the sulfite process, the main reactions that cause lignin solubilization are sulfonation and acid hydrolysis (Elumalai and Pan 2011). The mechanisms involve the loss of a hydroxyl group or the cleavage of the ether bond (α -O-4), generating quinone methide intermediates by means of a resonance-stabilized benzylic cation (Figure 3) (Doherty *et al.* 2011; Matsushita 2015). Subsequently, large amounts of sulfur become covalently bonded with the lignin as sulfonate groups ($-\text{SO}_3^-$) attach to α -carbon in amounts ranging from 0.4 to 0.5 sulfonate groups per C9 unit (Goring 1971; Sjöström 1993; Gellerstedt and Henriksson 2008; Lora 2008; Calvo-Flores *et al.* 2015). Instead of sulfonation, there may be a condensation reaction involving the benzylic carbon of one molecule and another electron-rich carbon atom due to the presence of the benzylic cation (Figure 4). This condensation tends to block the sulfonation reaction from occurring in the α -position (Doherty *et al.* 2011; Matsushita 2015).

Figure 3: Sulfonation reaction occurring during acidic sulfite pulping.



Source: Figure adapted from Matsushita (2015)

Figure 4: Condensation reaction occurring during acidic sulfite pulping.



Source: Figure adapted from Matsushita (2015)

Sulfite pulping does not selectively remove lignin; thus, carbohydrates are highly

solubilized (particularly hemicelluloses). The liquor resulting from the sulfite process contains a high content of sugars and chemicals used during the process. The sugar content is an important property of the industrial lignosulfonates because their presence may have negative implications in some applications (Forss *et al.* 1985). Several purification steps are necessary to obtain lignosulfonates with a higher purity and added value, including fermentation to convert the residual sugars into ethanol, membrane separation, and ultrafiltration (Lora 2008; Aro and Fatehi 2017).

The lignosulfonates generated by the sulfite process have two main ionizing groups, the sulfonates ($\text{pK}_a \leq 2$) and the phenolic hydroxyl groups ($\text{pK}_a \sim 10$), in addition to approximately 5% by weight of sulfur content (Doherty *et al.* 2011). The high water-soluble characteristic attributed to lignosulfonates is due to the low pK_a of the sulfonate groups, the variety of functional groups, and other structural characteristics that provide unique colloidal properties to these lignins (Areskog *et al.* 2010; Areskog and Henriksson 2011; Duval and Lawoko 2014).

When compared to kraft lignin ($\text{MW} = 1,000$ to $5,000$ g/mol), lignosulfonates generally have higher molecular weights, since only a small part of the more frequent β -O-4-ether bonds reacts in the pulping process (Aro and Fatehi 2017; Kun and Pukánszky 2017). However, molecular weights may also vary depending on the raw material, with hardwood lignosulfonates exhibiting lower molecular weights ($\text{MW} = 5,700$ to $12,000$ g/mol) compared to softwood lignosulfonates ($\text{MW} = 36,000$ to $61,000$ g/mol) (Braaten *et al.* 2003).

The conditions of the pulping process result in different physicochemical properties of lignosulfonates (Aro and Fatehi 2017). For example, the use of sodium cations produces extended lignin chains, which are more suitable for use as dispersants, while calcium cations produce compact lignin chains (Doherty *et al.* 2011). The lignosulfonates generally have a wide range of uses, such as dispersants, surfactants, animal feed, pesticides formulation, petroleum drilling additives, stabilizers in colloidal suspensions, and as plasticizers in concrete mixtures, which comprise cement, sand, and aggregate (Lora 2008; Fatehi and Ni 2011; Vishtal and Kraslawski 2011; Zhou *et al.* 2013).

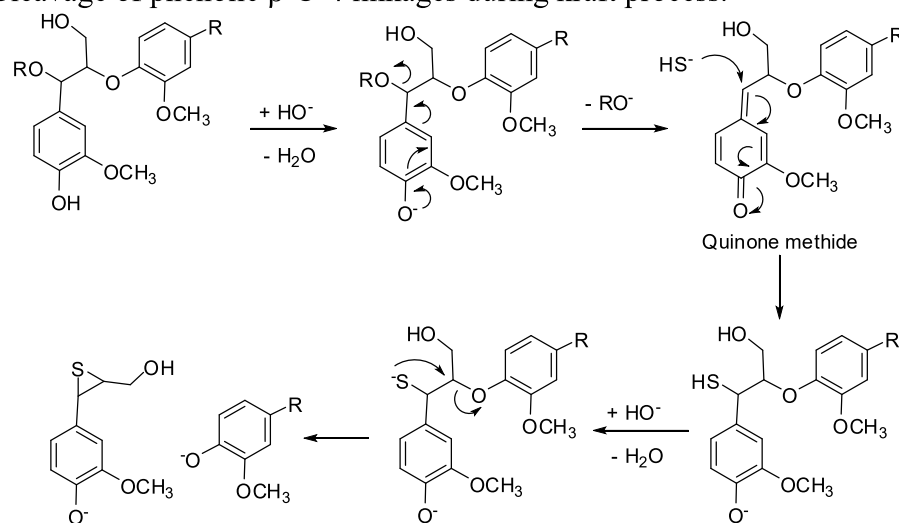
3.2 Kraft Process

Kraft is the world's dominant pulping process. During the kraft process, wood is converted into pulp using a solution of Na_2S and NaOH (white liquor) at a temperature of 155 °C to 175 °C. In addition, the lignin macromolecule must be degraded and solubilized to a

large extent, and the pulping conditions are highly dependent on the chemical structure of the macromolecule (Potthast 2006).

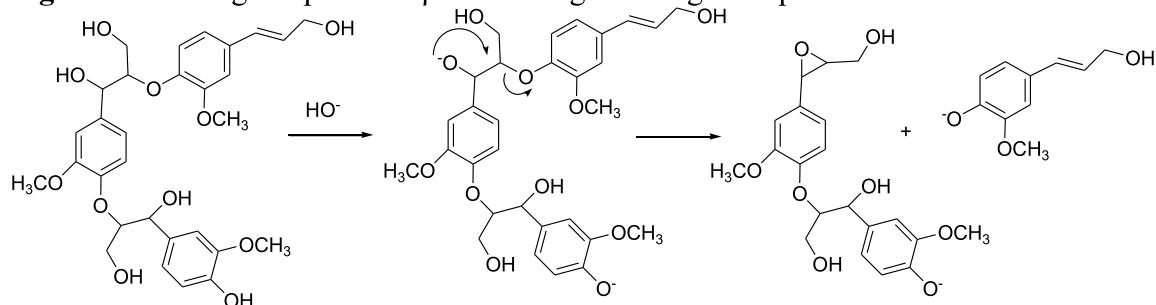
During pulping under alkaline conditions, the degradation or dissolution of phenolic lignin units involves the ionization of phenolic groups and the formation of the quinone methide, an unstable intermediate species (Figure 5). The bisulfide ions (HS^-) are strong nucleophiles. When present in the liquor, they react with the quinone methide, resulting in the hydrolysis of β -aryl ether bonds (Gierer 1980). A common characteristic of the kraft process is the nucleophilic reaction of species such as HO^- , HS^- , and S^{2-} (their nucleophilicity increases in the order $\text{HO}^- < \text{HS}^- < \text{S}^{2-}$) with electron-deficient centers in the lignin molecule, resulting in the cleavage of lignin interconnections and a higher hydrophilicity of resulting lignin fragments and thus, a better dissolution in the cooking liquor (Potthast 2006). Additionally, the breakage of β -aryl ether bonds occurs in non-phenolic structures of lignin under specific conditions (*e.g.*, the presence of an HO^- group in the α -carbon) (Figure 6).

Figure 5: Cleavage of phenolic β -O-4 linkages during kraft process.



Source: Figure adapted from Gierer (1980)

Figure 6: Cleavage of phenolic β -O-4 linkages during kraft process.



Source: Figure adapted from Gierer (1980)

The hydrolysis of the β -aryl ether bonds is important because it comprises 40% to 70% of the lignin interunit linkages. However, the hydrolysis of the α -aryl and α -alkyl ether bonds occurs during the kraft pulping process, in addition to the β -aryl ether bonds (Gierer 1980).

The reactivities of the lignin subunits differ greatly, with the phenolic lignins being noticeably more reactive than the non-phenolic lignin units. Additionally, softwood lignin is less reactive than hardwood lignin, which is due to the G-lignin containing higher amounts of C-C bonds at the C5 position (Sjöström 1993). In general, the kraft lignin contains characteristics that differentiate it from both native lignin and other classes of lignins. Kraft lignin has abundant phenolic hydroxyl groups, which arise due to the extensive breakage of β -O-4 linkages during the kraft cook (Chakar and Ragauskas 2004).

In addition to the degradation reactions of lignin, condensation reactions occur during kraft pulping, which increase the molecular size of the lignin fragments. Despite having the opposite effect in the delignification process, these two types of reactions are closely related because they proceed through common intermediates (Gierer 1980).

Black liquor is generated by the kraft process as a residual liquor, characterized by the presence of inorganic components as well as organic components that have been removed from the wood. The organic material consists of lignin fragments and hydroxy acids derived from carbohydrates (mainly hemicelluloses) that have been degraded by alkali-catalyzed reactions. According to Krotscheck and Sixta (2006), the black liquor chemical composition depends on the wood species, the composition of and amount of white liquor (solution of Na_2S and NaOH), the unbleached pulp yield, and the volume of recycled filtrates from the oxygen delignification stage (O-stage). This O-stage uses alkali and oxygen to remove a substantial portion of the residual lignin in the unbleached pulps before a bleaching process. In the pulp mill, the filtrate from the O-stage can be incorporated into the chemical recovery system together with the black liquor, if the recovery boiler has sufficient capacity to handle the extra load (Kvarnlöf and Germgård 2015).

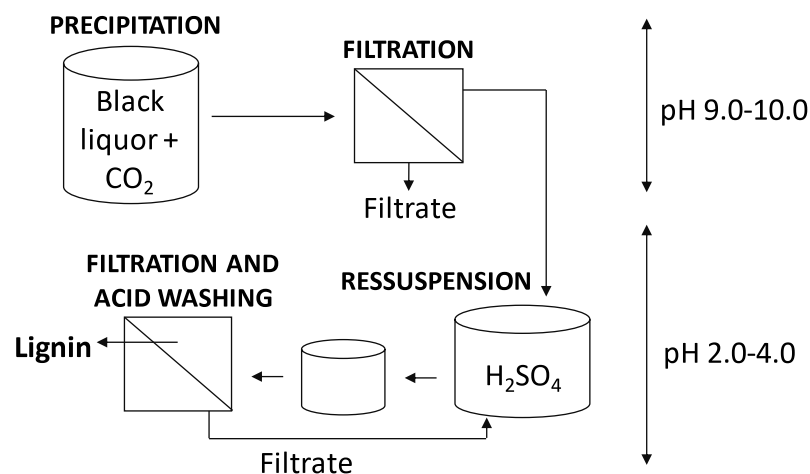
In pulp and paper mills, black liquor is burned in the recovery boiler, which serves as a source of steam for electricity generation and for the drying of paper. Through the kraft recovery cycle, it is possible to recover the inorganic chemical compounds used in the cooking process, providing lower production costs and a considerable reduction of effluents production (Reeve 2002; Tran and Vakkilainen 2008).

The isolation of lignin from black liquor is an important step when converting the pulp mill into a biorefinery to improve the pulp mill throughput and increase the added value of lignin *via* the generation of usable products (Zhu *et al.* 2014). Several methods have been

evaluated for the separation and purification of lignin (Jönsson *et al.* 2008; Bhattacharjee *et al.* 2006; Arkell *et al.* 2014). The extraction process should be simple and easy, producing a high-yield, isolated lignin, that is free of contaminants (Lin and Dence 1992). Currently, the most commercialized process to recover lignin from black liquor is known as “LignoBoost” (Theliander 2008).

In this process, a black liquor stream is withdrawn from evaporators of the kraft process recovery (dry solid content of 30% to 45%) and is acidified with CO₂ to a pH of 9.0 to 10.0 at 60 °C to 80 °C. The lignin is precipitated at this pH in a precipitation tank and filtered. The precipitated lignin is re-dispersed in an acidic filtrate suspension tank with pH controlled at 2 to 4 (Figure 7). The resulting lignin is then filtered and washed by acid displacement washing (pH of 2 to 3) (Kalogiannis *et al.* 2015). Unlike the lignin separation process during a single stage, the change in pH, ionic strength, and lignin solubility occur mainly in the re-dispersion tank and not during the final stage of lignin washing, and this improves the properties of the precipitated lignin (Öhman *et al.* 2007; Tomani 2010; Fatehi and Chen 2016).

Figure 7: The LignoBoost process for isolation of kraft lignin.



Source: Author

The LignoBoost process has a high lignin yield, high-purity lignin with low ash and carbohydrate contents, low investment costs due to reductions in acid wash volume, and low operating costs due to a reduction in the amount of H₂SO₄ required (Tomani 2010). According to Hu *et al.* (2018), the plant at the Stora Enso Sunila Mill (Kotka, Finland) and the plant at the Domtar Plymouth Mill (Plymouth, NC, USA) manufacture 75,000 tons of kraft

lignin per year using the LignoBoost process.

The pH of black liquor is high (pH of 13 to 14), contributing to a high solubility of lignin due to the ionized phenolic groups present in the molecules. The lignin precipitation results from the acidification of black liquor, which results in the protonation of these ionized phenolic groups, reducing the electrostatic repulsive forces between lignin molecules, and making them less hydrophilic (Sundin 2000; Vainio *et al.* 2004). Protonation takes place to a greater extent at a given pH, in cases where the pKa value is higher, which is influenced by the temperature, the ionic strength of the solution, and the molecular structure of the lignin (Rudatin *et al.* 1989; Norgren and Lindström 2000; Ragnar *et al.* 2000).

The structural difference of softwood and hardwood lignins, according to the type of monolignol units present [softwood (G) or hardwood (G and S)], has implication for the reactivity of lignin during kraft pulping, and for the kraft lignin extracted properties. Due to availability of the C5 position, G-type lignins contain more C-C bonds, *e.g.* β -C5 and C5-C5, when compared to S-type lignins (Sjöström 1993). According to Zhu and Theliander (2015), precipitated softwood lignin specimens contain lower amounts of methoxyl groups than a mix of hardwood and softwood lignin.

In addition, kraft lignin properties can be altered according to the conditions used during the LignoBoost process. A lower pH and/or lower temperature and a greater ionic strength in black liquor results in a higher precipitation yield. Under these conditions, the precipitated kraft lignin has a lower average molecular weight and the lignin has a higher number of phenolic groups (Zhu and Theliander 2015).

The main factors that limit the large-scale use of precipitated lignins in biorefineries are the large chemical and molecular variation, their complex structure, low reactivity, and low solubility (Vishtal and Kraslawski 2011; Park *et al.* 2018). Studies in order to improve solubility and reactivity of lignin may be developed to potentiate the production and generation of high value-added products.

To improve homogeneity and reduce the complexity of lignin, fractionation techniques by an eluotropic series of organic solvents and precipitation by the pH effect are potential solutions (García *et al.* 2009; Wang and Chen 2013; Li and McDonald 2014; Santos *et al.* 2014; Duval *et al.* 2015). In addition, the use of ceramic membranes having different cut-offs has been widely researched (Wallberg *et al.* 2003; Toledano *et al.* 2010). These techniques allow lignin to be produced with more uniform molecular weights and low polydispersity fractions (Francuskiewicz 1994; Li and McDonald 2014; Duval *et al.* 2015; Jääskeläinen *et al.* 2017).

Based on the chemical and molecular variations of the precipitated lignins, many possibilities of modifying its structure have been studied to increase the reactivity, to enhance its applications, and to increase the added value of this pulp industry by-product (Hu *et al.* 2011; Laurichesse and Avérous 2014).

4. KRAFT LIGNIN MODIFICATION

Kraft lignin has limited industrial applications, and it requires modifications to increase its potential for use as a starting material for polymer and chemical synthesis. However, due to the structural complexity and heterogeneity of lignin, such modifications are challenging. Without any modification, the most reactive site in the kraft lignin is the α -position of the phenylpropene subunits (Heden and Holmberg 1936). However, this reactive α -site can be occupied by ether bonds (*e.g.*, α -O-4 aryl), or be sterically hindered because of β -O-4 linkages and other interconnecting bonds, lowering the reactivity of kraft lignin (Inwood 2014).

According to Laurichesse and Avérous (2014), the chemical modification of lignin can be performed through the fragmentation of lignin, the chemical modification of hydroxyl groups, and the creation of new chemically-active sites. To increase the reactivity of the lignin, various methods have been described for modifying its structure, including demethylation, oxidation, hydrolysis, reduction, phenolation, and hydroxymethylation (Li and Geng 2005; Effendi *et al.* 2008; Hu *et al.* 2011; Inwood 2014; Dai *et al.* 2016; Zuluaga *et al.* 2018).

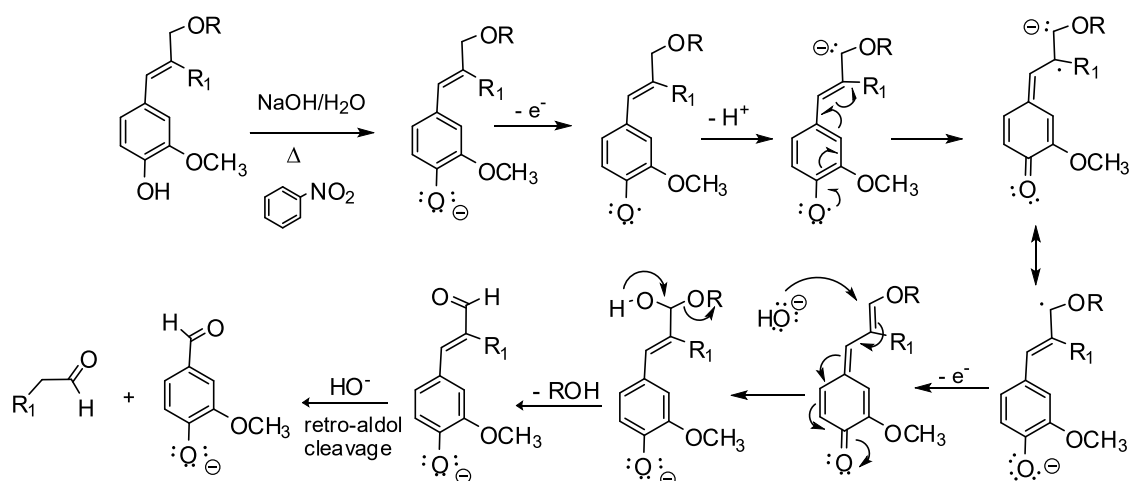
In the lignin structure, the C3 e C5 positions of the aromatic ring can be substituted by one or two methoxyl groups (-OCH₃), and these groups can interfere with the reactivity of the free phenolic hydroxyl group. The demethylation results in lignin with free phenolic groups instead of modifying lignin to form catechol groups (Okamoto *et al.* 1996; Hu *et al.* 2011). Sulfur-mediated demethylation and enzymatic oxidative cleavage can remove the methyl groups (Wu and Zhan 2001; Filley *et al.* 2002). However, in recent studies, a thermal treatment of black liquor prior to the lignin extraction was performed to obtain a significant level of demethylation and demethoxylation in the kraft lignin, a technology known as catechol (CAT) lignin (Wikberg *et al.* 2017). During the CAT lignin process, a lignin rich in catechol is produced, thus increasing the number of reactive sites. According to Leppävuori *et al.* (2017), in hardwood lignins, the methoxycatechol units that are formed primarily by demethylation and the demethoxylation will activate the *ortho* positions of the lignin phenolic

unit (C3 and C5).

Lignin oxidation is one way to obtain phenolic derivatives, and the oxidative lignin depolymerization increases the reactivity of lignin through selective bond cleavage of the β -O-4, aryl ether, and C-C types (Dai *et al.* 2016). The application of different oxidants (*e.g.*, nitrobenzene, oxygen gas, hydrogen peroxide, and metal oxides) allows the production of functionalized products that range from aromatic aldehydes (vanillin and syringic) to acids (vanillic and syringic). Nitrobenzene is the aromatic oxidant that promotes the highest yield of derivatives from lignin (Laurichesse and Avérous 2014). To obtain fractions with high value-added compounds, lignins are oxidized under the optimized conditions of temperature, time, and air pressure, with vanillin being considered the most well-known and valuable product from lignin.

The formation of an aldehyde through the oxidative degradation of lignin using alkaline nitrobenzene has been described as a one-electron transfer process (Nandanwar *et al.* 2016; Fache *et al.* 2016; Tarabanko and Tarabanko 2017). This process is demonstrated in Fig 8 with nitrobenzene, but another oxidant can be used. According Fache *et al.* (2016), there are many parameters influencing the process, which increase the complexity of the mechanism.

Figure 8: Reaction pathway of softwood lignin oxidation giving rise to vanillin.



Source: Figure adapted from Fache *et al.* (2016)

Hydrolysis is a method to break the ether bonds of lignin, which results in the production of low molecular mass phenolic compounds (Hu *et al.* 2011). This process can be performed with near- and super-critical water using a batch type reactor and an alkaline treatment with NaOH (Nenkova *et al.* 2008; Wahyudiono *et al.* 2008). Despite the fact that

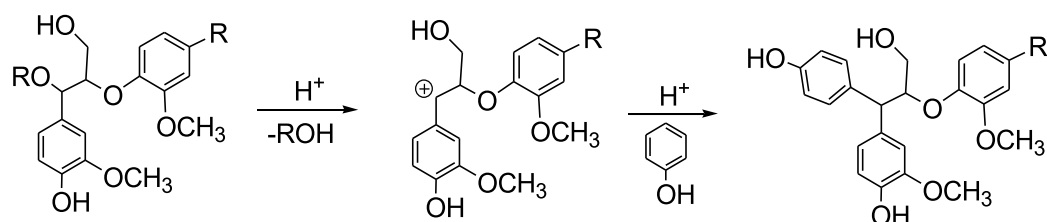
hydrolysis increases the lignin reactivity, it decreases the molecular weight, which is undesirable for some applications, *e.g.*, flocculants and dispersants.

The reduction of lignin takes place during the production of alcoholic groups through the reduction of aldehydes and ketones in the lignin. Some reducing reagents that can be used in this process are lithium aluminum hydride (LiAlH_4) and sodium borohydride (NaBH_4). According to Li and Geng (2005), a demethylated lignin reaction with NaBH_4 can form catechol groups, which are regarded as having a higher reactivity than phenol. A strong reagent for hydrogenation (*i.e.*, lithium aluminum hydroxide) can be used to reduce certain groups such as acid and ester, in addition to the aldehydes and ketones into alcohol, although this reagent is selective and does not react with the C-C bonds in lignin (Hu *et al.* 2011).

The phenolation process consists of the treatment of the lignin with phenol in a solution of organic solvents, *e.g.*, methanol or ethanol (Effendi *et al.* 2008). During the phenolation process in an acidic medium, the phenol condenses in the lignin's aromatic ring at the *ortho* site relative to the hydroxide group through aromatic substitutions as well as within the chain at the α position (Figure 9) (Brunow 2005; Inwood 2014; Jiang *et al.* 2018). Gao *et al.* (2019) demonstrated that the phenolation of lignin also can occur at the reactive γ position by substitution of aliphatic hydroxyl groups. The phenolation reaction is an acidolytic process, where electrophilic substitution reactions of phenolation and condensation occur simultaneously (Huang *et al.* 2017; Gao *et al.* 2019).

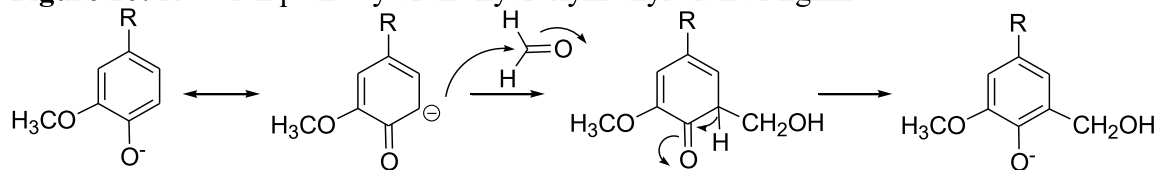
According to Hu *et al.* (2011), the phenolation process, as well as hydroxymethylation, are more effective at increasing the reactivity of lignin when compared with reduction, oxidation, and hydrolysis. The goal of the hydroxymethylation process is to introduce hydroxymethyl groups ($-\text{CH}_2\text{OH}$) to lignin molecules (Figure 10), which increases the reactivity of the *ortho* bonding site in relation to the hydroxide group on the phenyl propene subunit (Yasuda *et al.* 1999; Zuluaga *et al.* 2018).

Figure 9: Reaction pathway of the phenolation of β -O-4 structure of lignin



Source: Figure adapted from Jiang *et al.* (2018)

Figure 10: Reaction pathway of the hydroxymethylation of lignin.



Source: Figure adapted from Zuluaga *et al.* (2018)

5. KRAFT LIGNIN AS HIGH ADDED VALUE PRODUCT

Kraft lignin has a combination of a growing market and a high-level purity in its end-product, which increases its potential for applications in high value-added products. Based on the biorefinery concept, several studies are being carried out to develop wider uses for kraft lignin. In many cases, it is necessary to tune the extraction process or add a process step to reach a specific requirement. When the goal is to improve the reactivity and homogeneity of kraft lignin to compete with petroleum products, depolymerization techniques and chemical modification should be adopted.

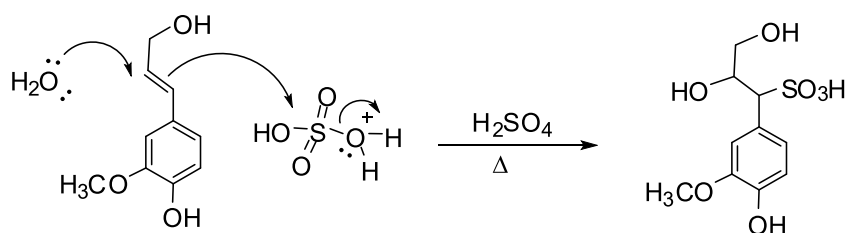
5.1 Lignin as liginosulfonates and dispersants

The production of liginosulfonates from kraft lignin through sulfonation reactions give rise to a wide range of lignins with different degrees of sulfonation, molecular weights, and functional groups. Although kraft lignin dissolves readily at a high pH, it exhibits poor solubility at a near-neutral pH, and this hinders its use in many systems involving aqueous solutions (Helander *et al.* 2013). Due to the presence of sulfonic groups, the liginosulfonates are both anionically charged and water-soluble, improving the properties of solubility and charge density of kraft lignin (Aro and Fatehi 2017).

Due to the limited production of liginosulfonates by the sulfite process, an increasing amount of studies focusing on acid sulfonation or sulfomethylation of technical lignins have been performed for the generation of water-soluble sulfonated lignin to satisfy the market demand (He and Fatehi 2015; Konduri and Fatehi 2015). Acid sulfonation consists of the treatment of kraft lignin with sulfuric acid at high temperatures (Inwood 2014). According to Dilling (1991), depending on the degree of sulfonation, the sulfonated lignin may exhibit complete solubility in water at all pH levels.

In this sulfonation, the $-\text{SO}_3\text{H}$ groups are linked to the aliphatic side chain of the lignin molecule, and the reaction occurs at the α -carbon of the phenyl propane unit (Figure 11) (Inwood 2014; Sjöström 1993).

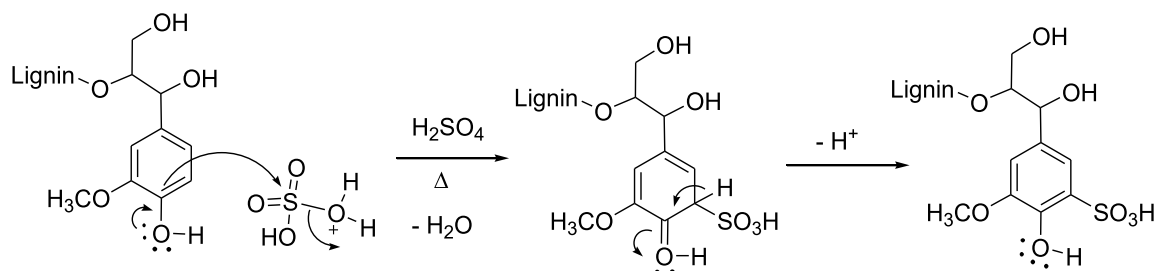
Figure 11: Sulfonation of kraft lignin with sulfuric acid ($-\text{SO}_3\text{H}$ groups linked on the aliphatic chain).



Source: Figure adapted from Inwood (2014)

According to Gao *et al.* (2019), the $-\text{SO}_3\text{H}$ groups can also be linked to aromatic groups, in H and G units of kraft lignin (Figure 12). A disadvantage of acid sulfonation is that kraft lignin may form condensed structures in the acidic conditions, impairing an extent of lignin sulfonation and its reactivity (Huang *et al.* 2017).

Figure 12: Sulfonation of kraft lignin with sulfuric acid ($-\text{SO}_3\text{H}$ groups linked on the aromatic groups).

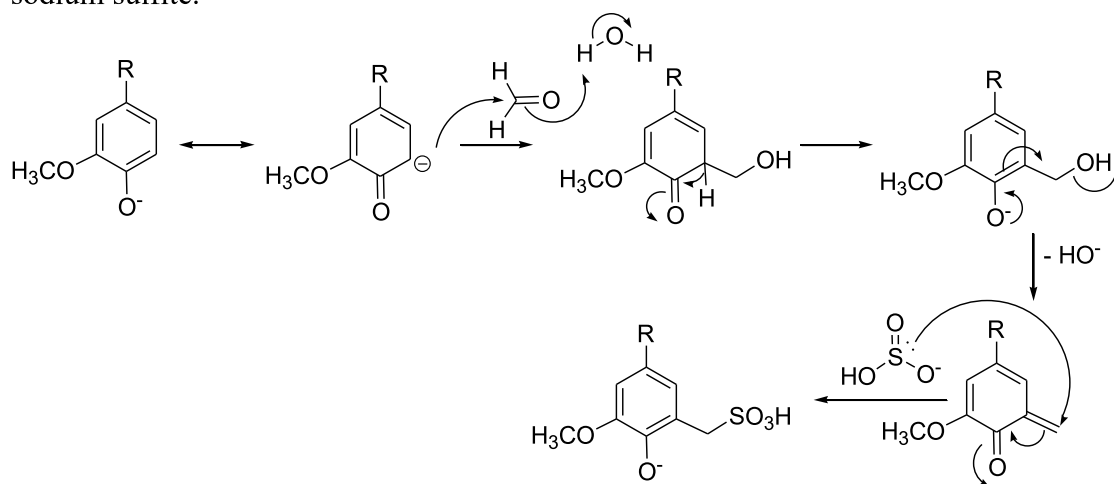


Source: Figure adapted from Gao *et al.* (2019)

Sulfomethylation is another alternative to produce sulfonated kraft lignin, and it consists of the treatment of purified lignin with sodium sulfite or sodium bisulfite in the presence of an aldehyde (formaldehyde). Therefore, hydroxymethylation occurs through the addition of formaldehyde, and sulfonation occurs through use of sodium sulfite or sodium bisulfite (Yu *et al.* 2013). The sulfomethylation reaction of the kraft lignin introduces $-\text{CH}_2\text{SO}_3\text{H}$ groups into the aromatic ring of the lignin structure, according to the mechanism proposed in Figure 13. Note that lignosulfonate production through sulfomethylation runs through a mechanism completely different from those of the sulfite pulping process and acid

sulfonation, in which the sulfonic acid groups are in the aliphatic chain (Berlin and Balakshin 2014). According to Kamoun *et al.* (2003), in the sulfomethylation reaction, the introduction of sulfonate groups into the aliphatic side chain of the lignin molecule may also occur in the presence of excess sulfite.

Figure 13: Proposed mechanism for sulfomethylation of kraft lignin with formaldehyde and sodium sulfite.



Source: Author

However, the sulfomethylation reaction in the aromatic ring is possible only in the guaiacyl lignin present in black liquor, which has the aromatic carbon at the C5 position available for sulfomethylation. Therefore, the sulfomethylation of hardwood kraft lignin is a challenging process due to the high content of low reactivity syringyl lignin present in the kraft liquor.

The kraft lignin can be sulfonated to various degrees, depending on the process conditions. Each water-soluble sulfonated lignin is evaluated through solubility, molar mass distribution, and hydrophilic character (Kamoun *et al.* 2003). Several applications have been suggested for sulfonated lignins, and the dispersants and additives for concrete (plasticizers) seem to have the most potential.

The preparation of water-soluble sulfonated lignin can be performed with both wood and non-wood lignins. Sulfomethylated lignin from sugarcane bagasse, esparto grass, and a mixture of hardwood were used as dispersant and cement additives (Kamoun *et al.* 2003; Li and Ge 2011; Konduri and Fatehi 2015). An increase in the degree of sulfonation through the sulfomethylation of kraft lignin will increase the charge density. This provides a lower viscosity to the cement paste in comparison to commercial lignosulfonates and acid

sulfonation. The sulfur content of sulfonated lignin is essential for its solubility and dispersion (Aro and Fatehi 2017).

In a study by Inwood (2014) with softwood kraft lignin, the acid sulfonation and sulfomethylation were evaluated, in addition to the application of the products as dispersants and flocculants. In the sulfuric acid treatment, adding charged groups to lignin at an α -position occurs on the aliphatic chain. However, lignin condensation (*i.e.*, the polymerization of lignin) can occur on the same site (Yasuda *et al.* 1999). Due to the balance of these possible reactions, some conditions may negatively influence sulfonation (*e.g.*, temperature). An increase in temperature decreased the charge density because the condensation reaction required less energy than lignin modification (Zoumpoulakis and Simitzis 2001). After optimizing the conditions, a sulfonated lignin with a charge density of 0.75 mEq/g and a solubility of 8% was produced.

However, Gao *et al.* (2019) showed that during acid sulfonation the $-\text{SO}_3\text{H}$ groups may also be linked on the aromatic chain, evidencing that this treatment can be effective in sulfonation of kraft lignin.

Sulfomethylation of softwood kraft lignin was performed on previously hydroxymethylated lignin (H-lignin) with formaldehyde (Inwood 2014). The sulfonation with sodium sulfite of this pretreated lignin yielded material having a charge density of 1.2 mEq/g and solubility of 100%, evidencing better results when compared with acid sulfonation. The molecular weight (MW) of kraft lignin increased from 25,100 g/mol to 37,161 g/mol, which indicates a slight condensation of lignin. The MW of hydroxymethylated lignin (prior to sulfonation) was 45,420 g/mol, with the decrease being attributed to hydrolysis, which occurs at a high pH (Mao *et al.* 2012). The hydrolysis of H-lignin is the dominant reaction, though in addition, condensation in alkaline conditions can occur (Gierer and Petterson 1977). According to Matsushita and Yasuda (2005), the increase in the molecular weight helps promote effective dispersion processes due to the application of a larger steric force, thus increasing the efficiency of the products as dispersants.

Sulfomethylated hardwood kraft lignin was successfully prepared by using sodium sulfite and formaldehyde (Konduri and Fatehi 2015). The conditions were optimized, and the unmodified lignin had a negligible charge density and 0.03 mmol/g of the sulfonate group, while the sulfomethylated lignin presented -1.6 mEq/g charge density and 1.48 mmol/g of the sulfonate group. The molecular weight increased *via* sulfomethylation from 22,746 g/mol to 53,360 g/mol, and the solubility analysis confirmed the high solubility (40 g/L) of sulfomethylated hardwood kraft lignin at a neutral pH. In contrast, the unmodified lignin was

insoluble at pH 7.

In addition to the benefits of increasing the charge density and sulfonic groups in kraft lignin for the various applications, Huang *et al.* (2018) observed a high lignosulfonate yield (94.9%) through the sulfomethylation of the bamboo kraft lignin with sodium sulfite and formaldehyde, evidencing that the process may be industrially viable.

5.2 Lignin as technical carbons

The structure and composition of lignin, which is the largest biomass source with aromatic properties and a carbon content above 60%, make it an ideal precursor to produce advanced carbon materials (Chatterjee and Saito 2015). Carbon fibers, activated carbons, and carbon black are some of the products that can be obtained by thermochemical conversion of kraft lignin (KL) (Rosas *et al.* 2014).

Carbon fiber is a material with excellent mechanical properties and low density. It is widely used in structures that need to be lightweight but strong, such as sports equipment and in the automotive and aerospace industries (Li *et al.* 2017a). Carbon fiber production from kraft lignin represents one of its highest value-added products and is discussed in the next topic.

Activated carbon (AC) usually exhibits properties suitable for use as adsorbents, and accordingly it is applied in gas and fluid streams, gas separation, catalyst supports, filtration systems, and electrochemical applications (Bansal and Goyal 2005; Puziy *et al.* 2018). Activated carbon has thermal and chemical stability in both acidic and alkaline media, easy modification of its chemical surface, well-developed porous structure (with a large internal surface area ranging from 500 m²/g to 2000 m²/g), and good adsorption capacities (Suhas *et al.* 2007; Rosas *et al.* 2010).

Non-renewable coal-based resources are used to produce approximately 80% to 85% of the total production of activated carbon (Ragan and Megonnell 2011). Kraft lignin can partially substitute these non-renewable resources in AC production, due to its high carbon content and high yield of carbon, which is beneficial for the manufacture of AC. In addition, the use of renewable resources reduces carbon emissions during the production process (Puziy *et al.* 2018). However, the low reactivity of lignin is a challenge for obtaining a quality technical carbon, with high yield and suitable textural properties (Li *et al.* 2014). Besides that, adjustments in the production process may be necessary.

The manufacture of activated carbon is a two-stage process: (1) carbonization and (2)

physical or chemical activation (Ragan and Megonnell 2011). In physical activation, the carbonization process is carried out to form a char (normally nonporous) *via* pyrolysis, in an inert atmosphere. The char is then activated through contact with an oxidizing gas, resulting in the formation of a well-developed micropore structure (Suhas *et al.* 2007; Rosas *et al.* 2014).

Preparation of activated carbons from eucalyptus kraft lignin through physical activation with CO₂ at 800 °C to 850 °C has been reported as a viable method (Rodríguez-Mirasol *et al.* 1993a,b; Bedia *et al.* 2007; Cotoruelo *et al.* 2012a, 2012b). The maximum specific surface area is found to range from 700 m²/g to 1900 m²/g. According to Suhas *et al.* (2007), although they observed high surface areas, the activation times were considerably long, which confirms the low reactivity of lignin due to its cross-linked nature. Fu *et al.* (2013) used black liquor to prepare AC through physical activation with steam and found the maximum specific surface area to be 310 m²/g. In this case, the specific surface area was negatively influenced by the higher periods and higher temperatures required for activation.

Impregnation with chemicals such as H₃PO₄, KOH, NaOH, Na₂CO₃, K₂CO₃, H₂SO₄, and ZnCl₂ was followed by heating under a nitrogen flow simultaneously with carbonization. Compared with the physical method, this method produces an activated carbon with higher micropore volumes and wider micropore sizes (Suhas *et al.* 2007; Supanchaiyamat *et al.* 2019). Among these activation agents, H₃PO₄ and KOH are preferred to produce AC from the kraft lignin in the range of 450 °C to 900 °C (Hayashi *et al.* 2000; Fierro *et al.* 2007; Li and Luo 2013). The textural properties and yield of ACs from kraft lignin are dependent on the lignin pretreatment methods, the activation methods, and the activation conditions (Li *et al.* 2014).

In a study performed by Gustafsson *et al.* (2017), AC derived from kraft lignin is produced as a potential sorbent for sediment remediation. Chemical activation *via* combination was performed with potassium hydroxide (KOH) (lignin/KOH, 1:3 by dry weight) at 700 °C. The sorption tests in water revealed that the softwood kraft lignin presented a similar value to other commercial activated carbons.

Carbon black (CB) is the trade name for a black powder used as a reinforcement filler in rubber products exposed to high wear and tear and plastics products. In addition, CB is used to make conductive polymer composites (Zhang *et al.* 2007). Several types of CBs are differentiated by particle size, surface area, and conductivity (Snowdon *et al.* 2014).

Currently, the raw material that is most used to produce carbon black is heavy fractions of oil. Replacing this compound with a renewable resource, such as kraft lignin, is a

great opportunity for the pulp and paper industries. According to Chatterjee and Saito (2015), lignin-based CB is a potential substitute for ordinary CB in ink, paint, reinforcing fillers, and other applications.

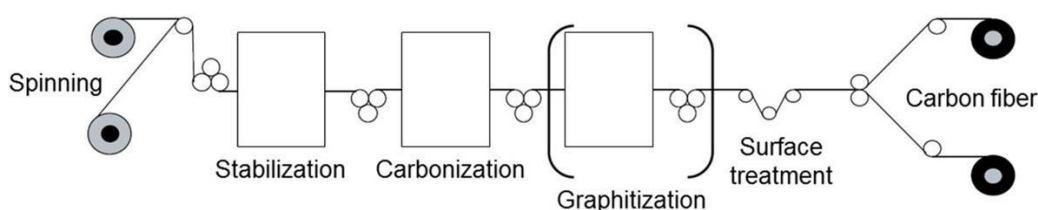
A new alternative that meets the specifications for several grades of CB is the high temperature carbonization process, which converts kraft lignin into CB of renewable resource and is used by the SunCoal Company. Snowdon *et al.* (2014) show that the surface area of lignin 654 m²/g was obtained with a high carbonization temperature (900 °C). Carbon black has a high surface area, but activated carbon has a higher surface area.

5.3 Lignin as carbon fibers

Carbon fiber is defined as a fiber containing at least 92 wt% carbon and generally has excellent mechanical properties, low weight, high thermal, chemical stabilities in the absence of oxidizing agents, and it conducts both heat and electricity well (Puziy *et al.* 2018). It has been used in composites, sporting goods, the automotive and aerospace industries, and in wind turbine blades (Mainka *et al.* 2015; Titirici *et al.* 2015; Li *et al.* 2017a).

The principal processing steps for the manufacture of carbon fiber (CF) are shown in Figure 14. Different methods of fiber spinning are used, depending on the raw material's properties, with the melt-spinning method being the most common and preferred method used (Baker and Rials 2013; Meek *et al.* 2016). Generally, the precursor fibers are first stabilized *via* oxidation at approximately 200 °C to 400 °C in air. After that, the carbonization process is performed at a high temperature (approximately 1,000 °C) in an inert atmosphere to remove hydrogen, oxygen, nitrogen, and other non-carbon elements. After carbonization, the fiber can be further graphitized at an even higher temperature (up to approximately 3,000 °C) to achieve a higher carbon content (Huang 2009). The surface treatment is performed to improve the interaction between the CFs and the resin matrix, which is when CFs are used as the strength bearing component in composites (Norberg 2012).

Figure 14: The principal processing steps for the manufacture of carbon fiber.



Source: Figure adapted from Norberg (2012)

Lignin is an attractive precursor to replace polyacrylonitrile (PAN) because of its low cost as a waste from pulp manufacturing facilities. Polyacrylonitrile is a petroleum-based synthetic polymer used to produce approximately 90% of commercial carbon fibers. Due to the high cost of PAN, production costs accounting for more than half the price tag, there is a cost-limitation for its CF applications (Baker and Rials 2013; Frank *et al.* 2014; Mainka *et al.* 2015). Petroleum pitch and regenerated cellulose (rayon) are alternative sources to produce CF. Of these two, lignin is the closest in properties of precursors to petroleum pitch (Norberg 2012).

Lignin as a precursor can promote a broader utilization of carbon fibers. The major advantages of using lignin are its availability, low cost, and high carbon content and high carbon yield during carbonization. In addition, using lignin helps to avoid elimination products such as HCN or nitrous gases released during PAN carbonization (Huang 2009). However, unlike the homogeneous PAN, lignin is a heterogeneous polymer, with different molecular weights, various functional groups, and various chemical linkages. This intrinsic heterogeneity is responsible for the lower mechanical performance of current lignin-based carbon fibers in comparison with petroleum-based carbon fibers (Li *et al.* 2017a).

The differences in structure between hardwood lignins and softwood lignins can affect the cross-linking ability of lignin and the spinning properties in the CF production process. The difficulties of spinning and thermal mobility of softwood kraft lignin are well-studied (Kadla *et al.* 2002; Norberg *et al.* 2013; Hosseinaei *et al.* 2016). In contrast, a condensed structure (C-C linkages) and unoccupied C5 sites in lignins with a high G content (grasses and softwood) result in faster thermostabilization and a reduction of CF production time (Norberg *et al.* 2013; Hosseinaei *et al.* 2016).

The main processing steps to produce carbon fiber include spinning, stabilization, carbonization, and sometimes graphitization. However, to use lignin as a precursor to carbon fiber, the lignin must undergo purification to attain less than 250 ppm ash in the final lignin product and pelletizing the lignin powder into pellets prior to the spinning process (Mainka *et al.* 2015).

Different methods of the spinning process have been investigated, focusing on the manufacture of lignin-based CFs, including both wet and dry spinning, melt-spinning, and electrospinning (Dallmeyer *et al.* 2010; Thunga *et al.* 2014; Zhang and Ogale 2014). During the oxidative stabilization, the main reactions in lignin are oxidative, caused by radicals (introduced by homolytic cleavage of the β -O-4' bond during heat treatment) and rearrangement reactions (Braun *et al.* 2005). During the carbonization step, the stabilized fiber

is converted into a CF, through the elimination of all elements except carbon. The formation of the graphite structure of the lignin-based CF during this process was established by Mainka *et al.* (2015).

Alternatives have been developed to potentiate the CFs production from lignin, mainly related to the spinning process enhancement, *e.g.*, chemical modification through the esterification of lignin phenolic groups, hydrogenation, and phenolation, plasticizing lignin through blending with synthetic polymers, such as polyethylene oxide (PEO), polyethylene terephthalate (PET), PAN, and reinforcement with clay or carbon nanotubes (Sudo and Shimizu 1992; Sudo *et al.* 1993; Uraki *et al.* 2001; Kadla and Kubo 2004; Kubo and Kadla 2005; Sevastyanova *et al.* 2010; Thunga *et al.* 2014; Ding *et al.* 2016; Liu *et al.* 2016; Wang *et al.* 2016; Youe *et al.* 2016). Additionally, purification and fractionation are used to obtain lignin with high thermal mobility and improved melt-spinning performance.

To improve the homogeneity and reduce the complexity of lignin, fractionation techniques by an elutropic series of organic solvents and precipitation by the pH effect are potential options; also, the use of membranes has been thoroughly studied (Brodin *et al.* 2009; Baker *et al.* 2012; Nordström *et al.* 2013; Wang and Chen 2013; Li and McDonald 2014; Duval *et al.* 2015; Kleinhans and Salmén 2016). These techniques allow lignin to be produced with more uniform molecular weights, thus improving the CF spinning ability and performance (Li and McDonald 2014; Duval *et al.* 2015).

Li *et al.* (2017) studied a new approach to fractionate and modify kraft lignin using an oxidation process to treat kraft lignin with laccase and a mediator. The process resulted in lignin fractions with different molecular weights, functional groups, and interunitary linkages. The insoluble fraction of the treated lignin was used with PAN (1:1 ratio) as the starting material for carbon fiber production. The results suggest that the spinnability was improved due to the better miscibility. The elastic modulus of lignin-PAN carbon fiber was similar to those of several commercial carbon fibers (PAN-CF).

5.4 Lignin as source of fuels and chemicals

Concepts of sustainability and a cleaner environment have encouraged research on replacing fossil fuels with renewable fuels. The development of the lignin-polymer platform in the pulp industry makes it a promising alternative to partially replace oil in the future (Laurichesse and Avérous 2014). Yet, the large-scale production of low-molecular-weight chemicals from lignin is still hindered by technological and economic challenges in relation to

hydrogenolysis, alkaline hydrolysis, solvent depolymerization, supercritical water, and alkaline oxidation are well-known depolymerization techniques (Pandey and Kim 2011; Azadi *et al.* 2013). According to Ponnusamy *et al.* (2019), the viability of lignin depolymerization depends on the depolymerization technique and the chemical composition of the technical lignin.

Among the depolymerization techniques can be mentioned the degradation by fungi and bacteria (microbial degradation), thermochemical depolymerization (base-catalyzed, acid catalyzed, metal catalyzed and, conventional pyrolysis of lignin) and electrochemical depolymerization of kraft lignin. All lignin degradation approaches are either expensive, consume more energy, or even produce toxic by-products, except for biological degradation. Then, it is a challenging process the controlled degradation of lignin into desired chemical compounds (Agarwal *et al.* 2018).

None of these processes will provide a high yield of monomers or high selectivity of the reaction products. However, lignin can be depolymerized into its aromatic monomer constituents (Azadi *et al.* 2013). These products can be blended into transportation fuels, given that aromatic hydrocarbons constitute approximately 35% to 50% of gasoline and 26% to 30% of diesel (Merker *et al.* 2011).

Regarding the use of kraft lignin for renewable chemicals, aromatic aldehydes such as vanillin (4-hydroxy-3-methoxybenzaldehyde) and syringaldehyde (4-hydroxy-3,5-dimethoxybenzaldehyde) are used as additives in foods, beverages, and pharmaceuticals (Pacek *et al.* 2013; Tarabanko and Tarabanko 2017). Currently, most of the vanillin is produced from petrochemical sources, but producing vanillin from kraft lignin is more environment-friendly and potentially economical than from guaiacol (Pinto *et al.* 2012).

Producing vanillin from kraft lignin faces challenges, such as having a low yield. This has been attributed to the difficulty purifying the vanillin products, mainly in hardwood, which contains less G-type lignin than softwood. In addition, lignin depolymerization has a high demand for energy, as well as high requirements for acids and organic solvents during the extraction process (Fache *et al.* 2016; Wongtanyawat *et al.* 2018).

The yield of aldehydes depends on the source of lignin, the condition of its isolation, and the condition of lignin oxidation (Tarabanko and Tarabanko 2017). In a study performed by Wang *et al.* (2018), three technical lignin samples were oxidized by alkaline nitrobenzene to evaluate their feedstock potential for vanillin production. They showed that the β -O-4 linkages in lignin affected its aldehyde yield. Kraft lignin showed a lower vanillin yield when compared to alkali lignin and sodium lignosulfonate.

Yoshikawa *et al.* (2013) performed an optimization of a two-step process to produce phenols from kraft lignin. First, lignin was depolymerized into liquid products with lower molecular weights using a H₂O/BuOH solution. Next, lignin catalytic cracking was carried out in the lignin-derived slurry liquid over ZrO₂-Al₂O₃-FeOX, and there was an increase in the total recovered fraction of phenols.

5.5 Lignin as bioplastics and coatings

A continuous increase in oil prices and an environmental concern with the use of common petroleum-based plastics has resulted in a growing interest in eco-friendly materials. Kraft lignin can be used as an additive or raw material to produce new plastics (Kun and Pukánszky 2017). Currently, the most common commercial thermoplastics used by the polymer industry for food packaging and bottles are polypropylene (PP), polyethylene (PE), polystyrene (PS), and polyethylene terephthalate (PET) (Gordobil Goñi 2018).

Lignin can be used in polymer-lignin blends (*e.g.*, plastics blends), as an ultraviolet and thermal stabilizer, and to improve the mechanical properties and processability (Stewart 2008; Doherty *et al.* 2011; Laurichesse and Avérous 2014). In addition, the phenolic structure inherent in lignin enables it to function as a free radical scavenging antioxidant in plastics, similar to the commercial phenol-based antioxidants (Egüés *et al.* 2012; Lu *et al.* 2012).

The depolymerization of kraft lignin is required for its use in polymers (*e.g.* polyethylene and polypropylene) because the unmodified lignin exhibits a large molecular mass as well as low reactivity and low compatibility with other polymers. This process has the potential of decreasing the molecular weight, reducing the hydrophilicity, increasing the phenolic content, and decreasing the aliphatic hydroxyl content of lignin (Kabir 2017). These characteristics increase the antioxidant activity of the lignin (Pan *et al.* 2006; Ugartondo *et al.* 2008).

In a study performed by Kabir (2017), the depolymerized kraft lignin presented more thermo-oxidative stability than unmodified species and used a 5% addition of kraft lignin as an antioxidant for polyethylene (PE) and polypropylene (PP). Additionally, the depolymerization improved the compatibility of the lignins with the non-polar polymer matrix by decreasing the aliphatic hydroxyl content and improving the hydrophobicity.

Chemical modification may be performed to achieve a uniform distribution of lignin with non-polar polymers in order to not affect the polymer's mechanical properties. Esterification is often used as a chemical pre-treatment when manufacturing lignin-based

polymers to reduce the polarity (Maldhure *et al.* 2011; Maldhure *et al.* 2012; Gao 2017). However, alkylation can be performed to decrease the number of hydroxyl groups responsible for lignin's polar character (Chen *et al.* 2011; Maldhure *et al.* 2012).

Acetylated softwood kraft lignin (ASKL) was used as filler in synthetic polymers (PE, PP, PS, and PET), and the acetylated lignin was more thermally-stable than the unmodified lignin (Jeong *et al.* 2012). The miscibility between ASKL and the synthetic polymers was favorable, reflecting positively on the tensile properties of ASKL and synthetic polymers. In another study, the properties of lignin-polyethylene blends were evaluated according to the raw material used (Dehne *et al.* 2016). Kraft lignin of hardwood and softwood were esterified and the results did not show any clear influence of the source of the raw material on mechanical properties. Despite this, the esterification of lignin turned out to be beneficial for the blend properties.

The use of kraft lignin is also being studied to improve biodegradable polymers. A known biodegradable thermoplastic is polylactic acid (PLA), which can be manufactured from renewable resources, and processed in conventional equipments by condensation of lactic acid or ring opening polymerization of lactide. It has desirable properties such as high strength and high stiffness, but it is too expensive to be widely used and possesses low thermal resistance and flexibility, which could be overcome by using lignin as an additive (Spiridon *et al.* 2015; Vila *et al.* 2016; Gao 2017). In a study performed by Spiridon *et al.* (2015), new bioplastics were obtained by melt compounding softwood kraft lignin (7%) with PLA. Adding lignin improved the thermal stability and the mechanical properties (elastic modulus and impact strength) of PLA. Gordobil Goñi *et al.* (2015) observed an increase in the thermal stability of PLA when kraft lignin is added; however, they recommend adding no more than 5% of lignin. Performing lignin chemical modification (acetylation) resulted in improving the compatibility with the PLA matrix, which was reflected in the observed mechanical properties.

For use in coating, kraft lignin needs to be depolymerized and/or chemically modified (Mulder *et al.* 2011; Gao 2017). An industrial softwood kraft lignin was used for coating in combination with PLA to improve the slow release of urea. The lignin was esterified for hydrophobicity development, which improved the water barrier property of the coating, thus increasing the efficiency of the nitrogen fertilizer (Li *et al.* 2017b). Additionally, the esterified kraft lignin is a potential material for sustainable coating applied to replace the conventional petroleum-based materials. According to Hult *et al.* (2013), kraft lignin can be used as a barrier in fiber-based packaging materials.

Softwood kraft lignin was used as polyurethane coatings (Griffini *et al.* 2015). Solvent extraction with MeTHF was used to improve the homogeneity of kraft lignin, and the MeTHF-soluble lignin fraction was used to polyurethane synthesis. The results showed that a viable strategy for the development of advanced lignin-based PU thermosetting systems can be obtained with the direct reaction of fractionated lignin with polyisocyanates. Besides that, the authors highlighted the potential of lignin-based thermoset PUs as sustainable bioderived materials for application in the field of high performance coatings and adhesives. Klein *et al.* (2018) considers the kraft lignin as a renewable resource for the production of bio-based polyurethane coatings for application in areas such as construction.

Hajirahimkhan *et al.* (2019) performed a reaction with kraft lignin and methacrylic anhydride in tetrahydrofuran solvent. They demonstrated that the obtained methacrylated lignin (ML) is curable in a UV-cured coating system with positive effects on the hydrophobicity, crosslinking percentage, and thermal stability of the coating system in which it was incorporated. Thus, the ML as an environmentally friendly UV-curable material for UV-cured coatings.

In addition to the necessary changes in kraft lignin, another challenge is the odor found in lignin-based composites, such as bioplastics, coating, binders, or adhesives because the characteristic odor can persist even when using pure lignin (Kalliola *et al.* 2012). The compounds that contribute to the scent are guaiacol and ethyl-guaiacol and not the sulfurous compounds (*i.e.*, dimethyl disulfide, dimethyl trisulfide, and dimethyl tetrasulfide). Softwood kraft lignin is primarily composed of G-type lignin, a potential source for guaiacol production, which is an important aromatic monomer in depolymerized lignin (Barton *et al.* 2018; Feng *et al.* 2019).

Therefore, the guaiacol must be removed from the lignin to be applied in situations that require a totally odorless material. Two pending patents have been developed to accomplish the removal of guaiacol: (1) the guaiacol removal treatment takes place during the lignin precipitation and washing process, removing approximately 60% of the compound, and (2) the washed lignin is treated, *i.e.*, after the lignin extraction and washing treatment; the latter approach is considered efficient due to the removal of approximately 97% of the guaiacol (Valmet 2017).

5.6 Lignin as adhesives and binders

The adhesives based on phenol-formaldehyde (PF) are used as a binder to produce

wood-based composites such as plywood, laminated veneer lumber, glue-laminated timber, fiberboard, and particleboard (Malutan *et al.* 2007; Bertaud *et al.* 2012). Reacting phenol with formaldehyde is conducted in an alkaline medium, and the process conditions (*e.g.*, phenol-formaldehyde ratio, pH, time, and temperature) determine certain physical and chemical properties of the adhesives, such as viscosity and the overall mechanical properties of the final glued product (Xu *et al.* 2012; Ghorbani *et al.* 2016).

Due to the possible future scarcity of fossil resources and global environmental concerns, the consumption of synthetic adhesives needs to be reduced (Solt *et al.* 2018a). Due to its availability and low cost, kraft lignin is a potential source of bio-phenol to substitute as the petroleum-based phenol when manufacturing phenolic resins (Yang *et al.* 2019).

Currently, the use of kraft lignin in PF resins is limited in its commercial application because lignin has a lower reactivity with formaldehyde compared with phenol, and the lignin-phenol-formaldehyde requires higher curing temperatures (Siddiqui 2013). Chemical modifications in the complex structure of lignin to improve its reactivity for use as adhesives have been studied with moderate success, *e.g.*, phenolation and demethoxylation (Hu *et al.* 2011; Laurichesse and Avérous 2014; Ghorbani *et al.* 2018).

In addition, the technique of solvent fractionation to improve the lignin homogeneity was studied and resulted in resins of lower strength values compared with commercial PF resins (Solt *et al.* 2018b). Fractions with lower molecular mass are more reactive due to increased content of phenolic hydroxyl groups from the depolymerization of kraft lignin and reduced steric hindrance (Mahmood *et al.* 2013; Siddiqui 2013). However, fragments with a high molar mass have a better chance of contributing to polymerization (Tejado *et al.* 2007).

Despite the large variety of lignin's molar mass, the functional groups of different lignin raw materials can impair its applicability as a binder in adhesives. Unlike phenol, in which electrophilic aromatic substitution can take place at the *para* and the two *ortho* positions, many reactive sites of lignin's aromatic ring are methoxylated or occupied by other groups, which impedes the reactions with formaldehyde (Hu *et al.* 2011; Ghorbani *et al.* 2016).

Another chemical property of lignin involved in polymerization reactions is the presence of hydroxyl groups (phenolic and aliphatic). According to Yang *et al.* (2019), because of activation of the aromatic ring in the *ortho* position, phenolic hydroxyl groups increase the reactivity of lignin with formaldehyde.

Hardwood lignin is less reactive than the softwood type because S-type lignin contains both *ortho* positions occupied by methoxyl groups. Ghorbani *et al.* (2016) substituted 20% of

phenol with pine kraft lignin and the phenol-formaldehyde adhesive performed similarly. The G-type kraft lignin of pine is superior to the hardwood lignin with respect to phenol replacement due to its high molecular weight and high amount of activated free ring positions (Ghorbani *et al.* 2016).

Presently, a promising method to increase lignin's applicability is the conversion of the polymer into smaller fragments through depolymerization. These fragments exhibit increased chemical reactivity because they are structurally similar to phenol (Cheng *et al.* 2013; Wang *et al.* 2013; Rößiger *et al.* 2018). Therefore, the depolymerized lignin is an interesting alternative to phenol substitution. In this case, higher substitution levels are achieved due to increased reactivity of the low-molecular-mass lignin fragments (Siddiqui *et al.* 2017; Solt *et al.* 2018a).

Pine kraft lignin was cracked using a base-catalyzed depolymerization process (250 bar, 320 °C, and 10 min) to obtain oligomeric lignin units (Solt *et al.* 2018a). The results demonstrated that the lignin oligomers can successfully replace phenol in PF resins at high substitution levels (up to 70%). No penalties were observed on the final dry or wet tensile shear strength, and the time of bond strength development was fully comparable with that of the PF reference at the 120 °C hot pressing temperature. However, the high viscosity of the lignin-phenol-formaldehyde (LPF) resin still poses a challenge for industrial applications.

In addition to the substitution of phenol to manufacture adhesives, lignin has been studied as binder material for eco-friendly Li-ion batteries. To assemble electrodes in Li-ion batteries, three components are employed: an active material, a conductive material, and a binder (the conventionally-used binding material is polyvinylidene fluoride (PVDF)) (Chen *et al.* 2003). Currently, it is essential to develop alternative binders that are non-fluorinated, less costly, and more environment-friendly (Lu *et al.* 2016; Nirmale *et al.* 2017).

The main study using lignin as a binding material for Li-ion battery electrodes was performed by Lu *et al.* (2016). A lignin pretreatment needs to be performed to remove the soluble, low-molecular-weight fractions of lignin. Electrodes based on pretreated lignin exhibit a relatively high specific capacity and a good stability, evidencing that lignin is a promising binding material for electrodes.

6. SUMMARY AND OUTLOOK

A steady increase in the interest of producing high value-added products from kraft lignin is evident based on the combination of a growing market, increasing environmental

restrictions with the use of non-renewable fuels, and the economic return of the lignin biorefinery.

The potentials and opportunities of providing the pulp and paper industries with the capacity to act as a biorefinery based on lignin are being exhaustively studied. Kraft lignin can be used as lignosulfonates and dispersants, technical carbons (*e.g.*, carbon fibers), transportation fuels, bioplastics, and adhesives. For some end markets, however, specific lignin requirements and/or specifications are needed to reach the conditions set for the final product (*e.g.*, a water-soluble lignin is a prerequisite for producing lignosulfonates from kraft lignin).

In order to exploit different applications, challenges remain, especially in terms of the structure complexity, heterogeneous nature, and low reactivity of lignin. The lignin from different raw materials (hardwood, softwood, and grasses) is different, which may have a direct impact on the final product. In some cases, changes in the extraction process to reach a specific requirement may additionally be necessary to enable current pulp industries to act as lignin biorefineries and expand their commercial potential.

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CAPÍTULO 2

IMPROVING LIGNIN REACTIVITY BY THERMAL TREATMENT OF EUCALYPT KRAFT BLACK LIQUOR

ABSTRACT

Kraft lignin is considered a potential valuable by-product in the pulp industry within the biorefinery concept. However, kraft lignin is characterized by a complex chemical structure, having a low reactivity and a high heterogeneity. Technical options to increase the reactivity of eucalypt kraft lignin are important to produce lignin-based materials. This study evaluates the effect of thermal treatment on the chemical composition of extracted kraft lignin from eucalypt kraft black liquor. The black liquor was heat-treated at temperatures of 175, 200 and 225 °C at reaction times of 30, 90 and 150 minutes. The lowest process yield (93%) was found for the treatment where more drastic conditions (225 °C and 150 minutes) were applied, with a minimum thermal degradation of the liquor, analyzed by TG/DTG curves. The lignins from the original liquor and the heat-treated liquors were extracted and characterized by their chemical composition, elemental analysis, heating value and Py-GC-MS to evaluate the changes caused by the thermal treatment. The thermal treatment promoted demethylation and demethoxylation on the eucalypt kraft lignin. A reduction in soluble lignin, oxygen and hydrogen content and an increase in insoluble lignin and carbon content were observed when higher temperature and retention time in the thermal treatment was applied. A reduction in the lignin S/G ratio of heat-treated lignins and an increase in the catechol and methoxycatechol content in the treatment of 225°C and 150 minutes period were also observed when compared to the reference. The eucalypt kraft lignin isolated from the heat-treated liquor may be more reactive than the original lignin due to changes in its chemical composition, and should be considered in the production of high-added value lignin-based products.

Keywords: Eucalypt kraft lignin. Demethylation. Demethoxylation. Chemical modification

1. INTRODUCTION

The pulp and paper industry is one of the largest in the world. Global Pulp and Paper Market Research Report (2019) shows that the global pulp and paper market was valued at 63.3 billion US\$ in 2018 and, by the end of 2025, it is expected to reach 76.8 billion US dollars, meaning a compound annual growth rate of 3.56% during 2019-2024.

The kraft pulping technology is the most used worldwide for converting wood or lignocellulosic biomass into pulp. During the kraft process, a water solution of sodium sulphide (Na_2S) and sodium hydroxide (NaOH), called white liquor, at a temperature of 155 °C to 175 °C is used to produce kraft pulp. The main objective is to degrade and solubilize the lignin macromolecule separating the fibers. The pulping conditions are highly dependent on the chemical structure of the lignin macromolecule and the raw material used (Potthast, 2006).

The residual liquor generated by the kraft process is called black liquor and consists of organic and inorganic components resulted from the wood delignification reaction. During the kraft cooking, lignin must be degraded and solubilized to a large extent in the residual cooking liquor (Potthast, 2006; Zhou and Lu, 2014). Lignin fragments and hydroxy acids derived from carbohydrates (mainly hemicelluloses), that have been degraded by alkali-catalyzed reactions, are the main components of the organic fraction in the black liquor (Demuner et al., 2019).

Black liquor is an extremely complex mixture and may contain in addition to lignin and carbohydrates, a fraction of acetic acid, formic acid, saccharinic acids, methanol, and other components (Bajpai, 2018). However, the chemical composition of this liquor depends on the wood species used as raw material, the pulp yield target, the composition and amount of white liquor applied, the end kappa number target and the volume of the recycled filtrates from the oxygen delignification stage (Krotscheck and Sixta, 2006).

A pulp mill that produces bleached kraft pulp generates 1.7-1.8 t of black liquor (measured as dry content) per ton of pulp (Das, 2020). Currently, the black liquor is sent to the chemical recovery cycle to recover the inorganic reagents used in pulping and to generate steam and energy for the process. The kraft recovery cycle is extremely efficient and promotes a lower production cost and a considerable reduction of effluents in the pulp mill (Reeve, 2002; Tran and Vakkilainen, 2008). Moreover, modern kraft mills can be suppliers of renewable energy (Bajpai, 2018).

Approximately 50 million tons of lignin are produced worldwide annually, of which 98% to 99% is incinerated to produce energy in kraft process, and 1% to 2% are

lignosulfonates generated in the sulfite process (Mohan et al., 2006; Gellerstedt et al., 2013; Inwood, 2014; Norgren and Edlund, 2014). Most of the black liquor generated in the kraft process, will remain being burned for energy generation and recovery of process reagents. However, part of lignin present in this liquor may become valuable by-product.

Kraft lignin is a potential adding value by-product in the concept of biorefinery in kraft pulp mills (Thakur et al., 2014; Jiang et al., 2018; Dessbesell et al., 2020; Kumar et al., 2020). An important step to convert a pulp mill into a biorefinery mill in order to improve the pulp mill revenue and increase the value of lignin via production of by products is the isolation of lignin from the black liquor (Zhu et al., 2014).

Currently, “LignoBoost” is the most widespread and commercially industrialized process for kraft lignin extraction, which is now owned and commercialized by Valmet (Dessbesell et al., 2020; Torres et al., 2020). In this process, black liquor is partly withdrawn from evaporators (dry solid content of 30% to 45%) and acidified with CO₂ to a pH of 9.0 to 10.0 at 60°C to 80°C, leading to the precipitation of lignin. After filtration, the precipitated lignin is re-dispersed in an acidic filtrate suspension tank with pH controlled at 2 to 4. The resulting lignin is then filtered and washed by acid displacement washing (pH of 2 to 3) (Kalogiannis et al. 2015).

Another important step for a pulp mill biorefinery is to expand the industrial applications of kraft lignin. Demuner et al. (2019) reported that kraft lignin may be used as lignosulfonates and dispersants, technical carbons (e.g., carbon fibers), transportation fuels, bioplastics, adhesives, among others. However, kraft lignin requires modifications to increase its reactivity to be used for polymer manufacturing and chemical synthesis.

Hardwood kraft lignin is considered less reactive than softwood kraft lignin, because of the higher syringyl/ guaiacyl (S/G) ratio in the lignin structure. The *ortho* positions of the aromatic ring can be substituted by one (G-lignin) or two methoxyl groups (S-lignin), and these groups may interfere in the reactivity of the free phenolic hydroxyl groups (Okamoto et al., 1996; Hu et al., 2011).

In order to remove the methoxyl groups (-OCH₃) present in hardwood kraft lignin, the demethylation and demethoxylation are potential modifications. In addition, many other methods have been described for modifying the kraft lignin structure, including oxidation, hydrolysis, reduction, phenolation, and hydroxymethylation (Li and Geng, 2005; Effendi et al., 2008; Hu et al., 2011; Inwood, 2014; Dai et al., 2016; Zuluaga et al., 2018). Controlled chemical modifications need to be developed to increase the compatibility of the lignin with the existing materials (Bertella and Luterbacher, 2020).

The demethoxylation and demethylation result in modifying lignin structures with free phenolic groups to form catechol and methoxycatechol groups (Okamoto et al., 1996; Hu et al., 2011). Methyl groups can be removed by enzymatic oxidative cleavage and sulfur-mediated demethylation (Wu and Zhan, 2001; Filley et al., 2002). However, a thermal treatment of black liquor prior to the lignin extraction can be performed to obtain a significant level of demethylation and demethoxylation in the kraft lignin (Wikberg et al., 2017; Leppävuori et al., 2017).

The dominant production of pulp in South America is made from eucalypt wood and an in-depth study of kraft lignin from this species is required. The objective of this study was to evaluate the effect of thermal treatment on black liquor from kraft eucalypt pulping. In addition, the research highlights the possible modifications in the chemical structure of eucalypt kraft lignin and its potential applications.

2. MATERIALS AND METHODS

Black liquor from eucalypt wood kraft cooking was supplied by a Brazilian pulp and paper mill. The eucalypt black liquor was treated by a thermal treatment carried out on a Parr digester, model 4848M. The process operating conditions optimization was carried out evaluating three temperatures: 175, 200, 225°C and three reaction times: 30, 90 and 150 minutes. The factorial arrangement resulted in nine treatments (175°C - 30 min; 175°C - 90 min; 175°C - 150 min; 200°C - 30 min; 200°C - 90 min; 200°C - 150 min; 225°C - 30 min; 225°C - 90 min; 225°C - 150 min) which were performed in duplicate. The thermal treatment yield was calculated by measuring the initial volume (black liquor) and final volume (thermal-treated liquor) of the process.

Kraft lignin was extracted from black liquor and thermal-treated liquors according to the methodology adapted from Lin (1992). The liquors were heated in a hot plate under rapid stirring and acidified carefully with 20% (by weight) sulfuric acid to pH 2.0. The acidified liquor was filtered through a Whatman No. 4 filter paper. After several washings with hot water at pH 2.0, the lignin was dried at 40°C.

For characterization of the chemical composition of black liquor and kraft lignins extracted from liquors, the total lignin was measured by the sum of acid-soluble lignin and acid-insoluble lignin, which were measured according to TAPPI UM 250 and TAPPI T 222 om-02, respectively. Sugar composition, ash and metals were measured according to SCAN-CM 71:09, TAPPI T211 om-93, TAPPI T266 om-94, respectively.

Elemental analysis was performed using CHNS-O model LECO equipment for black liquor and extracted lignins. The carbon, hydrogen, nitrogen and sulphur percentages were determined in the TruSpec CHNS Micro module and the oxygen percentage in the TruSpec Oxygen Add-On module. The TAPPI Test T684 om-90 standard was used for the analysis of the higher and lower heating value of kraft lignins extracted from liquors.

The thermogravimetric analysis of the black liquor (TG/DTG) was performed under a nitrogen gas atmosphere, at a constant flow rate of 100 mL/min, in the DTG-60H (Shimadzu). Thermogravimetric curves (TG) were obtained from 25 °C to a maximum temperature of 1100 °C, with a heating rate of 10 °C min⁻¹, to evaluate the mass loss as a function of temperature. From the first derivative of the mass loss, the second curve (DTG) was generated, which allows the determination of the maximum temperatures for thermal degradation.

For pyrolysis coupled to gas chromatography and mass spectrometry (Py-GC/MS) the isolated kraft lignins (ca. 0.1 mg) from black liquor were used for calculating the lignin S/G ratio and degraded products. The pyrolysis were performed in a micro-furnace pyrolyzer (Frontier Laboratories Ltd., Fukushima, Japan) connected to a GC-MS apparatus (Shimadzu, model QP2020), using an Ultra-ALLOY[®] Capillary Column (UA5, 30m x 0.25 mm ID, 0.25 µm film thickness). The pyrolysis was carried out at 550 °C for 10s, as previously described (Del Río et al., 2005; Barbosa et al., 2008; Schorr et al., 2014). The pyrolysis chamber was purged with helium (100kPa) to transfer the pyrolysis products as quickly as possible to the GC column. The injector temperature was 100°C and the chromatograph oven was ramped from 45°C (4 min) to 240°C at a rate of 4°C min⁻¹. The final temperature was kept for 10 min. The temperatures of the detector and the GC-MS interface were 250 and 290 °C, respectively. Mass spectrometer was operated by the electron impact ionization mode at 70 eV and mass scan range was 50-350. The compounds released were identified by comparing their mass spectra with the GC-MS spectral library (Willey and NIST), with data from the literature (Ralph and Hatfield, 1991; Del Río et al., 2005; Barbosa et al., 2008; Oudia et al., 2007; Fernández-Rodríguez et al., 2020; Silva et al., 2020) and when necessary by mass fragmentography. In duplicate, the peaks with the largest area were measured and the average was reported. The lignin S/G ratio was calculated by dividing the sum of area percentage of syringyl-type (S) lignin per the sum of area percentage of guaiacyl-type (G) lignin.

3. RESULTS AND DISCUSSION

3.1 Characterization of black liquor

Black liquor generated by the kraft process is composed of organic and inorganic components that have been removed from the wood during the delignification reactions. Table 1 shows the characterization of the eucalypt black liquor regarding to organics and inorganics, lignin and sugars.

Table 1: Characterization of the eucalypt black liquor as to organics and inorganics, lignin and sugars.

Constituents		Eucalypt black liquor
Organics (%)		50.7
Inorganics (%)		49.3
Soluble lignin (%)		14.5
Insoluble lignin (%)		29.2
Total lignin (%)		43.7
Sugars (%)	Glucan	0.8
	Xylan	0.7
	Mannan	0.1
	Galactan	0.4
	Arabinan	0.2
Inorganics (ppm)	Ca	393.5
	Na	153442.1
	Mg	736.6
	K	13304.4
	Fe	385.5
	Cu	88.6
	Mn	35.6
	Cl	2067.1

Source: Author

The percentage of organics present in the black liquor was 50.7%. The main component of organic fraction present in the black liquor is lignin fragments. However, also have carbohydrates that have been degraded by alkali-catalyzed reactions (Demuner et al., 2019). Kraft cooking typically removes 85 to 93% of the lignin and 56 to 71% of the hemicelluloses present in wood (Nagy et al., 2010).

The concentration of total lignin in eucalyptus black liquor was 43.7% (14.5% of soluble lignin and 29.2% of insoluble lignin) and the total content of sugars was 2.2%

(Glucan 0.8%; Xylan 0.7%; Mannan 0.1%; Galactan 0.4% and Arabinan 0.2%). Cardoso et al. (2009) observed a concentration of lignin between 40.2-42.3% in black liquor from the eucalypt kraft process, quantified by the lignin precipitation methods. The content of lignin and sugars in the black liquor may vary according to the conditions of the kraft process and the wood species (Hubbe et al., 2019). Colodette et al. (2013) observed a concentration of lignin and sugars of 40.9 and 3.5%, respectively, to produce pulp with kappa number 20. For pulp with kappa number 15, the values were 44.0% (lignin) and 4.1% (sugars).

In addition to fragments of lignin and sugars, the organic components may contain a fraction of acetic acid, formic acid, saccharinic acids, methanol, and hundreds of other components (Bajpai, 2018; Hubbe et al., 2019). In addition, cellulose and hemicelluloses are degraded to aliphatic carboxylic acids (Speight, 2019). These components have not been measured, but it is believed that they make up the percentage of organic components (50.7%).

The percentage of inorganics in the black liquor was 49.3%. Magdeldin and Järvinen (2020) reported that the presence of inorganic chemicals in liquors is approximately 45%. The inorganic content of black liquor depends on wood feedstock, alkali charge, sulfidity and cooking conditions (Hubbe et al., 2019). The main inorganic components present in black liquor are NaOH and Na₂S, from white liquor used in kraft pulping, and others sodium compounds (Na₂CO₃, Na₂S₂O₃, Na₂SO₃ and Na₂SO₄) (Venkatesh and Nguyen, 1992; Niemelä and Alén, 1999; Hubbe et al., 2018).

High content of sodium and potassium in the liquor was observed. The sodium content is explained by the absence of the chemical recovery cycle step (recovery boiler and causticizing), since this liquor was removed after the evaporation step (Cardoso et al., 2009). The potassium content may come from the wood used in the kraft process. Besides these major components other inorganic components are present, some of them occurring in trace amounts (Hubbe et al., 2019). These elements are challenges for the process as they cause corrosions and heat transfer surface fouling (Magdeldin and Järvinen, 2020).

Krotscheck and Sixta (2006) reported that the chemical composition of black liquor may vary according to the wood species, the composition and the amount of white liquor, pulp yield, kappa number of the brown stock and the volume of recycled filtrates from the oxygen delignification stage.

The solids content, higher and lower heating values, and ultimate analysis of the black liquor sample are presented in Table 2. Ultimate analysis of black liquor is defined as the determination of the carbon, hydrogen, nitrogen, oxygen, sulfur and ash in the material.

Table 2: Characterization of the eucalypt black liquor regarding to solids content, higher and lower heating values, and ultimate analysis

Parameters		Eucalypt black liquor
Solids content (%)		51.1
Heating value (MJ/Kg)	Higher	13.9
	Lower	13.2
Ultimate analysis (%)	Carbon	36.7
	Hydrogen	2.95
	Oxygen	40.0
	Nitrogen	0.046
	Sulfur	3.41
	Sodium	15.3
	Potassium	1.33
	Chlorine	0.207

Source: Author

At the end of the kraft process, the residual black liquor is sent to recovery of inorganics materials used in the wood cooking process (Tran and Vakkilainen, 2008). The first stage of the kraft recovery cycle is the washing of the brown stock. Pulp washing provides desirable benefits associated with increased efficiency in both pulp screening and bleaching (Santos and Hart, 2014). After washing, the weak black liquor has a solids content of about 15-20% (Nikolskaya et al., 2019). However, as the liquor needs to be burned in the recovery boiler, it undergoes an evaporation step to increase the solids content higher than 64%.

The black eucalypt liquor in this study had a solids content of 51.1%, showing that it was removed in the evaporation stage of the kraft recovery cycle. The solids content is used to control and estimate the efficiency of the evaporation process (Nikolskaya et al., 2019). In a typical pulp mill, the strong black liquor has a solid content of approximately 65–75% (Leite et al, 2013; Vähä-Savo, 2014), even reaching up to 80–85% (Tran and Vakkilainen, 2008) for energy production and chemical reduction reactions in the recovery boiler. The solids content of the black liquor is associated to its heating value.

The higher and lower heating values of the black liquor were 13.9 and 13.2 MJ/Kg, respectively. The higher heating value (HHV) and lower (LHW) differ from each other because for the HHV calculation the energy that the water vapor particles release when changing to liquid phase is considered. The LHW calculation assumes that the water formed by the combustion remains in vapor state (Jenkins and Ebeling, 1985; Acar et al., 2012).

The results of HHV and LHW show lower values than other raw materials used for burning, such as wood. These values have a major impact on the steam generation and therefore on the pulp production, due to the recovery boiler solids load (Frederick, 1997). The content of organics and sulfur components in the black liquor contributes to the increase in the heating value, while other inorganic compounds contribute negatively to this value (Venkatesh and Nguyen, 1992; Magdeldin and Järvinen, 2020).

The heating value (HV) of kraft black liquor is equal to the sum of the heating value of each individual component, multiplied by its mass fraction. The HV for carbohydrates (13.5 MJ/kg) is lower than that of hardwood lignin (25.1 MJ/kg) and softwood lignin (26.9 MJ/kg) (Green and Grace, 1984).

Magdeldin and Järvinen (2020) observed that the heating value of black liquor vary between 12 to 15 MJ/kg. Cardoso et al. (2009) reported the average heating value of the eucalypt black liquor of 14.6 MJ/kg and Adams (1997) reported a HHV of 13.9 MJ/kg and LHV of 12.0 MJ/kg. The heating value of black liquor (12-15 MJ/kg) is lower when compared to the extracted kraft lignin (21-26 MJ/kg), due to the lower carbon content and higher oxygen content of black liquor when compared to the kraft lignin (Carneiro et al., 2014; Freitas et al., 2017).

Kraft black liquor contains mainly carbon, oxygen, sodium, sulfur and hydrogen and small amounts of potassium, chloride and nitrogen. The ultimate analysis of kraft black liquor consists of a range of 34 to 39% for carbon and 33 to 38% for oxygen. In addition to these elements, there is a variation of 3 to 5% for hydrogen, 17 to 25% for sodium, 3 to 7% sulfur, 0.1 to 2% potassium, 0.2 to 2% chloride and 0.04 to 0.2% nitrogen (Frederick, 1997).

Casademont et al. (2020) detected values of C (34.86%), H (2.13%); N (0.20%); S (0.30%); O (33.43%); Na (26.34%), K (1.84%) for eucalypt black liquor. Cardoso et al. (2009) in a study with eucalypt kraft liquors extracted from different pulp mills, observed the following values of carbon (29.6-37.3%), hydrogen (3.4-3.5%), nitrogen (0.01-0.04%), sulfur (3.0-4.4%), oxygen (30.5-38.9%), sodium (17.3-21.8%), potassium (1.8-2.2%) and chloride (0.3-4.3%), showing a large variation in elemental composition of black liquors.

The value found for oxygen (40.0%) was higher and the value for sodium (15.3%) was lower than that reported by other authors. This variation may be directly associated with the conditions of the kraft process. Colodette et al. (2013) observed a variation in the elemental composition of eucalypt black liquors, according to the kappa number target in the pulping process. Kappa number 20 present a higher carbon content (42.0%) and a lower sulfur content (3.6%) when compared to kappa number 15 (C: 39.2% and S: 4.5%).

3.2 Thermal treatment process

The optimization of a thermal treatment of eucalypt black liquor was carried out with three temperatures (175, 200, 225°C) and three reaction times (30, 90 and 150 minutes). Table 3 shows the yield and pH results of these processes.

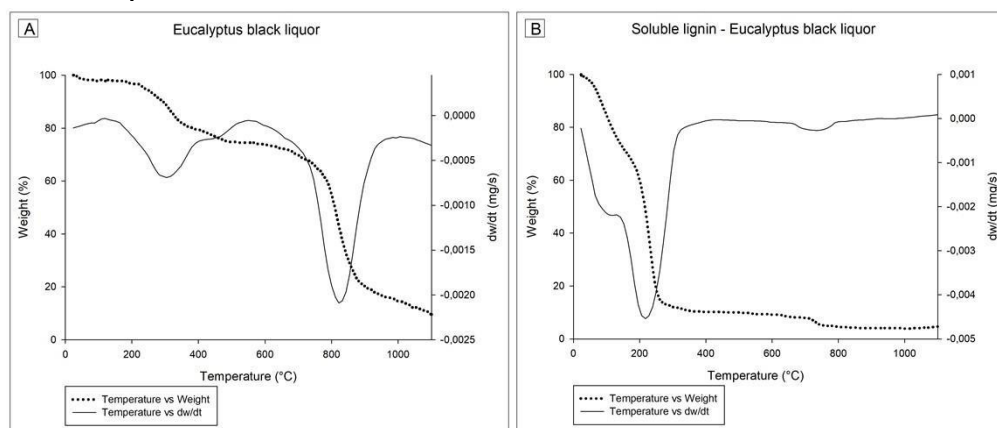
Table 3: Yield and pH results of thermal treatment process

Samples		Yield (%)	Initial pH	Final pH
175°C	30'	97.6	13.0	12.8
	90'	97.0	13.0	12.7
	150'	96.3	13.0	12.4
200°C	30'	95.6	13.0	12.0
	90'	94.9	13.0	11.9
	150'	94.4	13.0	11.7
225°C	30'	93.7	13.0	11.5
	90'	93.1	13.0	11.3
	150'	93.0	13.0	11.0

Source: Author

The highest yield (97.6%) was obtained in the treatment with lower temperature and shorter reaction time. The lowest yield (93.0%) was observed in the treatment with more drastic conditions (225 °C and 150 minutes). According to thermogravimetric analysis of eucalypt black liquor, minimal thermal degradation was observed up to a temperature of 225 °C. However, this minimal degradation and black liquor incrustation in the digester justify the low loss yield (Figure 1A).

Figure 1: Thermogravimetric analysis: (A) Eucalypt black liquor; (B) Soluble lignin of eucalypt black liquor



Source: Author

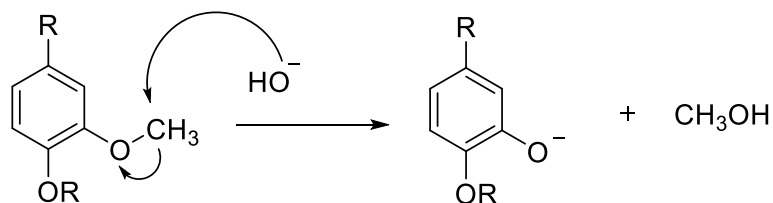
The thermogravimetric method (TG) showed the percentage of mass loss as a function of temperature. The DTG curves correspond to the first derivative of the TG curves and show the mass variation in relation to time, reported as a function of temperature (Janković et al., 2020). From the thermogravimetric analysis it was observed that up to 225°C (the maximum temperature used for the thermal treatment of the black liquor) there was a maximum mass loss of about 5%. At higher temperatures (225 °C) there were no significant yield losses and thermal degradation of chemical constituents of this liquor.

It was observed two main peaks of maximum temperatures during thermal degradation in the eucalypt black liquor sample (Figure 1A). The first peak showed a thermal degradation in the temperature range between 250 and 350°C and in the second peak showed a significant loss of mass in the range 800 to 900°C.

Between 200 and 400°C, the mass loss is characterised by degradation of hemicelluloses and cellulose (Chen et al., 2019). However, the sugars content found in the black liquor was low (2.2%) as showed in Table 2. The percentage of soluble lignin found in the black liquor (14.5%; Table 1) also undergoes thermal degradation in a temperature ranging between 200 and 300°C (Figure 1B). Mass loss between 150 and 300 °C can be attributed to the elimination of formic acid, formaldehyde, carbon dioxide and sulphur dioxide resulting from the degradation of phenylpropane side chains of lignin (Fenner and Lephardt, 1981). Fang et al. (2015) attributes that between 200-300°C, the decomposition of low molar mass phenols, such as guaiacol, can also occur.

The loss of mass observed between 400 to 800°C may be attributed to the decomposition and the condensation of the aromatic ring of lignin (Fang et al., 2015; Brazil et al., 2018). The second major loss of mass (800-900°C) is characterised by the melting of salts. The ash fusion is accompanied by a great loss of mass, since the inorganic components are present in a high percentage in the black liquor (Nassar, 1984).

The treatment with the highest temperature and reaction time (225°C and 150 minutes) showed the greatest pH drop during the thermal treatment (Final pH 11.0). This drop in pH is attributed to the alkali consumption due to the hydrolysis of methoxyl groups in lignin aromatic ring, forming methanol and a free phenolic hydroxide (Gomide and Gomes, 2015). Figure 2 shows this reaction that probably occurs during thermal treatment of black liquor, highlighting that demethylation and modification of kraft lignin occur.

Figure 2: Hydrolysis reaction in thermal treatment of black liquor.

Source: Adapted from Gierer (1970)

3.3 Characterization of isolated kraft lignins

The kraft lignin was extracted from the original black liquor and from the thermal-treated liquors for characterization in order to evaluate possible chemical modifications.

3.3.1 Chemical characterization

Lignins extracted from the original eucalypt black liquor (Reference) and from the thermal-treated liquors were characterised by lignin (soluble, insoluble, and total), sugars, and ash content (Table 4).

Table 4: Characterization of the extracted kraft lignin as to lignin (soluble, insoluble and total), sugars, and ash content.

Temperature and time		Constituents (%)				
		Soluble lignin	Insoluble lignin	Total lignin	Sugars	Ash
Reference		5.64	91.30	96.94	0.88	2.06
175°C	30'	5.84	90.51	96.35	1.32	2.17
	90'	6.14	91.02	97.16	1.07	1.71
	150'	6.02	91.32	97.34	0.94	1.50
200°C	30'	6.07	91.15	97.22	0.80	1.96
	90'	5.97	91.41	97.38	0.80	1.56
	150'	5.16	92.40	97.56	0.69	1.42
225°C	30'	2.89	95.17	97.24	0.54	1.87
	90'	2.01	96.03	98.04	0.55	1.34
	150'	1.63	96.63	98.26	0.40	1.15

Source: Author

The values found for lignin extracted from black liquor (Reference) were soluble lignin (5.64%), insoluble lignin (91.30%), total lignin (96.94%), sugars (0.88%) and ash (2.06%). Boschetti et al. (2019a) in a study with eucalypt kraft lignin extracted from black

liquor found similar values of soluble lignin (5.9%), insoluble lignin (91.3%), total lignin (97.2%) and ash (2.1%). In other researches evaluating eucalypt kraft lignin, Zhou and Lu (2014) found 97.57% of total lignin and Diestes et al. (2016) found total lignin values of 94.1% and low carbohydrate content (0.7%).

Treatments at 175°C showed a higher percentage of carbohydrates (0.94 to 1.32%) and total lignin ranging between 96.35 and 97.34%. Ponomarenko et al. (2014) found these values for hardwood kraft lignin: total lignin ($97.4 \pm 0.5\%$) and sugars ($2.50 \pm 0.04\%$). The treatments at 200 and 225°C showed an increase in the total lignin value, reaching up to 98.26%, and low values of carbohydrates (0.40 to 0.80%) due to the degradation that occurs during the thermal treatment. Zhou and Lu (2014) also found a similar carbohydrate value (0.81%), however, these authors also observed lower ash content (0.84%).

The ash and carbohydrate contents in kraft lignin are variable. Gordobil et al. (2016) found 22.4% of ash and 2.2% of sugars in eucalypt kraft lignin. However, this ash and carbohydrates content is directly related to the purity of the kraft lignin, and high values may be related to the raw material or to the extraction process. According to Tomani (2010), the LignoBoost process presents a high lignin yield and high-purity lignin with low ash and carbohydrate contents. Although the same raw material and extraction process was adopted for all studied liquors, they had an initial pH variation according to the heat treatment (Table 3).

Lignin becomes soluble in alkaline aqueous solutions (high pH of black liquor) due to the ionized phenolic groups in the molecules (Demuner et al., 2019). When the black liquor is acidified, the protonation of these phenolic groups makes the lignin less hydrophilic (Vainio et al., 2004). Protonation is influenced by the molecular structure of the lignin, the solution ionic strength and temperature (Rudatin et al., 1989; Norgren and Lindström, 2000; Ragnar et al., 2000; Zhu and Theliander, 2015). It is believed that changes have occurred in the molecular structure of the lignin with the heat treatment of the liquor, as already shown by Wikberg et al. (2017) and Leppävuori et al. (2017).

Although there was no significant variation in the total lignin content among the treatments, a difference was found in the levels of soluble and insoluble lignin. In the reference, soluble and insoluble lignin of 5.64 and 91.30% were found, respectively. However, the most drastic heat treatment (225 °C and 150 minutes) showed a lower content of soluble lignin (1.63%) and a higher content of insoluble lignin (96.63%).

These values at 225 °C and 150 minutes are similar to those found by other authors for kraft lignin extracted from softwood black liquor: $96 \pm 1\%$ of insoluble lignin (Jablonskis

et al., 2018); 2.5% for lignin soluble (Domínguez-Robles et al., 2018); 93.1% of insoluble lignin and 2.9% of soluble lignin (Jääskeläinen et al., 2017). According to Yasuda et al. (2001), low-molecular degradation products and hydrophilic derivatives of lignin form the soluble lignin fraction.

This similarity with softwood lignin indicates that demethoxylation of eucalypt kraft lignin occurred during the heat treatment, forming more G-units. In softwoods, the G-unit is dominant and form condensed bonds because it has C-5 available to make C-C linkages (Sjöström, 1993). Stronger and more condensed bonds result in low cleavage and degradation during acid hydrolysis. Gomes et al. (2015) demonstrated that lignin containing high lignin S/G ratio will condensate less during the acid hydrolysis and produce more acid-soluble lignin in the filtrates.

3.3.2 Elemental analysis and heating value

Elemental analysis and heating value of lignins extracted from the original black liquor (Reference) and from the thermal-treated liquors are presented in Table 5.

Table 5: Characterization of the extracted kraft lignin as to elemental analysis and heating value

Temperature and time		Elemental analysis (%)					Higher heating value (MJ/Kg)
		Carbon	Hydrogen	Nitrogen	Oxygen	Sulfur	
Reference		63.52	5.68	0.12	27.63	3.01	25.43
175°C	30'	64.03	5.66	0.14	28.12	1.95	25.73
	90'	64.20	5.85	0.14	27.67	2.03	26.13
	150'	65.36	5.61	0.09	27.01	1.73	26.43
200°C	30'	65.13	5.81	0.11	27.06	1.78	26.47
	90'	66.30	5.63	0.11	26.07	1.70	26.52
	150'	66.39	5.32	0.11	26.22	1.87	26.70
225°C	30'	67.14	5.28	0.17	25.75	1.57	26.51
	90'	69.43	5.07	0.13	24.21	1.10	26.70
	150'	70.73	4.94	0.13	23.02	1.06	26.73

Source: Author

The values of the reference were carbon (63.52%), hydrogen (5.68%), nitrogen (0.12%), oxygen (27.63%) and sulfur (3.01%), similar to those found by Dou et al. (2019) for eucalypt kraft lignin: C (62.96%), H (5.82%), O (28.32%), N (0.72%) and S (1.68%). Tagami

et al. (2019) also in a study with eucalypt kraft lignin found values: C (62.4%); H (4.5%); S (2.6%) and O (30.3%). The nitrogen content found in the isolated lignins varied between 0.09 and 0.17%. The variation in the sulfur content was 1.06 to 3.01%. According to Doherty et al. (2011), kraft lignin has a sulfur percentage between 1 and 3%, which are present as aliphatic thiol groups in kraft lignin (Inwood, 2014).

There was an increase in the carbon content and a reduction in the hydrogen, oxygen and sulfur contents as the temperature and reaction time increased. For treatments at 200 °C, the values were similar to those found for softwood kraft lignin: C (66.2%), H (4.7%), O (26.9%), S (2.0%) as reported by Tagami et al. (2019) and C (66.9 %), H (5.2%), N (0.1%) and O (25.4%) as reported by Mukundan et al. (2019).

The elemental analysis of the most drastic treatment (225°C – 150 minutes) showed the values of 70.73, 4.94 and 23.02% for carbon, hydrogen and oxygen, respectively. These values point out that there was demethylation (cleavage of groups -CH₃) and demethoxylation (cleavage of groups -OCH₃) of the eucalypt kraft lignin, decreasing the hydrogen and oxygen content and, proportionally, increasing the carbon content. Wikberg et al. (2017) observed a significant demethylation and demethoxylation in the hardwood kraft lignin after a thermal treatment of black liquor prior to the lignin extraction.

The higher heating value found for kraft lignin extracted from black liquor (Reference) was 25.43 MJ/kg. Boschetti et al. (2019a) reported the same HHV value for eucalypt kraft lignin. This value may be quite variable for eucalypt kraft lignin. Tagami et al. (2019) found a value of 22.2 MJ/kg for higher heating value of eucalypt kraft lignin with elemental composition similar to this study. Murphy and Masters (1978) reported a value of 21.13 and Dieste et al. (2016) a value of 26.0 MJ/kg for eucalypt kraft lignin. The variation observed in those studies is directly related to the chemical composition and the elemental analysis of kraft lignins. The heating values were similar, but an increase with the conditions of the thermal treatment of liquor was observed, which can be explained by the higher carbon content and lower oxygen content found in the samples (Carneiro et al., 2014; Freitas et al., 2017). The high ash content can also negatively influence the heating value (Boschetti et al., 2019b).

The heating value of the sample obtained after the most drastic treatment (225 °C and 150 minutes) was 26.73 MJ/kg. This value is similar to the heating value reported for softwood kraft lignins. Gellerstedt et al. (2013) reported the range of 26 to 28 MJ/kg (HHV) for softwood kraft lignins. Green and Grace (1984) reported a value of 26.9 MJ/kg for that same type of lignin. This fact shows that the demethoxylation of eucalypt kraft lignin may

have occurred, since the results are similar to a softwood lignin, that predominates the G-type lignin and lower levels of methoxyl groups.

3.3.3 Fractionated lignin by Py-GC-MS

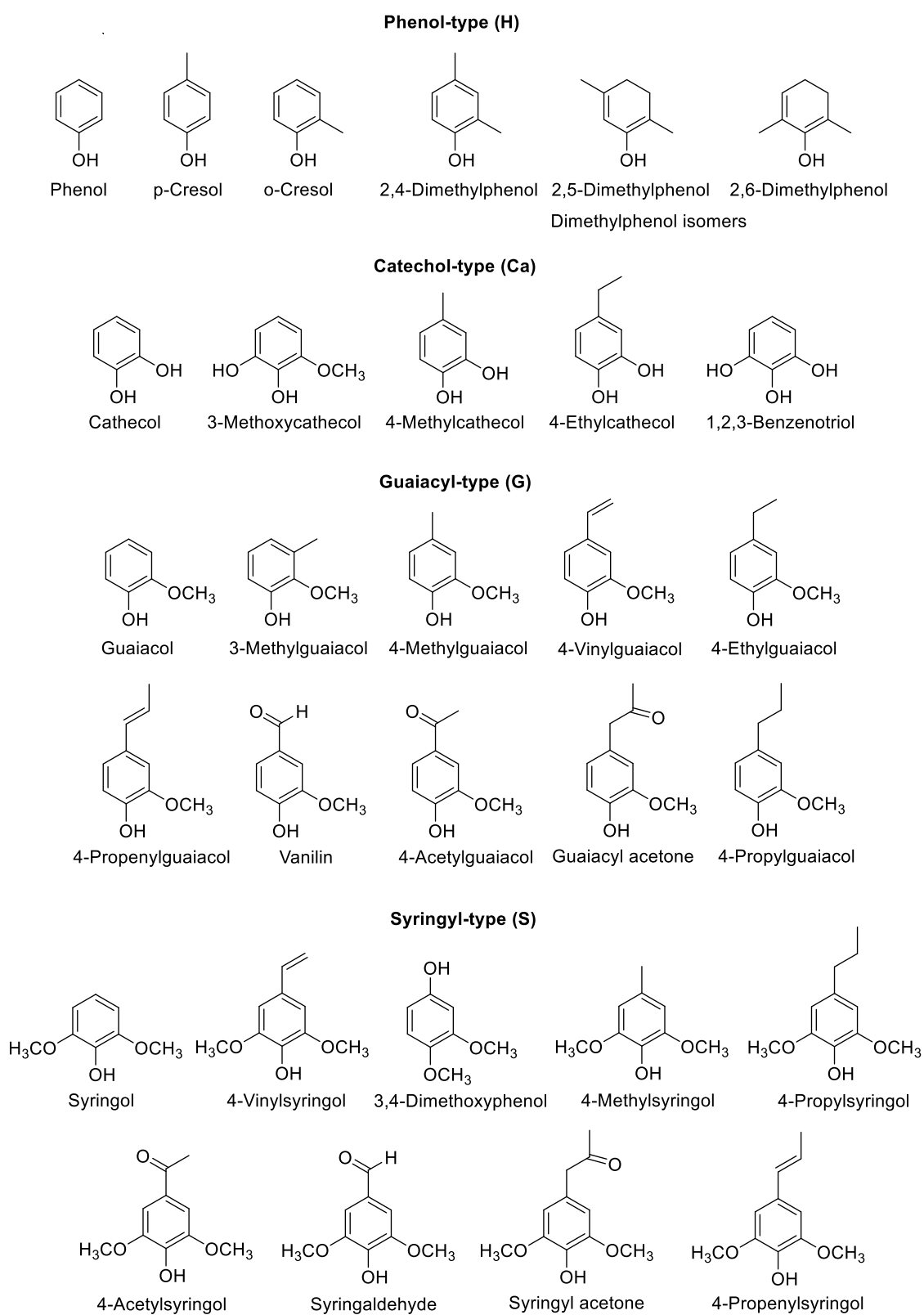
The monomeric compositions of isolated lignins and lignin syringyl/guaiacyl ratio (S/G) are showed in Table 6. The analytical pyrolysis was carried out at 550 °C, temperature in which it was achieved the maximum yield of phenolic compounds (Schorr et al., 2014). The identified phenolic compounds were classified into four categories, based on Fernández-Rodríguez et al. (2020) and Silva et al. (2020): phenol-type (H), catechol-type (Ca), guaiacyl-type (G) and syringyl-type (S), which are illustrated in Figure 3. The analysis provided the identification of 28 phenolic compounds, which represents 93–96% of the lignin samples (Silva et al., 2020).

Table 6: Py-GC/MS results and S/G ratios

Compound	Origin	Mass fragments	Reference	Area percentage (%)											
				175°C			200°C			225°C					
				30'	90'	150'	30'	90'	150'	30'	90'	150'			
Phenol	H	94/66/65	-	0.45	-	-	-	0.54	0.61	0.61	0.88	1.48	1.74		
p-Cresol	H	107/108/77/79/51	0.50	0.32	0.61	0.67	0.66	0.88	1.00	1.00	1.29	2.09	2.37		
o-Cresol	H	108/107/79/77/90	0.37	0.48	0.45	0.50	0.49	0.58	0.65	0.65	0.81	1.10	1.25		
Dimethylphenol isomers	H	122/107/91/77/51	0.23	-	0.30	0.30	0.24	0.24	0.45	0.45	0.56	0.53	0.88		
Cathecol	Ca	110/81/64	2.83	3.02	3.45	3.72	4.18	5.37	6.35	6.35	8.85	12.71	15.20		
3-Methoxycathecol	Ca	140/125/97	9.18	9.75	11.72	12.40	14.05	16.06	17.29	17.29	19.46	20.05	19.70		
4-Methylcatechol	Ca	24/123/78	1.76	1.60	1.70	1.88	1.97	2.44	2.76	2.76	3.53	4.87	5.96		
4-Ethylcatechol	Ca	138/123/77	0.82	0.74	1.13	1.19	-	0.98	1.01	1.01	1.27	1.59	2.04		
1,2,3-Benzenetriol	Ca	126/80/108/52	1.05	0.85	1.16	-	1.50	2.06	2.76	2.76	4.08	4.90	4.36		
Guaiacol	G	109/124/81/53	3.39	3.53	3.70	3.76	3.86	4.27	4.12	4.12	4.24	4.10	3.91		
3-Methylguaiacol	G	123/138/77/95/67	0.86	0.89	1.05	1.10	1.14	1.25	1.17	1.17	1.19	1.07	1.00		
4-Methylguaiacol	G	138/123/95	4.45	3.72	3.98	3.85	3.75	3.61	3.35	3.35	3.31	2.96	2.77		
4-Vinylguaiacol	G	150/135/107/77	3.00	2.16	1.96	1.82	1.88	1.47	1.44	1.44	1.29	1.23	1.39		
4-Ethylguaiacol	G	137/152	2.45	1.90	2.17	2.08	1.94	1.85	1.57	1.57	1.32	1.12	1.08		
4-Propenylguaiacol	G	164/77/149	0.55	-	-	0.22	-	-	-	-	0.20	0.20	0.22		
Vanilin	G	151/152/109/81	0.80	-	-	-	-	-	-	-	-	1.18	1.16		
4-Acetylguaiacol	G	166/151/123	0.77	0.96	0.89	0.81	0.78	0.70	0.76	0.76	0.62	0.63	0.58		
Guaiacyl acetone	G	137/180/122	0.88	-	-	-	-	-	-	-	-	-	-		
4-Propylguaiacol	G	137/166/122	0.40	0.47	0.23	0.26	0.30	0.29	0.35	0.35	-	-	-		
Syringol	S	154/139/111/96	12.89	12.59	14.18	14.00	14.04	13.66	12.23	12.23	10.11	7.40	6.31		
4-Vinylsyringol	S	180/165/137	7.95	6.61	6.45	6.34	6.33	4.61	4.14	4.14	2.52	1.41	1.17		
3,4-Dimethoxyphenol	S	154/139/111	4.83	4.11	4.50	4.68	4.93	5.34	5.04	5.04	4.28	3.70	3.25		
4-Methylsyringol	S	168/153/125	14.64	11.65	13.48	13.01	12.98	11.75	10.20	10.20	8.23	5.47	4.07		
4-Propylsyringol	S	167/196/168/123	-	0.62	0.59	-	0.56	0.77	-	-	-	-	-		
4-Acetylsyringol	S	196/181/153	1.83	2.19	2.31	2.01	1.87	1.36	1.92	1.92	1.07	0.75	0.57		
Syringaldehyde	S	182/181/111	2.40	3.02	3.16	2.83	2.98	2.87	2.65	2.65	2.18	1.75	1.12		
Syringylacetone	S	167/210	0.69	0.69	0.61	0.56	0.41	0.42	0.32	0.32	-	-	-		
4-Propenylsyringol	S	194/91/151	5.96	2.05	1.92	2.24	1.53	1.38	0.97	0.97	0.71	0.49	0.20		
Lignin S/G ratio			2.92	3.20	3.38	3.29	3.34	3.14	2.94	2.94	2.39	1.68	1.38		

Source: Author

Figure 3: Phenolic compounds into four categories: phenol-type (H), catechol-type (Ca), guaiacyl-type (G) and syringyl-type (S)



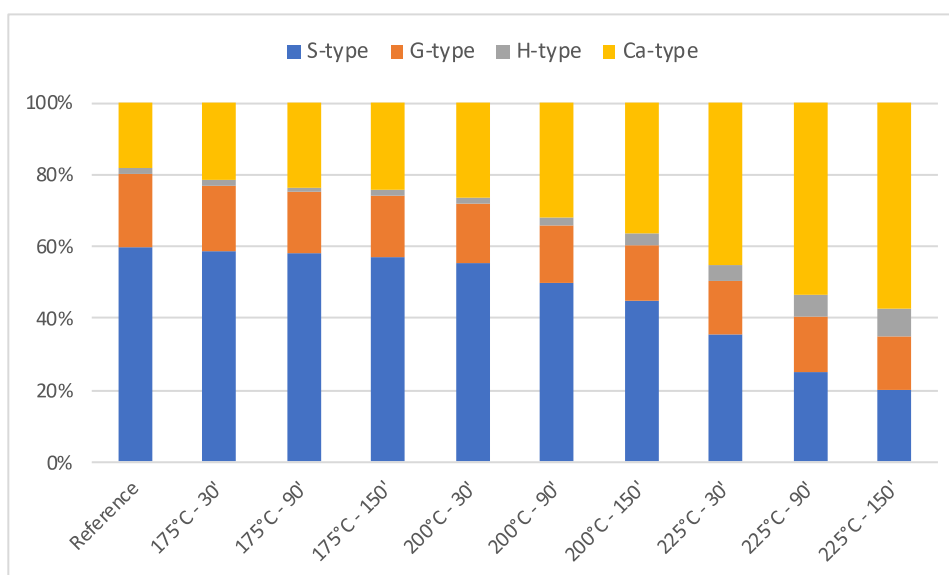
Source: Author

Lignin S/G ratio values ranged from 1.38 to 3.38. There was no significant variation between the S/G values of the reference and treatments of 175 and 200°C. However, a reduction of 53% in the S/G ratio of the reference treatment (lignin S/G ratio: 2.92) compared to the treatment of 225°C and 150 minutes (lignin S/G ratio: 1.38) was observed. In addition, the proportion of lignin with the absence of methoxyl groups (H-type) also increased significantly. This trend shows that demethoxylation of eucalypt kraft lignin occurred during the thermal treatment.

In the reference treatment, a content of 59.90, 20.52, 1.27 and 18.31% of S-type, G-type, H-type and Ca-type of lignin was observed (Figure 4). In the treatment carried out with the most drastic conditions (225°C and 150 minutes), these values were 20.28% (S-type), 14.70% (G-type), 7.56% (H-type) and 57.45% (Ca-type) significant reduction in S-type lignin (66%) and in G-type lignin (28%), showing that demethoxylation happened during heat treatment.

In addition, a significant increase in H-type lignin (495%) and modified catechol-type lignin (214%) was observed. A strong increase in the catechol and methoxycatechol content was observed in the treatment of 225°C and 150 minutes compared to lignin extracted from untreated liquor, showing that the demethylation of eucalypt kraft lignin occurred during the thermal treatment.

Figure 4: Effect of thermal treatment in the percentage of phenolic compounds



Source: Author

According to Fernández-Rodríguez et al. (2020), base catalysis depolymerization occurs by hydrolysis of ether bonds, reactions of demethoxylation, demethylation and dealkylation. Guaiacol may be a direct product of demethoxylation (removal of $-OCH_3$) from syringol. From guaiacol, phenol groups may be formed through demethoxylation and catechol may be formed through demethylation (Mukundan et al., 2019). The 1,2,3-benzenetriol compound is generated through the demethylation of syringol.

Leppävuori et al. (2017) performed the thermal treatment of softwood and hardwood black liquor and observed that the content of catechol groups increased from 0.3 mmol/g to 2.2 mmol/g in the modified black liquor. During the thermal process a lignin rich in catechol is produced, and an increase in the number of reactive sites is observed (Wikberg et al., 2017). According to some authors, catechol groups are regarded as having a higher reactivity than phenol (Kallury et al., 1985; Li and Geng, 2005; Davis et al., 2016).

Hardwood kraft lignin is less reactive than the softwood type because S-type lignin contains both *ortho* positions occupied by methoxyl groups (Demuner et al., 2019). The modification in the chemical structure of eucalypt kraft lignin is important for several uses. The eucalypt kraft lignin isolated from the heat-treated liquor may be used with greater success in the production of high-added value products based on lignin, as lignosulfonates and adhesives.

During lignosulfonates production through sulfomethylation of kraft lignin, first occurs hydroxymethylation reaction through the addition of formaldehyde. Then the sulfonation occurs through use of sodium sulfite or sodium bisulfite (Yu et al, 2013). The hydroxymethylation is one of the most common reactions that may be performed on the aromatic rings (Bertella and Luterbacher, 2020). However, it is possible the sulfomethylation reaction occurs only in the guaiacyl lignin, which has the aromatic carbon at the C5 position available (Demuner et al., 2019). Therefore, as the sulfomethylation of hardwood kraft lignin is a challenging process due to the high content of low reactivity syringyl lignin present, the thermal treatment can be an excellent pre-treatment of black liquor to increase the reactivity of kraft lignin for this purpose.

For adhesives production, G-type kraft lignin also is superior to S-type due to its free ring position (Ghorbani et al., 2016). According to Yang et al. (2019), because of activation of the aromatic ring in the *ortho* position, phenolic hydroxyl groups increase the reactivity of lignin with formaldehyde to produce lignin-phenol-formaldehyde resin. Therefore, chemical modifications in the structure of hardwood lignin to improve its reactivity are essential for successful use as adhesives.

4. CONCLUSIONS

The eucalypt black liquor used for the heat treatment showed typical characteristics of chemical composition, elemental analysis and heating value when compared with the literature. The lowest thermal process yield (93.0%) was found for the treatment with more drastic conditions (225 °C and 150 minutes), with minimal thermal degradation of the liquor analyzed by TG/DTG curves. It was observed that the mass loss between 200 and 400°C is characterised by degradation of hemicelluloses and cellulose, but mainly due to the degradation of soluble lignin.

After extracting the lignins from the original liquor and the heat-treated liquors, it was evidenced that the heat treatment promoted demethylation and demethoxylation of eucalypt kraft lignin. A reduction in soluble lignin, oxygen and hydrogen content and, an increase in insoluble lignin and carbon content were observed in the treatments with higher temperatures and times reaction. Heat-treated lignins presented characteristics similar to those found for softwood kraft lignin, whose predominant lignin is G-type.

There was a reduction of 53% in the lignin S/G ratio of the reference treatment (lignin S/G ratio: 2.92) compared to the treatment of 225 °C and 150 minutes (lignin S/G ratio: 1.38). Besides the reduction in the lignin S/G ratio of heat-treated lignins, a significant increase in H-type lignin (495%) and modified catechol-type lignin (214%) was observed in the treatment of 225°C and 150 minutes compared to lignin extracted from untreated liquor.

The eucalypt kraft lignin isolated from the heat-treated liquor may be more reactive than the original lignin due to changes in its chemical composition and molecular structure. This lignin should be considered in the production of high-added value lignin-based products.

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CAPÍTULO 3

PRODUCTION OF LIGNOSULFONATES FROM EUCALYPT KRAFT LIGNIN BY THE SULFOMETHYLATION AND ACID SULFONATION PROCESSES

ABSTRACT

Biorefinery is a promising approach to promote a wider use of kraft lignin, which is currently incinerated in kraft recovery boilers for power and steam generation. The production of lignosulfonates is one of possible uses of technical lignin for the production of lignin derivative bioproduct. This study evaluates the production of lignosulfonates from eucalypt kraft lignin by two processes: sulfomethylation and acid sulfonation. For sulfomethylation process, three temperatures (100, 130 and 160 °C) and three molar ratios of sodium hydroxymethylsulfonate/lignin (0.8; 1.2 and 1.6) were evaluated. For acid sulfonation process, the temperatures of 80, 100 and 120 °C and molar ratio H₂SO₄/lignin of 10, 20 and 30 were considered. The acid sulfonation was not efficient for the production of lignosulfonates from kraft lignin. On the other hand, the lignosulfonate produced by the sulfomethylation process (160 °C and molar ratio of 1.6) presented a sulfur content (5.23%) similar to that found for commercial lignosulfonate (5.28%). A reduction of acid-insoluble lignin content and increase of acid-soluble lignin content was also observed compared to unmodified kraft lignin. In addition, it was confirmed the insertion of sulfonate groups verified through FTIR analysis. Some lignosulfonates produced by sulfomethylation obtained solubility values similar to the commercial lignosulfonate, showing that the chemical modification of kraft lignin was achieved.

Keywords: Eucalypt kraft lignin. Lignosulfonates. Sulfonation process. Chemical modification

1. INTRODUCTION

Lignin is the second most abundant natural polymer on Earth, next to cellulose, and constitutes approximately 15-30% weight of the lignocellulosic biomasses (Gnansounou and Pandey, 2017; Ahmad et al., 2018). Lignin is responsible for the hardness and resistance of lignocellulosic cell walls, characterized by the presence of phenolic hydroxyl groups, high molecular weight and amorphous structure (Demuner et al., 2019). In pulp production, lignin must be degraded and solubilized to promote the individualization of wood fibers (Potthast, 2006).

As a by-product of the pulp and paper industry, approximately 50 million tons of lignin are produced worldwide annually, of which 98% to 99% is incinerated to produce fuel in the kraft process. Only 1-2% are lignosulfonates generated in the sulfite process (Mohan et al., 2006; Gellerstedt et al., 2012; Inwood, 2014; Norgren and Edlund, 2014; Shrotri et al., 2017). Most of the black liquor generated in the kraft process, will remain being burned for energy generation and recovery of process reagents. However, the value equivalent of lignin used as a fuel is much lower than the value of lignin used in chemical conversion into high-value products (Macfarlane et al., 2009; Vishtal and Kraslawski, 2011).

Traditionally, lignosulfonates are obtained as by-products of sulfite pulping and are the main components in the spent liquors (Feizi et al., 2019; Hanhikoski et al., 2019; Dessbesell et al., 2020). In the sulfite process, the wood delignification is carried out by SO_2 and HSO_3^- (acid sulfite), HSO_3^- (bisulfite), or HSO_3^- and SO_3^{2-} (neutral sulfite), usually in the presence of a cation (Fan and Zhan, 2008; Calvo-Flores and Dobado, 2010).

Lignosulfonates generated by the sulfite process are composed of phenyl propane units with sulfonic groups, carboxylic acids and phenolic-OH groups (Woiciechowski et al., 2020). They are water soluble and anionically charged (Aro and Fatehi, 2017). Because of these characteristics, lignosulfonates are widely used as dispersants, surfactants, wastewater treatment flocculants, animal feed, pesticides, petroleum drilling additives, stabilizers in colloidal suspensions, and plasticizers in concrete mixtures (Fatehi and Ni, 2011; Vishtal and Kraslawski, 2011; Zhou et al., 2013; Nasser et al., 2013; Rybczyńska-Tkaczyk and Kornilowicz-Kowalska, 2017).

However, due to the limited production of sulfite pulp, an increasing number of studies focusing on sulfonation of technical lignins have been performed to enable the generation of water-soluble lignin and satisfy the market demand for lignosulfonates (He and Fatehi, 2015; Konduri and Fatehi, 2015). Since kraft pulping is the world dominant process,

kraft lignin is considered an important potential by-product of adding value within the concept of biorefinery in the pulp industry (Jiang et al., 2018; Kumar et al., 2020). An increased by 150% in their production from 2014 to 2018 was observed (Dessbesell et al., 2020).

The biorefinery concept of the pulp mills is a promising approach to promote a wider use of kraft lignin. This lignin valorization may be associated to the improving of the pulping process, more efficient and less costly extraction technologies and the opportunity of portfolio diversification and generation from lignin (Dessbesell et al., 2020).

Johansen (2018) reported that the lignin market pull is expected between 2023 and 2028. However, new kraft lignin applications are already being studied and improved to meet market specifications and become adequate to end-users (McCoy, 2016). Kraft lignin can be used as lignosulfonates and dispersants, technical carbons (e.g., carbon fibers), transportation fuels, bioplastics, adhesives, etc.

The production of lignosulfonates from kraft lignin consists in the sulfonation process, which can be carried out using acid sulfonation or sulfomethylation methods. Sulfonation aims to improve the solubility and charge density of kraft lignin, because although the lignin dissolves readily at a high pH, it exhibits poor solubility at a neutral and acid pH, and this hinders its use in many systems involving aqueous solutions (Helander et al., 2013).

Acid sulfonation consists of treating lignin with concentrated sulfuric acid at high temperatures (Compere et al., 2005). During sulfonation, the $-SO_3H$ groups are attached to the aliphatic side chain of lignin, on the alpha carbon of the phenylpropane unit (Fengel and Wegener, 1989; Sjöström, 1993). According to Gao et al. (2019a), the $-SO_3H$ groups can also be linked in the aromatic groups.

Another alternative for sulfonated kraft lignin production is the sulfomethylation, which consists of treating the purified lignin with sodium sulfite or sodium bisulfite, in the presence of an aldehyde (for instance formaldehyde). A hydroxymethylation occurs through the addition of formaldehyde and the sulfonation through the use sodium sulfite (Yu et al., 2013). Berlin and Balakshin (2014) report that the kraft lignin sulfomethylation reaction introduces $-CH_2SO_3H$ groups in the aromatic ring of the lignin structure.

However, the sulfonation of hardwood kraft lignin is a challenging process due to the high content of low reactivity syringyl lignin (S-type) present in the kraft liquor. Possible acid sulfonation and sulfomethylation reactions in the aromatic ring occurs only in guaiacyl lignin (G-type), which presents the aromatic carbon in the C-5 position available for reaction or in the aliphatic side chain of lignin (Gao et al., 2019a).

Sulfonation studies of softwood and grasses kraft lignin have already been carried out (Inwood, 2014; Huang et al., 2018; Gao et al., 2019a). However, as the production of short fiber pulp is dominant in South America, an in-depth study of kraft lignin from the eucalypt specie is necessary. The objective of this study was to assess conditions of temperature and molar ratio of reagents/lignin to produce eucalypt sulfonated kraft lignin through the process of acid sulfonation and sulfomethylation.

2. MATERIALS AND METHODS

2.1 Kraft lignin characterization

Kraft lignin from eucalypt wood kraft cooking was supplied by a Brazilian pulp and paper company. For characterization of the chemical composition, the total lignin was measured by the sum of acid-soluble and acid-insoluble lignin, measured according to TAPPI UM 250 and TAPPI T 222 om-02, respectively. Sugar composition, ash and metals were measured according to SCAN-CM 71:09, TAPPI T211 om-93, and TAPPI T266 om-94, respectively.

For pyrolysis coupled to gas chromatography and mass spectrometry (Py-GC/MS) was used the kraft lignin (ca. 0.1 mg) for calculating the S/G ratio. The pyrolysis was performed in a micro-furnace pyrolyzer (Frontier Laboratories Ltd., Fukushima, Japan) connected to a GC-MS apparatus (Shimadzu, model QP2020), using an Ultra-ALLOY[®] Capillary Column (UA5, 30m x 0.25 mm ID, 0.25 μ m film thickness). The pyrolysis was carried out at 550 °C for 10s, as previously described (Del Río et al., 2005; Barbosa et al., 2008; Schorr et al., 2014). The pyrolysis chamber was purged with helium (100kPa) to transfer the pyrolysis products as quickly as possible to the GC column. The injector temperature was 100°C and the chromatograph oven was ramped from 45°C (4 min) to 240°C at a rate of 4°C min⁻¹. The final temperature was kept for 10 minutes. The temperatures of the detector and the GC-MS interface were 250 and 290 °C, respectively. Mass spectrometer was operated by the electron impact ionization mode at 70 eV and mass scan range was 50–350. The compounds released were identified by comparing their mass spectra with the GC-MS spectral library (Willey and NIST), with data from the literature (Del Río et al., 2005; Barbosa et al., 2008; Fernández-Rodríguez et al., 2020; Silva et al., 2020) and when necessary by mass fragmentography. Based on Fernández-Rodríguez et al. (2020) and Silva et al. (2020) studies, Guaiacol, 3-Methylguaiacol, 4-Methylguaiacol, 4-Vinylguaiacol, 4-Ethylguaiacol, 4-Propenylguaiacol, Vanilin, 4-Acetylguaiacol, Guaiacyl acetone and 4-Propylguaiacol were used as markers of

guaiacil lignin (G-type). Syringol, 4-Vinylsyringol, 4-Methylsyringol, 4-Propylsyringol, 3,4-Dimethoxyphenol, 4-Acetylsyringol, Syringaldehyde, Syringylacetone and 4-Propenylsyringol were used as markers of syringyl lignin (S-type). The lignin S/G ratio was calculated by dividing the sum of area percentage of syringyl-type (S) lignin per the sum of area percentage of guaiacyl-type (G) lignin.

The eucalypt kraft lignin elemental analysis was performed using CHNS-O model LECO equipment. The carbon, hydrogen, nitrogen and sulphur percentages were determined in the TruSpec CHNS Micro module and the oxygen percentage in the TruSpec Oxygen Add-On module. The eucalypt kraft lignin higher and lower heating values were measured according to TAPPI Test T684 om-90 standard.

The thermogravimetric analysis of eucalypt kraft lignin (TG/DTG) was performed under a nitrogen gas atmosphere, at a constant flow rate of 100 mL/min, in the DTG-60H (Shimadzu). Thermogravimetric curves (TG) were obtained from 25 °C to a maximum temperature of 1100 °C, with a heating rate of 10 °C min⁻¹, to evaluate the mass loss as a function of temperature. The second curve (DTG) was generated from the first derivative of the TG curves.

Functional groups of samples were determined by using Fourier-transform infrared spectroscopy (VARIAN 600 with GladiATR) in the range of 400–4000 cm⁻¹ with a resolution of 4 cm⁻¹.

2.2 Sulfomethylation process

Eucalypt kraft lignin was mixed with sodium sulfite and formaldehyde according to methods mentioned by Huang et al. (2018) and Konduri and Fatehi (2015). During sulfomethylation, 1 mol of formaldehyde mixed with 1 mol of sodium sulfite generate 1 mol of sodium hydroxymethylsulfonate, the reactive reagent for sulfomethylation. The eucalypt kraft lignin was mixed with formaldehyde (37% by weight) and sodium sulfite. The investigated parameters were molar ratio between sodium hydroxymethylsulfonate and lignin (0.8; 1.2; 1.6 mol/mol) and three temperature (100; 130; 160°C). The reaction was carried out in stainless steel reactors inserted in a pressurized rotary digester. The time to temperature was 80 minutes and time at temperature was 240 minutes. The concentration of lignin adopted was 25 g/L and the pH of the final reaction was maintained at 8.0. After the reaction, the hot reactor was cooled immediately in an ice bath and the liginosulfonate solution was neutralized to pH 5.0 by adding sulfuric acid to precipitate the un-reacted lignin.

2.3 Acid sulfonation process

Eucalypt kraft lignin was mixed with highly concentrated sulfuric acid (98%) according to the method described by Inwood (2014). Three lignin molar ratios H₂SO₄/lignin (10, 20 and 30) and three reaction temperatures (80, 100 and 120 °C) were evaluated. Lignin and sulfuric acid were inserted into glass bottles, sealed and vortexed at 2500 rpm for 1 minute using a Fisher Scientific Mini Vortex or to ensure a homogenous mixture. The samples were placed in a bath with temperature control. The time reaction was 60 minutes and the concentration of lignin adopted was 25 g/L. After removing samples from the bath, the sulfonation reaction was stopped by neutralization with NaOH to pH 5.0 and the solutions were cooled to room temperature.

2.4 Yields of sulfomethylation and acid sulfonation processes

After sulfomethylation and acid sulfonation processes, the remaining solids and lignosulfonates were separated by filtration within a crucible system with aluminum oxide. The remaining solids were dried at 105°C for 5 hours to calculate the amount of undissolved lignin. The lignosulfonates yields were calculated based on the Equation 1, where w is the amount of kraft lignin used in the process and w_1 is the amount of remaining solid after sulfomethylation and acid sulfonation process.

$$\text{Lignosulfonate yield (\%)} = \left(\frac{w - w_1}{w} \right) \times 100 \quad \text{Eq. 1}$$

2.5 Lignosulfonates characterization

The produced lignosulfonates were purified through a dialysis membrane (molecular weight cut-off of 1000 g/mol – MWCO1000) for 48 h. For the first 6 hours, the water was changed every 2 hours and after the water was changed every 12 hours to separate the lignosulfonates and un-reacted chemicals. The samples collected from membrane were dried in a 60°C oven overnight. Subsequently, the samples were characterized by chemical composition, elemental analysis, S/G ratio and FTIR using the same methodology adopted for the eucalypt kraft lignin characterization.

To measure the water solubility, 200 mg of lignosulfonates samples were suspended in 20 ml of deionized water, the pH was adjusted to 7.0, and the suspension was stirring at 100 rpm for 2 h at 25°C (Ouyang et al., 2009; Konduri and Fatehi, 2015). After that, the samples

were centrifuged at 1000 rpm for 5 min, and the supernatant was dried overnight in a 105°C oven. The solubility of lignosulfonates in the supernatants was determined according to Equation 2.

$$\text{Solubility (\%)} = \left(\frac{\text{Mass of dissolved lignin}}{\text{Initial mass of lignin}} \right) \times 100 \quad \text{Eq. 2}$$

3. RESULTS AND DISCUSSION

3.1 Kraft lignin characterization

Eucalypt kraft lignin was characterized by lignin (soluble, insoluble, and total), lignin S/G ratio, sugars, ash, and inorganics (Table 1).

Table 1: Characterization of the eucalypt kraft lignin regarding to lignin (soluble, insoluble and total), S/G ratio, sugars, ash and inorganics

Constituents		Eucalypt kraft lignin
Acid-soluble lignin (%)		9.8
Acid-insoluble lignin (%)		85.5
Total lignin (%)		95.3
S/G ratio		3.1
Ash (%)		2.2
Sugars (%)	Glucan	0.9
	Xylan	1.3
	Mannan	0.0
	Galactan	0.2
	Arabinan	0.1
Inorganics (ppm)	Ca	670.6
	Na	2207.9
	Mg	84.6
	K	268.6
	Fe	222.5
	Cu	14.7
	Mn	28.9
	Cl	574.9

Source: Author

The values found for total lignin, acid-soluble lignin and acid-insoluble lignin were 95.3%, 9.8% and 85.5%, respectively. Zhou and Lu (2014) in a study with eucalypt kraft

lignin found similar values of insoluble lignin (88.7%), soluble lignin (8.87%) and total lignin (97.57%). Dieste et al. (2016) found values of 94.1% (total lignin), 86.7% (acid-insoluble lignin), 7.4% (acid-soluble lignin) also in a study with eucalypt kraft lignin.

Ashes content in kraft lignin was 2.2% and the total content of sugars was 2.5% (Glucan 0.9%; Xylan 1.3%; Galactan 0.2% and Arabinan 0.1%). Gordobil et al. (2016) found 2.2% of sugars and Tagami (2019) found $2.1 \pm 0.2\%$ of ash, which were similar to those found in this study, both in eucalypt kraft lignin. However, lower values of carbohydrates (0.81%) and ash (0.84%) were also observed by Zhou and Lu (2014). Dieste et al. (2016) found a lower carbohydrate value (0.7%) than that found in this study, but a similar ash content (2.1%). The metals most found in lignin kraft were sodium, calcium, chloride and potassium. These elements are found in the wood and in the kraft black liquor (Frederick, 1997), and can remain in the kraft lignin after extraction. Besides these major components, other inorganic components are present, some of them occurring in trace amounts (Hubbe et al., 2019).

Sugars and ashes contents are directly related to the purity of kraft lignin, and high values may be related to the raw material or to the extraction process. Silva (2020) used different acids (sulfuric acid, acetic acid, citric acid and lactic acid) for precipitation of kraft lignin from eucalypt black liquor. The authors observed a great difference in the content of lignin, sugars and ash among the isolated lignins, showing that the extraction process interferes in the chemical composition of the isolated kraft lignin.

Cassales et al. (2020) reported that the purification of eucalypt kraft lignin can be carried out by washing with water to remove contaminants, such as sugars and inorganic residues. The ash content decreased from 1.8% to 0.1% after washing. Glucose content decreased from 3.0 to 2.7%, and xylose from 2.6 to 2.3%. Besides that, a difference was also observed in the content of total, soluble and insoluble lignin. Before purification the values were: total lignin (88.4%), acid-soluble lignin (8.4%) and acid-insoluble lignin (80.0%); and after washing they were total lignin (94.1%), acid-soluble lignin (9.0%) and acid-insoluble lignin (85.1%).

Lignin S/G ratio value of the eucalypt kraft lignin sample was 3.10 measured by Py-GC-MS. Normally in hardwood kraft lignin, the majority of compounds liberated during the pyrolysis are derived from syringyl units (S-type). Cassales et al. (2020) reported the lignin S/G ratio of 2.86 for eucalypt kraft lignin also measured by Py-GC-MS. Gordobil et al. (2019) and Tagami et al. (2019) in studies with eucalypt kraft lignin found a lignin S/G ratio of 3.8 and 2.5, respectively.

As well as the raw material used in the pulping process, the extraction process can interfere with the lignin S/G ratio. Cassales et al. (2020) demonstrated that ionic strength of the organic acid used for the precipitation modifies the content of methoxylated phenolic substructures in kraft lignin (S/G ratio of up to 5.16). The presence of methoxyl groups in C-5 positions of the aromatic ring (S-type lignin) avoid the formation of the condensed bonds (Holtman et al., 2006). However, *ortho* positions occupied by methoxyl groups reduce hardwood kraft lignin reactivity for the production of high-added value products based on lignin (Demuner et al., 2019). Tagami et al. (2019) reported that the lignin S/G ratio may also have an important effect on the chemical reactivity of extracted lignin.

Elemental analysis and heating value from kraft lignin is presented in Table 2. The values found for carbon (62.28%), hydrogen (4.62%) and oxygen (30.69%) were similar to those found by Tagami et al. (2019) for eucalypt kraft lignin: C (62.4%); H (4.5%) and O (30.3%) and Dou et al. (2019) for the same raw material: C (62.96%), H (5.82%), O (28.32%). Boschetti et al. (2019a) found the following values: carbon (61.8%), hydrogen (5.8%) and oxygen (28.2%) for eucalypt kraft lignin extracted by the Lignoboost process.

Table 2: Characterization of the kraft lignin as elemental analysis and heating value

Parameters		Eucalypt black liquor
Heating value (MJ/Kg)	Higher	25.39
	Lower	24.38
Elemental analysis (%)	Carbon	62.28
	Hydrogen	4.62
	Oxygen	30.69
	Nitrogen	0.09
	Sulfur	2.06

Source: Author

The nitrogen (0.09%) and sulfur (2.06%) contents are lower than those found for carbon, hydrogen and oxygen. Nitrogen values of 0.2% (Dou et al., 2019) and 0.72% (Boschetti et al., 2019a) have recently been reported in the literature. According to Doherty et al. (2011), kraft lignin has a sulfur percentage between 1 and 3%, which are present as aliphatic thiol groups in kraft lignin (Inwood, 2014). Sulfur values of 2.6% (Tagami et al., 2019), 1.68% (Dou et al., 2019) and 2.5% (Boschetti et al., 2019a) were reported in the literature, similar to those found in this study.

The elemental analysis, chemical composition, lignin/carbohydrates ratio and raw material influence on the lignin heating values (Maksimuk et al., 2020). The lower heating value (LHV) and higher (HHV) differ because, in the first, it is considered that the water formed by the combustion remains in a vapor state. In the second it is considered the energy that the water vapor particles release when changing to liquid phase (Jenkins and Ebeling, 1985; Acar et al., 2012).

The lower and higher heating values of the eucalypt kraft lignin were 24.38 and 25.39 MJ/Kg, respectively. Boschetti et al. (2019a) reported the same HHV for eucalypt kraft lignin and Dieste et al. (2016) reported the value of 26.0 MJ/kg for this type of raw material.

For lignin, the heating value (HV) is equal to the sum of the heating value of aromatic and carbohydrate parts (Maksimuk et al., 2020). About the elemental analysis, the higher carbon and lower oxygen contents positively influence on the HHV (Carneiro et al., 2014; Freitas et al., 2017) and the high ash content can negatively influence on the heating value (Boschetti et al., 2019b).

The heating value is an important parameter to indicate the energetic potential of lignin. Related to this parameter, the thermogravimetric analysis (TG) provides important information concerning to lignin energetic profile, technique frequently used to characterize pyrolyzed lignin (Malucelli et al., 2019).

The thermogravimetric method (TG) shows the percentage of mass loss as a function of temperature. The DTG curves (first derivative of the TG curves) show the mass variation in relation to time, reported also as a function of temperature (Janković et al., 2020). The TG/DTG thermogravimetric curves of the lignin sample are shown in Figure 1.

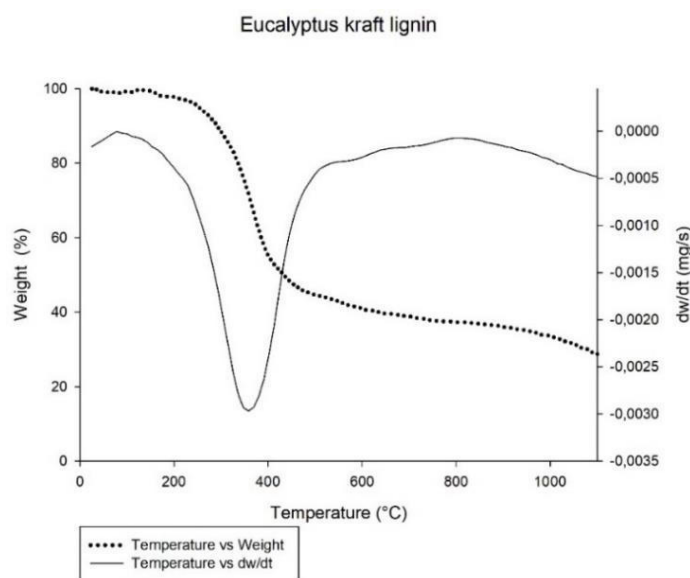
The maximum temperature of approximately 360°C observed in this work is similar to that found by Ponomarenko et al. (2014) with hardwood lignin isolated by the LignoBoost process (365°C). A significant weight loss between 250 and 400°C was observed. According to Sen et al. (2015), kraft lignin has a great loss of mass (about 40%) between 200 and 600°C, mainly up to 400°C. Fenner and Lephardt (1981) reported that the weight loss of kraft lignin between 150 and 300°C is attributed to the formic acid, formaldehyde, carbon dioxide and sulphur dioxide elimination resulting from the degradation of phenylpropane side chains of lignin. Between 200-300°C, it also can occur the decomposition of low molar mass phenols (Fang et al., 2015) and degradation of hemicelluloses and cellulose (200 to 400°C) present in the kraft lignin (Chen et al., 2019).

The weight loss observed between 400 to 800 °C can be attributed to the decomposition and the condensation of the aromatic ring of lignin (Fang et al., 2015; Brazil et

al., 2018). After 800 °C, lignin exhibits less weight loss, a behavior that can be attributed to the process of condensation or relocation of aromatic rings (Hua et al, 2016), and the fusion of inorganic elements in the kraft lignin.

Decomposition over a wide range in temperature occurs due to the complex structure of lignin, composed of aromatic rings, with C-C and C-O-C side chains and various types of functional groups (Wang et al., 2008; Kim et al., 2014). In addition, the large distribution of molar mass and other elements present in lignin also contribute to the wide thermal decomposition of this polymer.

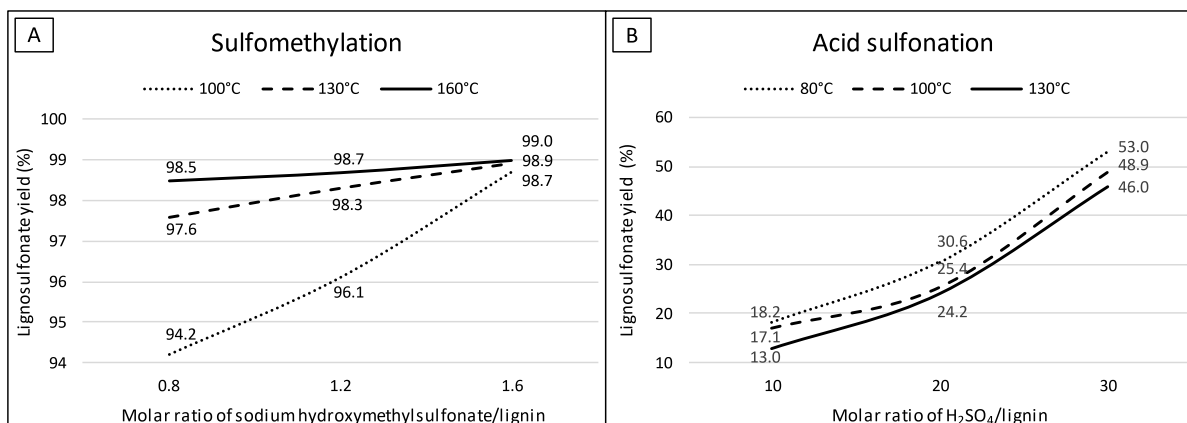
Figure 1: Thermogravimetric analysis of eucalyptus kraft lignin



Source: Author

3.2 Yields of sulfomethylation and acid sulfonation processes

Eucalypt kraft lignin was used for the sulfomethylation process investigated with three molar sodium hydroxymethylsulfonate/lignin ratios (0.8; 1.2 and 1.6) and three temperatures (100, 130 and 160 °C) (Figure 2A). This same raw material was used for the acid sulfonation process evaluated with three molar H₂SO₄/lignin ratios (10, 20 and 30) and three temperatures (80, 100 and 120 °C) (Figure 2B).

Figure 2: Yields of the sulfonation processes: A) Sulfomethylation; B) Acid sulfonation

Source: Author

The yields of the sulfomethylation process ranged from 94.2 to 99.0%. Huang et al. (2018) also observed high yield of lignosulfonates (94.9%) through sulfomethylation of bamboo kraft lignin with sodium sulfite and formaldehyde. The unmodified bamboo kraft lignin also had a total lignin content of 94.2%, similar to that found in this study for eucalypt kraft lignin of 95.3% (Table 1).

In the sulfomethylation process, it was observed that the increase of the molar ratio and temperature increased the yield of lignosulfonates. The highest yield was obtained in the treatment with the highest temperature and molar ratio (160°C – 1.6), although the yield values among treatments were similar, mainly in the 1.6 molar ratio.

Treatments at a temperature of 160°C, the yield values were also similar for the molar ratio of 0.8 (98.5%), 1.2 (98.7%) and 1.6 (99.0%). In the temperature of 100°C, increasing the ratio from 0.8 mol/mol to 1.6 mol/mol resulted in an increase of lignosulfonate production from 94.2% to 98.7%. Other authors have reported that the dosage of sodium hydroxymethylsulfonate is the foremost parameter affecting the degree of lignin sulfonation during the process (He and Fatehi, 2015; Konduri and Fatehi, 2015; Huang et al., 2017).

Huang et al. (2018) in the optimization of the sulfomethylation process of bamboo kraft lignin observed that the yield also increased with the increase of the molar ratio; however, higher temperatures did not favor the lignosulfonate production from bamboo kraft lignin. Although the bottleneck of sulfomethylation reactions may be due to a finite amount of reaction sites in lignin (Huang et al., 2017), it was evidenced in this study that the eucalypt kraft lignin showed good results of lignosulfonates yield through the sulfomethylation process.

The yield of the acid sulfonation process ranged from 13 to 53%. It was observed that the increase in the molar ratio increased the yield of lignosulfonates in acid sulfonation process. However, higher temperatures did not favor the production of lignosulfonates. The highest yield was obtained in the treatment with the molar ratio $\text{H}_2\text{SO}_4/\text{lignin}$ of 30 and temperature of 80°C .

In the temperature of 80°C , increasing the molar ratio from 10 mol/mol to 30 mol/mol resulted in a considerable increase of lignosulfonate production from 18.2% to 53.0%. At a temperature of 120°C , increasing the molar ratio from 10 mol/mol to 30 mol/mol resulted in an increase of lignosulfonate production from 13.0% to 46.0%. However, the variation in temperature within the same molar ratio resulted in minor variations of lignosulfonate yields. For example, at the molar ratio of 30, the lignosulfonate yields in the temperatures of 80, 100 and 120°C were 46.0, 48.9 and 53.0%, respectively.

Inwood et al. (2018) studied acid sulfonation of softwood kraft lignin and the temperatures from 100°C to 160°C and $\text{H}_2\text{SO}_4/\text{lignin}$ molar ratios from 6.5 to 32.5 were evaluated. The optimum $\text{H}_2\text{SO}_4/\text{lignin}$ molar ratio was 15.2 mol/mol and the best temperature condition was at 100°C , showing that the temperature negatively influenced the process.

3.3 Lignosulfonates characterization

3.3.1 Chemical characterization

The lignosulfonates produced by the sulfomethylation process (temperatures of 100, 130 and 160°C and sodium hydroxymethylsulfonate/lignin molar ratios of 0.8; 1.2 and 1.6) and acid sulfonation process (temperatures of 80, 100 and 120°C and $\text{H}_2\text{SO}_4/\text{lignin}$ molar ratios of 10, 20 and 30) were characterized by lignin (soluble, insoluble and total) sugars, ash and lignin S/G ratio. A commercial lignosulfonate was also chemically characterized (Table 3).

Commercial lignosulfonate showed the highest content of acid-soluble lignin (68.78%) and the absence of acid-insoluble lignin. Doherty et al. (2011) reported that the lignosulfonates generated by the sulfite process have two main ionizing groups, the sulfonates ($\text{pK}_a \leq 2$) and the phenolic hydroxyl groups ($\text{pK}_a \sim 10$). The high acid-soluble characteristic attributed to lignosulfonates is due to the low pK_a of the sulfonate groups and a variety of functional groups that provide unique colloidal properties to these lignins (Areskog et al., 2010; Areskog and Henriksson, 2011; Duval and Lawoko, 2014). In addition to fragments of

lignin, sugars and ash, the liginosulfonate may contain a fraction of phenols, alcohols and carboxylic acids in its chemical composition (Woiciechowski et al., 2020)

Table 3: Chemical characterization of commercial liginosulfonate and liginosulfonates produced by the sulfomethylation and acid sulfonation processes

Liginosulfonates			Constituents (%)					Lignin S/G ratio
Process	T (°C)	Molar ratio	Soluble lignin	Insoluble lignin	Total lignin	Sugars	Ash	
Sulfomethylation	100	0.8	11.57	79.56	91.13	1.77	6.17	2.21
		1.2	11.69	77.78	89.47	1.91	7.32	2.26
		1.6	14.46	74.01	88.46	1.72	8.52	2.20
	130	0.8	15.07	71.97	87.04	1.52	9.34	2.33
		1.2	15.43	70.89	86.31	1.56	9.99	2.39
		1.6	19.36	66.42	85.78	1.67	10.67	2.44
	160	0.8	28.36	56.58	84.94	1.47	9.83	2.61
		1.2	40.83	36.17	77.00	1.41	11.85	2.68
		1.6	44.59	30.31	74.90	1.47	12.25	2.77
Acid sulfonation	80	10	3.60	92.47	96.07	0.10	3.52	2.73
		20	3.64	90.10	93.74	0	6.23	2.88
		30	3.23	89.74	92.97	0	7.01	2.76
	100	10	4.01	90.01	94.01	0	5.93	2.68
		20	4.06	89.79	93.85	0	6.04	2.61
		30	4.90	89.82	94.72	0.05	4.96	2.74
	120	10	4.81	91.15	95.96	0	3.90	2.70
		20	4.97	89.30	94.27	0.10	5.46	2.70
		30	5.48	89.77	95.25	0.15	4.51	2.76
Commercial liginosulfonate			68.78	0	68.78	4.65	12.91	0

Source: Author

The contents of sugars and ash found in the commercial liginosulfonate were 4.65 and 12.91%, respectively. After sulfite pulping, the spent liquor contains a high content of sugars and residual chemicals used during the process (Restolho et al., 2009). Several purification steps are necessary to obtain liginosulfonates with a higher purity, because the presence of contaminants may have negative implications in some applications (Forss et al., 1985).

Fermentation to convert the residual sugars into ethanol, membrane separation, and ultrafiltration are some processes used for purification (Lora, 2008; Aro and Fatehi, 2017). In spent liquor, the sugar content can reach 30% by weight and inorganics represent

approximately 10% by weight (Aro and Fatehi, 2017), however these values are much lower after purification.

Reknes (2003) reported values of sugars (2.0%) and inorganics (6.1%) for hardwood lignosulfonate "Borresperse CA-AS" (Borregaard Ind. Ltd. LignoTech South Africa - LTSA) and values of sugars (6.6%) and inorganics (8.3%) for softwood lignosulfonate "Borresperse CA" (Borregaard Ind. Ltd. LignoTech Norway - LTN). In the commercial lignosulfonate used in this study, only derivatives of lignin G and H (lignin S/G ratio equal to zero) were found in the Py-GC-MS analysis, showing that it is a softwood lignosulfonate.

The chemical composition of the lignosulfonates obtained by the sulfomethylation and acid sulfonation processes was quite different. Based on the chemical composition of unmodified kraft lignin (Table 2), the lignosulfonates produced by sulfomethylation presented an increase in acid-soluble lignin and a reduction in acid-insoluble lignin. The values of acid-soluble lignin ranged from 11.57 to 44.59% and the values of acid-insoluble lignin ranged from 30.31 to 79.56%.

The sample with the highest temperature (160°C) and highest sodium hydroxymethylsulfonate/lignin molar ratio (1.6 mol/mol) showed values of 44.59 and 30.31% of acid-soluble and acid-insoluble lignin, respectively. This sample presented values of acid-soluble lignin closest to the commercial lignosulfonate (68.78%) and showed the highest lignosulfonate yield (Figure 2).

The increase in the acid-soluble lignin content was up to 74% and shows that the sulfomethylation process was effective in modifying and sulfonating the kraft lignin. The acid-soluble characteristic of lignosulfonates is due to the low pKa of the sulfonate groups (Areskog et al., 2010; Areskog and Henriksson, 2011; Duval and Lawoko, 2014) that were introduced in kraft lignin.

Other authors have already reported that kraft lignin can be sulfonated by formaldehyde and sodium sulfite treatment (Yu et al., 2013; Berlin and Balakshin, 2014; Matsushita, 2015; Aro and Fatehi, 2017; Gao et al., 2019a). The reaction is believed to occur preferentially in G-type lignin, for the introduction of the $-\text{CH}_2\text{SO}_3\text{H}$ groups in the aromatic ring.

In this study, it was observed that the lignosulfonate produced under the conditions of 160 °C and molar ratio of 1.6, presented a higher lignin S/G ratio (2.76) than other lignosulfonates produced by the same process. Thus, it was evident that, even with a high content of S-type lignin in kraft lignin, it was also possible to produce lignosulfonates. This

insertion of sulfonate groups probably occurs on aliphatic hydroxyl group (e.g. α -position), as reported by Gao et al. (2019a, b).

In acid sulfonation, a reduction in acid-soluble lignin and an increase in acid-insoluble lignin was observed compared to unmodified kraft lignin. The values of acid-soluble lignin ranged from 3.23 to 5.48% and the values of acid-insoluble lignin ranged from 89.30 to 92.47%. Among the treatments, an increase in acid-soluble lignin was observed according to the increase in the molar ratio and temperature. In this sulfonation, the $-\text{SO}_3\text{H}$ groups are linked to the aliphatic side chain of lignin at the α -carbon of the phenyl propane unit (Inwood, 2014; Sjöström, 1993) and at aromatic groups, in H and G units of kraft lignin (Gao et al., 2019a).

The lignin S/G ratio values for the lignosulfonates produced by acid sulfonation were similar, varying from 2.61 to 2.88%. As observed for the sulfomethylation process, despite the high content of S-type lignin in kraft lignin, the reaction can occur in the aliphatic chain. However, the chemical modification of lignin with sulfuric acid is a balance between the sulfonation and condensation reactions, mainly in the α -position on the aliphatic chain of lignin (Shimada et al., 1997; Yasuda et al. 1999; Zoumpoulakis and Simitzis, 2001). The condensation at the α -position of aliphatic chain could eliminate the occurrence of other modification reactions (Yasuda et al., 1999).

A disadvantage of acid sulfonation compared to the sulfomethylation process is the formation of condensed structures in kraft lignin in the acidic conditions, impairing an extent of lignin sulfonation and its reactivity (Huang et al., 2017). This has reflected in lower values of lignosulfonates yield and lower values of acid-soluble lignin in the lignosulfonates produced by acid sulfonation.

In the sulfomethylation process, a sugar variation of 1.41 to 1.91% was observed and the ash values varied from 6.17 to 12.25%. At the same temperature, an increase in the sodium hydroxymethylsulfonate/lignin molar ratio resulted in lignosulfonates with higher remaining inorganics content. In the acid sulfonation process, only traces of sugar were found in some samples due to the severity of the acidic conditions and the ash values varied from 3.52 to 7.01%.

The results of elemental analysis of commercial lignosulfonate and lignosulfonates produced by the sulfomethylation and acid sulfonation processes are showed in Table 4. In the sulfomethylation process, an increase in the percentage of sulfur from 2.06% of unmodified kraft lignin (Table 2) to 5.23% in the treatment with highest temperature (160°C) and highest sodium hydroxymethylsulfonate/lignin molar ratio (1.6) was observed. In the acid sulfonation

process, the increase in the percentage of sulfur was smaller than in the sulfomethylation process. The highest value (3.28%) was presented by the treatment at 80°C and with molar ratio H₂SO₄/lignin of 20.

Table 4: Elemental analysis of commercial lignosulfonate and lignosulfonates produced by the sulfomethylation and acid sulfonation processes

Lignosulfonates			Elemental analysis (%)				
Process	T (°C)	Molar ratio	Carbon	Hydrogen	Oxygen	Nitrogen	Sulfur
Sulfomethylation	100	0.8	62.70	4.79	30.04	0.18	2.19
		1.2	60.73	4.73	31.78	0.14	2.47
		1.6	60.17	4.61	32.12	0.12	2.71
	130	0.8	60.01	4.46	32.13	0.15	3.18
		1.2	59.03	4.57	32.43	0.08	3.74
		1.6	58.62	4.49	32.48	0.10	4.13
	160	0.8	58.07	4.53	32.74	0.09	4.41
		1.2	57.42	4.60	33.00	0.09	4.79
		1.6	56.37	4.62	33.64	0.08	5.23
Acid sulfonation	80	10	60.24	5.23	31.56	0.15	2.72
		20	59.38	5.15	31.87	0.10	3.28
		30	59.95	5.20	31.55	0.12	2.95
	100	10	60.22	5.25	31.68	0.05	2.66
		20	60.14	5.22	31.82	0.05	2.49
		30	60.10	5.11	31.55	0.09	3.10
	120	10	60.31	5.15	31.78	0.08	2.51
		20	59.80	5.04	31.76	0.08	3.13
		30	60.68	5.08	31.41	0.06	2.62
Commercial lignosulfonate			47.76	4.87	34.65	0.21	5.28

Source: Author

Kraft lignin has a sulfur percentage ranging from 1 to 3% (Doherty et al., 2011). An increase in the sulfur content evidences the success of the sulfonation reactions. These values are similar to the average percentage of sulfur (5.0% by weight) found for lignosulfonates produced by the sulfite process, which is highly soluble in wide pH range (Hawley and Wise, 1926; Wong, 1980; Matsushita and Yasuda, 2005; Alen, 2000; Doherty et al., 2011). The sulfur value found for the commercial lignosulfonate analyzed in this study was 5.28%.

Konduri and Fatehi (2015) in a study with hardwood kraft lignin found a sulfur percentage of 3.2±0.6% of lignosulfonates in the optimal conditions of sulfomethylation: 0.9

of molar ratio of sodium hydroxymethylsulfonate/lignin, 100°C, time reaction of three hours and lignin concentration of 20 g/L. Inwood et al. (2018) also found a sulfur percentage of 3.2% of lignosulfonates produced with softwood kraft lignin by sulfomethylation process. The same authors found a sulfur percentage of 8.2% through sulfuric acid treatment of softwood kraft lignin under the conditions of 100 °C, 0.5 h, and 15.2 of H₂SO₄/lignin molar ratio.

In the sulfonation processes, in addition to the increase in the percentage of sulfur, an increase in the percentage of oxygen was also observed. The oxygen content in kraft lignin was 30.69% (Table 2), while sulfomethylated lignin (160°C and molar ratio 1.6) and acid sulfonated lignin (80°C and molar ratio 20) presented 33.64 and 31.87% of oxygen, respectively. This trend was also observed by other authors and confirms the sulfonation of kraft lignin, since the sulfonic group (SO₃⁻) contributes to the increase in the sulfur and oxygen contents of the lignosulfonate produced (Lou et al., 2013; Inwood, 2014; Konduri and Fatehi, 2015; Inwood et al., 2018).

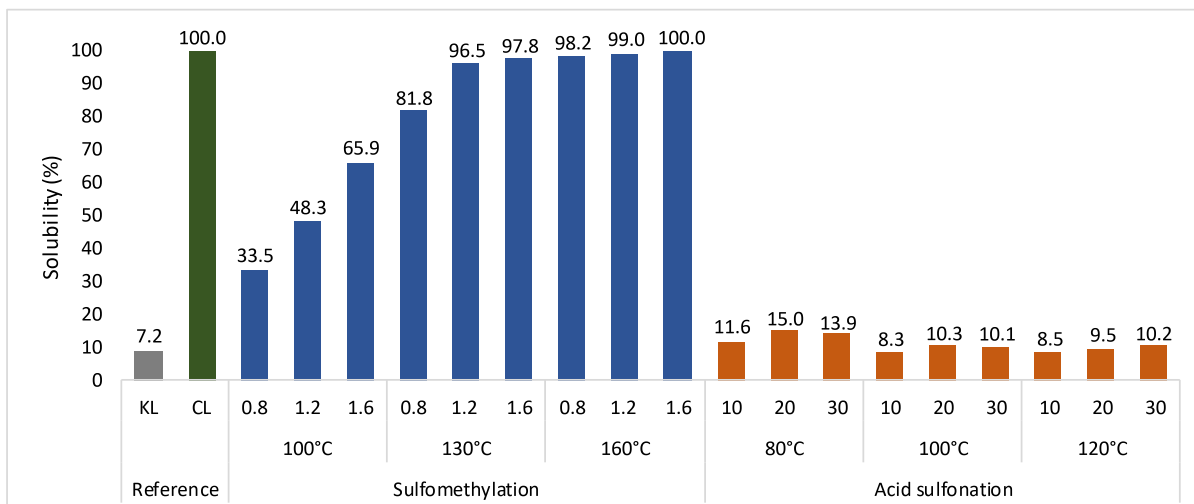
The amount of carbon dropped from 62.28% in kraft lignin to 56.37% in sulfomethylated lignin (160°C and molar ratio 1.6) and to 59.38% in acid sulfonated lignin (80°C and molar ratio 20). In commercial lignosulfonate, the percentage of carbon (47.76%) was lower and the percentage of oxygen (34.65%) was higher than those found for lignosulfonates produced in this study

The chemical formulas of unmodified kraft lignin, sulfomethylated lignin (160°C and molar ratio 1.6), acid sulfonated lignin (80°C and molar ratio 20) and commercial lignosulfonate were C₉H_{8.01}O_{3.33}S_{0.11}, C₉H_{8.85}O_{3.62}S_{0.28}, C₉H_{9.37}O_{3.59}S_{0.18} and C₉H_{11.00}O_{4.90}S_{0.37}, respectively. Nitrogen was omitted due to the presence in trace amounts.

3.3.2 Water solubility

The results of water solubility of reference (kraft lignin – KL and commercial lignosulfonates - CL), lignosulfonates produced by sulfomethylation (temperatures of 100, 130 and 160 °C and molar ratios sodium hydroxymethylsulfonate/lignin of 0.8; 1.2 and 1.6) and lignosulfonates produced by acid sulfonation (temperatures of 80, 100 and 120°C and molar ratios H₂SO₄/lignin of 10, 20 and 30) are showed in Figure 3.

Figure 3: Water solubility of kraft lignin (KL), commercial lignosulfonates (CL) and lignosulfonates produced by sulfomethylation and acid sulfonation



Source: Author

As lignin extracted from black liquor has different structures, molecular weights and high polydispersity (Kouisni et al., 2012; Jääskeläinen et al., 2017; Tagami et al., 2019), the solubility of 7.2% found for eucalypt kraft lignin may be associated with some low molecular weight fractions of this lignin that solubilized in water. Commercial lignosulfonates present total solubility in water. This material is water soluble due to the anion charges of the sulfonic groups, carboxylic acids and OH groups present in the structure of lignosulfonates generated by the sulfite pulping process (Aro and Fatehi, 2017; Woiciechowski et al., 2020).

In the sulfomethylation process, the solubility values ranged from 33.5 to 100%. Lignosulfonates produced at temperature of 160 °C and molar ratio of 0.8 (98.2%), 1.2 (99.0%) and 1.6 (100.0%), and also lignosulfonates produced at temperature of 130 °C and molar ratio of 1.2 (96.5%) and 1.6 (97.8%) showed similar values of solubility. In the acid sulfonation process, the solubility values ranged from 8.3 to 15.0%. The highest solubility value was obtained by the treatment with a molar ratio of 20 and a temperature of 80°C.

Konduri and Fatehi (2015) in a study with hardwood kraft lignin also found a solubility about 97 wt.% in the optimal conditions of sulfomethylation: 0.9 of sodium hydroxymethylsulfonate/lignin molar ratio, 100°C, time reaction of 3 hours and lignin concentration of 20 g/L. Inwood et al. (2018) in a study with softwood kraft lignin found a solubility remained under 8 wt.% in lignosulfonates produced from acid sulfonation process and a solubility of 100 wt.% in lignosulfonates produced from sulfomethylation process. These values were similar to those found in this study for the processes of sulfomethylation and acid sulfonation of eucalypt kraft lignin.

The lignosulfonates produced by sulfomethylation obtained solubility values similar/equal to the commercial lignosulfonate, showing that the chemical modification of kraft lignin occurred. The lignosulfonates produced by acid sulfonation obtained solubility values similar to unmodified kraft lignin, showing the inefficiency of the process. In agreement with the results of chemical characterization, it was evidenced that the sulfomethylation process was much better than the acid sulfonation process for the production of lignosulfonates.

3.3.3 FTIR analysis

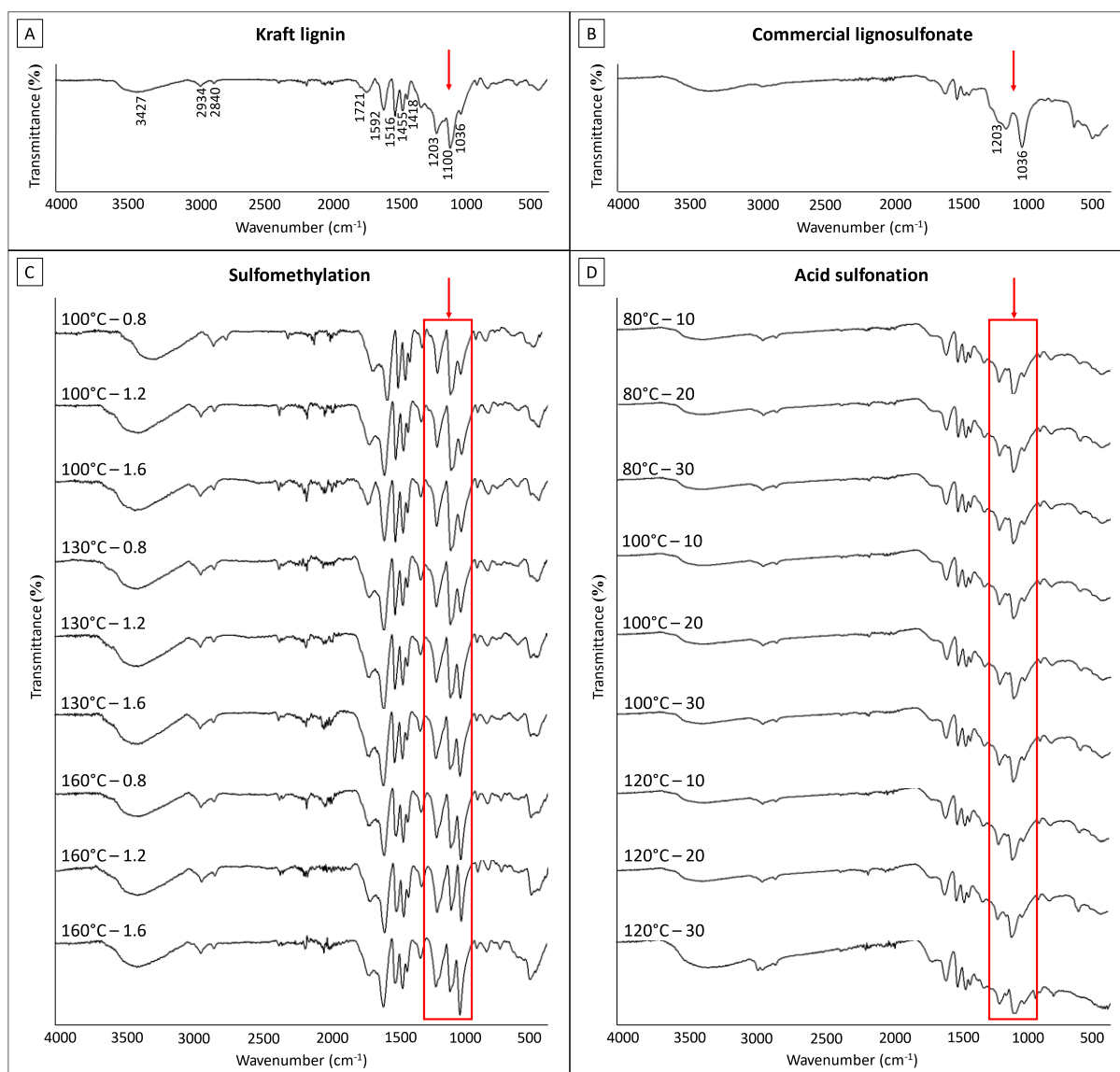
FTIR of functional groups of unmodified kraft lignin is presented in Figure 4A. The broad band at around 3427 cm^{-1} is typical of O-H stretching of alcohol or phenolic groups (Boeriu et al., 2004; Ibrahim et al., 2004; Iglesias, 2018). The peaks at 2934 and 2840 cm^{-1} are associated with CH stretching in aromatic methyl and methylene groups (Boeriu et al., 2004; Ibrahim et al., 2004; Inwood, 2014; Moradi et al., 2020) and CH vibration of the $-\text{OCH}_3$ groups (Sathawong et al., 2018).

C=O stretch in unconjugated ketone and carboxyl groups corresponds to the absorption peak at 1721 cm^{-1} (Inwood, 2014; Huang et al., 2016). The band at approximately 1592 cm^{-1} is the typical of aromatic skeletal vibrations together with C=O stretching and the peak at 1516 cm^{-1} is attributed to the aromatic skeletal vibrations (Faix, 1991; Gan et al., 2012; Melro et al., 2020).

The C-H bending of methyl or methylene groups is correspondent of the absorption peaks at 1455 cm^{-1} (Li and Ge, 2011; Inwood, 2014; Sathawong et al., 2018). The band at around 1418 cm^{-1} is the characteristic of aromatic skeletal vibration combined with CH asymmetric deformation of methyl groups (Faix, 1991; Moradi et al., 2020). The peak at 1203 cm^{-1} can be attributed to C-O and C=O stretching of the aromatic ring (Malutan et al., 2008; Melro et al., 2020).

Stretching of -CH-OH bonds of secondary alcohols can be observed in the peak at 1100 cm^{-1} (Faix, 1991). It is known that unmodified lignin kraft does not present stretching of sulfonate groups (Li and Ge, 2011; Konduri and Fatehi, 2015). Therefore, the small absorption peak at 1036 cm^{-1} on kraft lignin can be attributed to $\text{CH}_2\text{-OH}$ bonds of primary alcohols in the molecule (Faix, 1991; Huang et al., 2016).

Figure 4: FTIR analysis: A) Eucalyptus kraft lignin; B) Commercial lignosulfonate; C) Lignosulfonates produced from sulfomethylation; D) Lignosulfonates produced from acid sulfonation.



Source: Author

In the sulfomethylation process, it was possible to observe an increase in the peak of absorption at 1036, 1110 and 1200 cm⁻¹, with the increase in temperature and molar ratio sodium hydroxymethylsulfonate/lignin (Figure 4C). These peaks on lignosulfonates produced for sulfomethylation is attributed to stretching of S=O in sulfonate groups and sulfonic acid, which confirmed the grafting of sulfonate groups to the lignin in the sulfomethylation process (Li and Ge, 2011; Barbosa, 2013; Inwood, 2014; Konduri and Fatehi, 2015). In commercial lignosulfonate, it was also observed a large peak of absorption at 1036 cm⁻¹ and between 1100 and 1200 cm⁻¹, confirming that this peak corresponds to the sulfonate groups and sulfonic acid (Figure 4B).

In the acid sulfonation process, it was possible to observe that the peak attributed to sulfonate groups and sulfonic acid was similar to that observed for unmodified kraft lignin (Figure 4D). Therefore, it is evidenced that the acid sulfonation process was not effective for the lignosulfonate production.

4. CONCLUSIONS

The eucalypt kraft lignin used for the lignosulfonate production showed typical characteristics in chemical composition, elemental analysis, heating values and thermal analysis when compared to others reported previously in the literature.

The acid sulfonation process was not efficient for the production of lignosulfonates from kraft lignin. The best results were obtained with the H₂SO₄/lignin molar ratio of 20 and at 80 °C. The lignosulfonate produced in these conditions had a sulfur percentage of 3.28%, a solubility in water of 15.0% and a peak of absorption at FTIR analysis, similar to those found for unmodified kraft lignin. Therefore, it was clear that the acid sulfonation process was not effective for production of lignosulfonates.

Opposite to the acid sulfonation process, it was possible to produce lignosulfonates from eucalypt kraft lignin by the sulfomethylation process with yields close to 100%. The process was optimized, and the best results were obtained with the sodium hydroxymethylsulfonate/lignin molar ratio of 1.6 at 160°C. The lignosulfonate produced under these conditions showed a sulfur value (5.23%) similar to those found for commercial lignosulfonate (5.28%). It was also showed that the sulfonation occurred due to the reduction of acid-insoluble lignin content and increase of acid-soluble lignin and oxygen contents.

It was confirmed the insertion of sulfonate groups through FTIR analysis. The lignosulfonates produced by sulfomethylation obtained water solubility values similar to the commercial lignosulfonate, showing that the chemical modification of kraft lignin has occurred.

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CONCLUSÕES E CONSIDERAÇÕES FINAIS

O uso da lignina para geração de produtos de alto valor agregado é promissor, inserido no conceito de biorrefinaria das indústrias de celulose kraft. Após o processo de desconstrução da madeira pelo processo kraft, a lignina se caracteriza como um polímero altamente complexo e de baixa reatividade. No entanto, ficou evidenciado que o tratamento térmico do licor negro residual é uma forma de modificação química dessa lignina kraft, com a geração de novos sítios ativos de reação e grupos catecol em sua estrutura.

A lignina kraft pode ser utilizada para produção de lignosulfonatos pelo processo de sulfometilação. Ficou evidenciado a modificação química da estrutura da lignina pela inserção de grupos sulfonatos, aumento da solubilidade e do conteúdo de enxofre. Esses lignosulfonatos produzidos apresentaram características similares ao lignosulfonato comercial, produzido pelo processo sulfito, que é amplamente utilizado como dispersantes e floculantes.

Como possibilidade de novas pesquisas, é possível avaliar os benefícios do aumento da reatividade da lignina kraft com o tratamento térmico para produção de novos produtos, como os adesivos fenólicos. Além disso, é viável avaliar se esse aumento de reatividade gera efeitos positivos para produção de lignosulfonatos pelo processo de sulfometilação, realizando a comparação com os lignosulfonatos produzidos a partir da lignina kraft não modificada.