UNIVERSIDADE FEDERAL RURAL DO RIO DE JANEIRO
INSTITUTO DE FLORESTAS
PROGRAMA DE PÓS-GRADUAÇÃO EM CIÊNCIAS AMBIENTAIS E FLORESTAIS

DISSERTAÇÃO

Síntese de adesivo lignina-fenol-formaldeído para painéis de madeira

Rafael Eloy de Souza

Seropédica, RJ
Fevereiro, 2020

UNIVERSIDADE FEDERAL RURAL DO RIO DE JANEIRO
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E FLORESTAIS

SÍNTESE DE ADESIVO LIGNINA-FENOL-FORMALDEÍDO PARA PAINÉIS DE MADEIRA

RAFAEL ELOY DE SOUZA

Sob a Orientação do Professor
Fernando José Borges Gomes

Coorientação do Professor
Edvá Oliveira Brito

Coorientação do Professor
Roberto Carlos Costa Lelis

Dissertação submetida como requisito parcial para obtenção do grau de **Mestre em Ciências Ambientais e Florestais**, no Programa de Pós-graduação em Ciências Ambientais e Florestais, Área de Concentração em Ciência e Tecnologia de Produtos Florestais.

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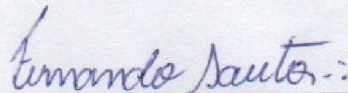
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DISSERTAÇÃO APROVADA EM: 18 DE FEVEREIRO DE 2020

_____
Fernando José Borges Gomes - Prof. Dr.UFRRJ
(Orientador)

_____
Fernando Almeida Santos - Prof. Dr.UERGS

_____
Dalton Longue Junior - Prof. Dr. UESB

_____
Larisse Aparecida Ribas Batalha - Dra. UFV

DEDICATÓRIA

Dedico aos meus avós, pelo exemplo, amor e dedicação.

AGRADECIMENTOS

Agradeço a Deus pela força e fé nessa caminhada e por ter me proporcionado essa grande trajetória em minha vida.

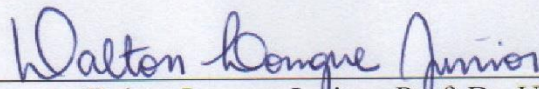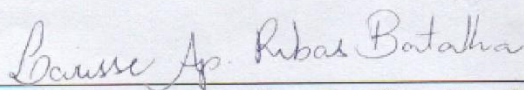Aos meus familiares, pai e mãe, que sempre me deram apoio em qualquer circunstância, obrigado por estarem aqui comigo.

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BIOGRAFIA

Rafael Eloy de Souza nasceu em 13 de abril de 1988, na cidade de Manhuaçu, Minas Gerais.

Cursou o ensino fundamental na Escola Estadual de Manhuaçu na cidade de Manhuaçu - MG, e o ensino médio na antiga Escola Agrotécnica Federal de Alegre, atual IFES *Campus* de Alegre, em Alegre - ES.

Em fevereiro de 2011, iniciou o curso de graduação em Engenharia Florestal na Universidade Federal Rural do Rio de Janeiro, cursou graduação sanduíche através do programa Ciência sem Fronteiras em Ontário, Canadá. Finalizou a graduação em dezembro de 2017.

Em março de 2018 iniciou o curso de Pós-Graduação em Ciências Ambientais e Florestais, em nível de mestrado, na Universidade Federal Rural do Rio de Janeiro.

RESUMO

SOUZA, Rafael Eloy de. **Síntese de adesivo lignina-fenol-formaldeído para painéis de madeira**. 2020. 40f. Dissertação (Mestrado em Ciências Ambientais e Florestais). Instituto de Florestas, Universidade Federal Rural do Rio de Janeiro, Seropédica, RJ, 2020.

A lignina é um subproduto gerado em larga escala no processo de polpação da madeira e atualmente tem sido utilizada para geração de energia na própria fábrica. Devido a sua estrutura fenólica, ela vem sendo estudada para diversos fins de aplicação em diferentes produtos no mercado. Uma alternativa para utilização dessa lignina tem sido a de usos em adesivos fenólicos para painéis de madeira. Porém, devido a baixa reatividade da lignina kraft de eucalipto com o formaldeído durante o processo de síntese do adesivo, muitos estudos vêm sendo realizados para melhorar essa característica da lignina e assim obter um adesivo com propriedades comparativas aos atuais adesivos para madeiras encontrados no mercado. A fenolação tem sido uma metodologia promissora para aumentar a reatividade da lignina. A partir dessa premissa, esse trabalho objetivou-se em fenolar a lignina kraft de eucalipto para síntese e caracterização de adesivos fenólicos. Foram sintetizados seis adesivos lignina-fenol-formaldeído usando lignina fenolada e não fenolada em proporções de substituição de 30%, 40% e 50% do fenol, e adicionalmente foi preparado uma amostra controle, em que não houve substituição do fenol por lignina. Utilizou-se também uma amostra de adesivo comercial a fim de comparação dos resultados, totalizando oito tratamentos. Para cada tratamento foram confeccionados um painel compensado sob mesmas condições (tempo, temperatura e pressão) e produzidos oito corpos de prova para realização do teste de resistência da linha de cola ao esforço de cisalhamento. O processo de fenolação aumentou em 14,7% a reatividade da lignina kraft, havendo incremento de componentes fenólicos nas estruturas da lignina. A utilização de lignina teve efeitos nas propriedades dos adesivos sintetizados, tanto para os de lignina não fenolada, quanto para os de lignina fenolada. De acordo com os resultados encontrados, não houve diferença estatística, ao nível de 95% de probabilidade pelo teste de Scott-Knott, entre os tratamentos para o teste de resistência da linha de cola ao esforço de cisalhamento, exceto pelos tratamentos com 30% de substituição por lignina fenolada e não fenolada, atendendo os requisitos mínimos de resistência ao cisalhamento especificado pela norma europeia EN 314-2 (1993). Foi possível a utilização da lignina kraft para síntese dos adesivos fenol formaldeído em substituição parcial ao fenol. O adesivo considerado melhor foi o de 50% de substituição de lignina fenolada devido a maior taxa de substituição e melhor tempo de formação de gel.

Palavras chave: lignina kraft, subproduto, eucalipto, fenolação, fenol formaldeído.

ABSTRACT

SOUZA, Rafael Eloy de. **Synthesis of lignin-phenol-formaldehyde adhesive for wood panels**. 2020. 4860f. These (Master's Degree in Environmental and Forestry Science). Forestry Institute, Federal Rural University of Rio de Janeiro, Seropédica, RJ,2020.

Lignin is a by-product generated on a large scale in the wood pulping process and has currently been used to generate energy in the pulp mill itself. Due to its phenolic structure, it has been studied for several application purposes in different products on the market. An alternative to the use of this lignin has been to use phenolic adhesives for wood boards. However, due to the low reactivity of eucalypt kraft lignin with formaldehyde during the adhesive synthesis process, many studies have been carried out to improve this characteristic of lignin and thus obtain an adhesive with properties comparable to the current wood adhesives found on the market. Phenolation has been a promising methodology for increasing the reactivity of lignin. Based on this premise, this work aimed to phenolate an eucalypt kraft lignin for the synthesis and characterization of phenolic adhesives. Six lignin-phenol-formaldehyde adhesives samples were synthesized using phenolated and non-phenolated lignin in substitution proportions of 30%, 40% and 50% of the phenol, in addition it was prepared a control sample, in which there was no substitution of phenol by lignin. A commercial adhesive sample was also used in order to compare the results, totalizing eight treatments. For each treatment, a plywood was made under the same conditions (time, temperature, and pressure), and eight specimens were produced to perform the test of resistance of the glue line to shear strength. The phenolation process increased the reactivity of lignin kraft by 14.7%, with an increase in phenolic components in the lignin structure. The use of lignin had effects on the properties of the synthesized adhesives, both for non-phenolated lignin and for phenolated lignin. According to the results found, there was no statistical difference, at the 95% probability level in the Scott-Knott test, among the treatments for the test of resistance of the glue line to shear strength, except for the treatments with 30% substitution by phenolated lignin and non-phenolated. The other treatments met the minimum requirements for shear strength specified by the European standard EN 314-2 (1993). Kraft lignin has shown promise in the production of lignin-based bioproducts. It was possible to use kraft lignin to synthesize phenol formaldehyde adhesives in partial replacement to phenol. The adhesive with 50% of replacement with phenolated lignin was considered the best from the adhesives synthesized due to higher percentage of replacement and faster gel time.

Key words: kraft lignin, byproduct, eucalyptus, phenolation, phenol formaldehyde.

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GENERAL INTRODUCTION

A huge challenge for the society is becoming a sustainable civilization based on more realistic needs and rational utilization of the natural resources. Concern for environmentally sustainable processes has led companies to adopt policies and laws that are specifically strategic and meet the assumptions of rational use of renewable resources in place of non-renewable resources for the biomaterials production, bioenergy and biochemicals. In this context, the concept of biorefineries arises that aims to produce a wide variety of products aiming at low waste and minimum amount of gas emissions.

A wide variety of lignocellulosic biomass sources may be used to produce bioproducts. These include agriculture residues, forestry residues, herbaceous crops and industrial residues/waste. Among these sources, lignin, obtained from the process of deconstruction of this biomass has been generated in large quantities in the industries that work with this raw material. Currently 50 million tons of lignin are generated in industrial processes using lignocellulosic material.

A wide range of applications of this lignin can be incorporated into the manufacturing processes of materials such as adhesives, bioplastics, carbon fibers, pellets, briquettes, dispersants, lignosulfonate, phenols, bio-oils, biokerosene, syngas, etc., giving it numerous high value-added applications, which has encouraged companies to invest in lignin extraction facilities.

According to Grand View Research Inc. (2019) the lignin market value is estimated in USD 954.5 million in 2019 and it is gaining more space in the world market. Its horizons are projected to expand in the coming years as a growing demand for this material for the production of macromolecules used in biofuel manufacturing, and a growing demand for binders in adhesives and concrete additives along with rising infrastructure development expenses. It should also drive the market over the next years, as the automobile market is expected to boost the demand for carbon fibers.

Wood adhesives have been widely used in industrial processing, mainly for the manufacture of wood boards, such as MDP, MDF, OSB, among others. The Brazilian wood board segment is among top ten in the global rankings of the largest producers (IBA, 2019). The panel companies have been optimistic with segment for the next years, foreseeing growth of the domestic market with the resumption of the economy and external through international trade agreements.

For the manufacture of these wood boards, it is necessary to use synthetic resins that have the function of adhering the wood to each other to form the board. These adhesives, which are phenol based, are of synthetic origin and not renewable, and their availability is directly linked to the cost and availability of fossil fuels. For instance, in the United State, from June 2014 to June 2017, average

price of phenol was USD1304/t, varying from 970 to 2028 USD/t in this period (DESSBESELL et al., 2020). Considering that the adhesive corresponds to most of the cost of producing these boards, it is justifiable to research possible substitutes for these commercial adhesives by others that are more efficient and economic (SANTOS et al., 2015). The phenolic resin market size is estimated in USD 11.17 billion in 2018, according to Grand View Research Inc. (2019).

In this context, the main goal of this work was to evaluate the use of lignin as a substitute for phenol in the adhesive type phenol-formaldehyde aiming its use in the wood board production. This dissertation was developed in two chapters, being in the Chapter 1 described the state-of-the-art of the lignin isolation and application by the forest base industry, and in the Chapter 2 an investigation of the kraft lignin phenolation method and its application in the synthesis of the phenol formaldehyde adhesive.

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CHAPTER I:

LIGNIN SOURCES AND APPLICATIONS: STATE OF THE ART

LIGNIN SOURCES AND APPLICATIONS: STATE OF THE ART

ABSTRACT

The efficient use of renewable resources has become a driving force for the worldwide industry in a quest for competitiveness. Considering the available natural raw materials, the lignin is one of the most abundant polymers in the world, being the unique plant source, therefore renewable, to present aromatic rings in its constitution. In this way, this review details the structure of native lignin as well as the technical lignin, including information on the characteristics that this polymer must have for the most promisor applications. Approximately 50 million tons of lignin are produced worldwide annually, of which 98% to 99% is incinerated to produce energy and steam in a pulp mill. Only a small fraction of the lignin, derived from the sulfite pulp mill is used in a biorefinery concept. Recent studies have shown that other lignin sources may also be used as feedstock for phenol derived products, technical carbons, fuels, and adhesives. On the other hand, there are some technological hurdles must be overcome to make these uses feasible.

Key words: biochemicals; biofuels; biorefinery; chemical modification; lignin.

1 INTRODUCTION

It was in 1838, when the French chemist Anselme Payen first treated the wood with nitric acid and sodium hydroxide, obtaining two distinct substances, which one was called cellulose and the second one, with high carbon content, where cellulose was soaked, was called it "encrusting material." This was considered the milestone in the history of lignin. Later, in 1865, F. Schulze named this "encrusting material" of lignin, from the Latin *Lignum*, which means wood. In 1868, E. Erdmann noted that the constituents of lignin were aromatic compounds. Benedikt and Bamberger in 1890 demonstrated that in this lignified wood material there were also methoxyl groups (ADLER, 1977; MAHMOOD, 2018).

The lignin is found in a large volume in the cell wall of lignocellulosic materials, such as wood, being a highly branched and amorphous biomacromolecule. Its composition can be diverse depending on the vegetal source (SJOSTROM, 1993). The chemical structure of lignin consists of phenylpropane units, which give rise to cinnamic alcohols, p-coumaryl alcohol, coniferyl and synaphyl alcohol, which differ in the degree of methoxylation at the C3 and C5 positions of the aromatic ring. After incorporation into the lignin structure, these alcohols are named p-hydroxyphenyl (H unit) where there are no methoxyl groups in the carbon C3 and C5, in guaiacyl (G unit) it can be found methoxyl group in the carbon C3 or C5, in syringyl (S unit) there are methoxyl groups in carbon C3 and C5 (Fig. 1) (KLASON, 1897) cited by (SARKANEN; LUDWIG, 1971).
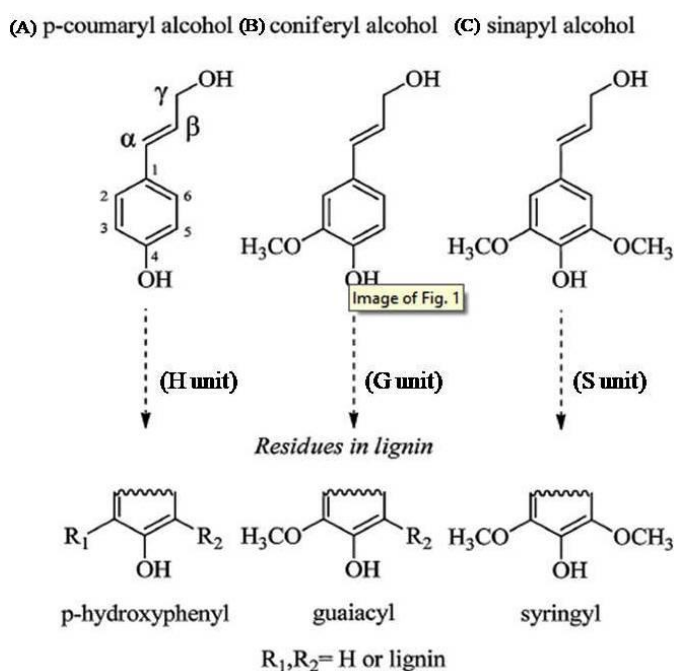
Figure 1. Monolignol species, being: (A) p-coumaryl alcohol (H unit); (B) coniferyl alcohol (G unit); and (C) sinapyl alcohol (S unit) (LAURICHESSE and AVÉROUS, 2014).

During the biological lignification process of plant species, the phenolic structure formed by the precursor alcohols is linked together, giving rise to a complex, three-dimensional structure formed by a wide variety of bonds. The main one is β-O-4 ether bonds. The composition and lignin content may vary from species to species and may also be influenced by the environment. Hardwood lignin consists mainly of guaiacyl and syringyl units and low levels of p-hydroxyphenyl. Softwood lignin has higher levels of guaiacyl units and low levels of p-hydroxyphenyl. Grasses comprise guaiacyl, syringyl and p-hydroxyphenyl units (UPTON and KASKO, 2015). An example of the main characteristic lignin bonds of softwood woods are shown in the Figure 2.
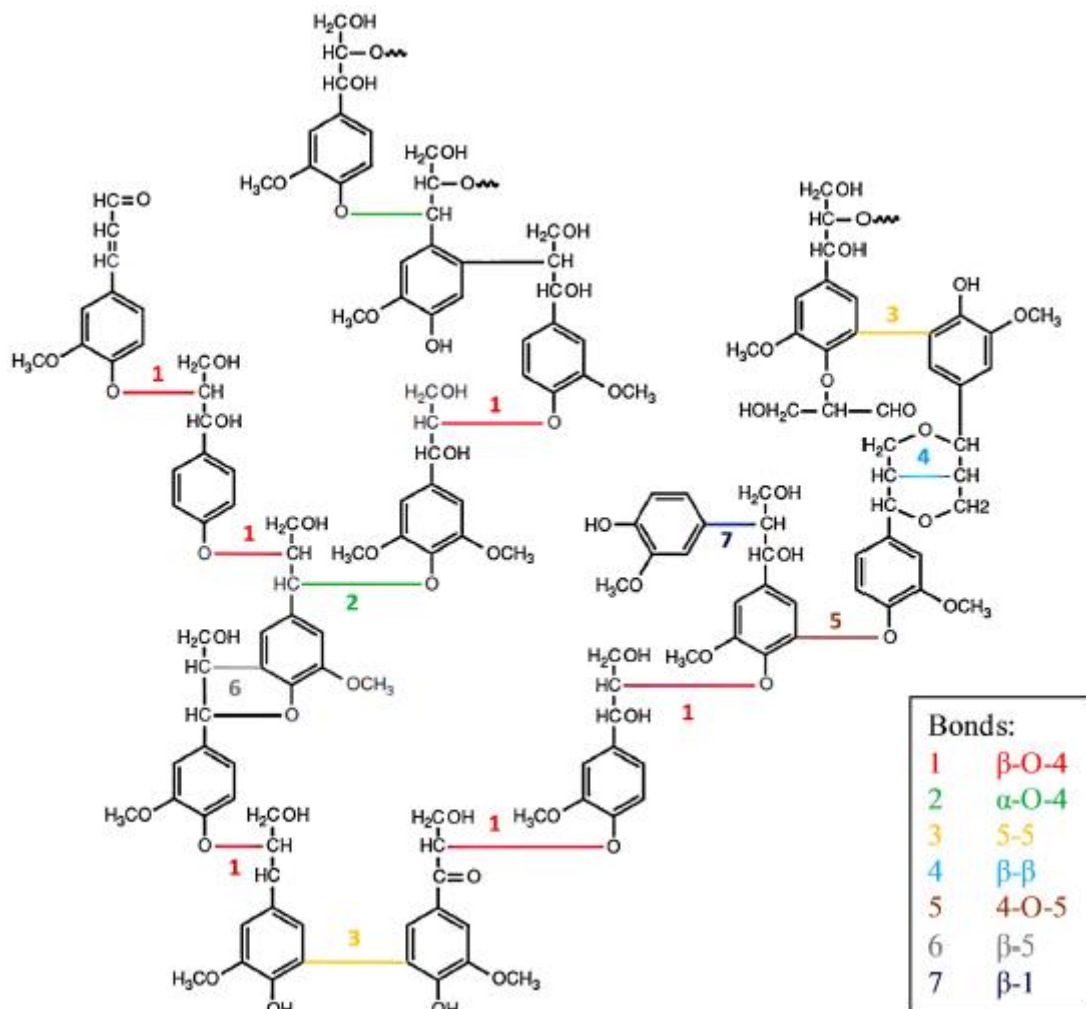
Figure 2. Main linkages in a softwood lignin (WINDEISEN and WEGENER, 2012).

The purpose of this brief review is to summarize the different types of technical lignin that are obtained in the market and the main pathways to treat this lignin for further application

to get high value-added products.

1.1 Industrial Sources of the Technical Lignin

Technical lignin is originated from different pretreatments or separation process, which affects its chemical properties such as composition, molecular weight, and molecular structure. They also differ in physical properties such as solubility, hydrophobicity, and hydrophilicity of lignin. Because of these differences, each technical lignin must be considered individually (VISHTAL and KRASLAWSKI, 2011; KUMAR et al., 2019). Currently the pulp mill is the main commercial source of lignin. The pulping processes are used to individualize the wood fibers in an extraction processes that depending on the technology applied, may occur in acid, alkaline media or using organic solvents. In all the processes the lignin is progressively broken into low molecular weight fragments (DOHERTY et al., 2011). The main commercial processes are kraft, sulfite, soda, and organosolv (pilot scale). Depending on the used process a significant degradation and change the structure of the native lignin may occur, with a reduction in the amounts of aliphatic OH groups, β-O-4, and β-β bonds. It is also possible to generate degraded products such as phenolic hydroxyl groups, carboxylic acids, and carbonyl groups (CAPANEMA and BALAKSHIN, 2015). Therefore, the structure of the technical lignin is typically dependent on the extraction method, as well as from the raw material of origin (softwood, hardwood, or grasses) (CAPANEMA and BALAKSHIN, 2014).

1.1.1 Kraft lignin

Obtained through the kraft pulping process, this lignin is highly condensed with strong ether bonds and high number of C-C bonds. Due to the chemical reagents used during the kraft pulping process, kraft lignin may have some impurities in its structure, such as sulfur. These impurities present in its structure may make its use unfeasible due to the venous nature of sulfur, or even prevent the action of catalysts (KUMAR et al., 2019).

Kraft lignin has a large number of phenolic hydroxyls due to breakage of β-aryl bonds during kraft pulping (Figures 3 and 4). Oxidative conditions during the delignification process may cause formation of quinone and catechol structure, as well the increase of carboxylic groups (CHAKAR; RAGAUSKAS, 2004). Kraft lignin has a small content of ash and carbohydrate (KUMAR et al., 2019). It also has aliphatic thiol groups, low molecular weight, and high polydispersity (LIN et al., 2014).

Luong et al (2012), facing the reality of the industries report that, with the growing production of pulp, a larger amount of lignin kraft has been generated, and the fact that the industries cannot burn all the produced black liquor, many studies about that are being made for conversion of the lignin extracted from the black liquor into high value-added products.
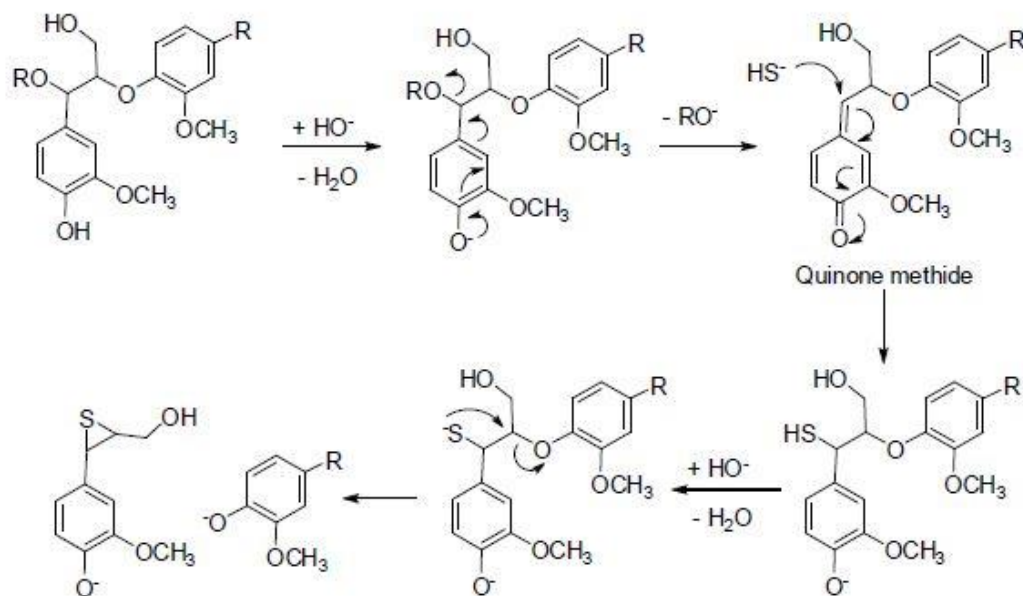
Figure 3. Cleavage of phenolic β-O-4 linkages (DEMUNER et al., 2019 adapted from GIERER, 1980).
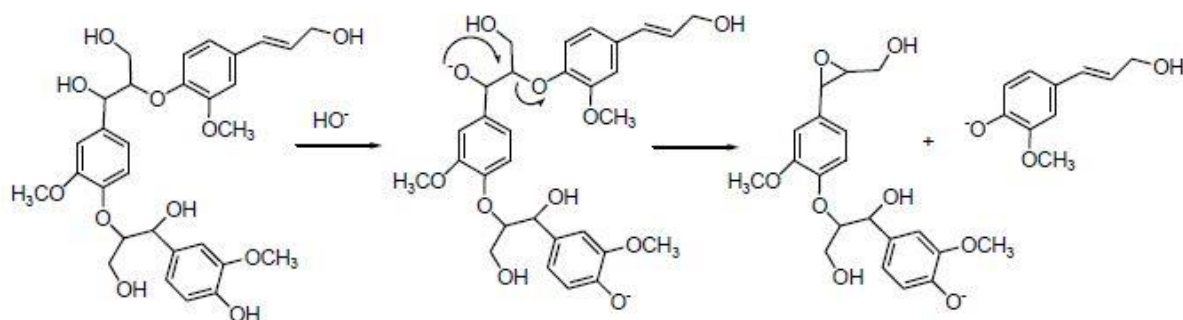
Figure 4. Cleavage of non-phenolic β-O-4 linkages (DEMUNER et al., 2019).

1.1.2 Lignosulfonate lignin

Lignosulfonate is the lignin obtained from the sulfite pulping process. In the cooking process, a mix of alkaline earth metal sulfite performs the delignification of wood, sulfonating the lignin (Figure 5). They have a variety of functional groups providing unique colloidal properties (KUMAR et al., 2019). Lignosulfonate lignin are soluble in water, present high

molecular weight, and higher ash content than kraft lignin, about 4 – 8 %. It has been used in different applications such as colloidal suspensions, stabilizers, dispersants, binders, detergents, adhesives, feed, surfactants, additives for concrete, among others (JABLONSKÝ et al., 2014).
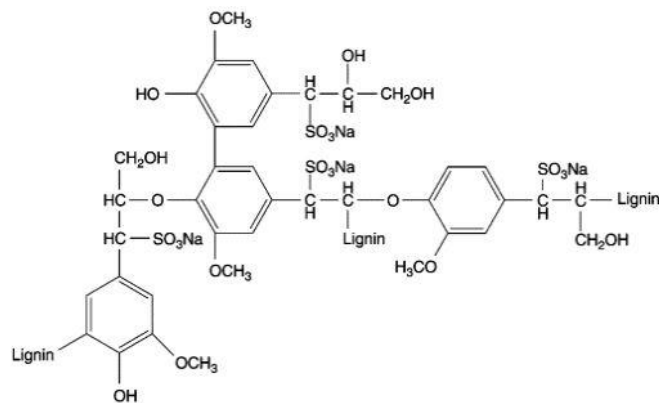
Figure 5. The main building blocks of the lignosulfonate molecule (FLATT and SCHOBER, 2012).

1.1.3 Soda lignin

Soda lignin is quite different from kraft lignin and lignosulfonates due to sulfur-free. Another different feature is the presence of vinyl ethers (KUMAR et al., 2019). Soda lignin has been applied for production of phenolic resins, animal feed, dispersants, polymers (JABLONSKÝ et al., 2014). On the other hand, the pulp mills using soda pulping process are becoming rarity, due to its low pulp yield performance and strength (ALMEIDA and GOMIDE 2013).
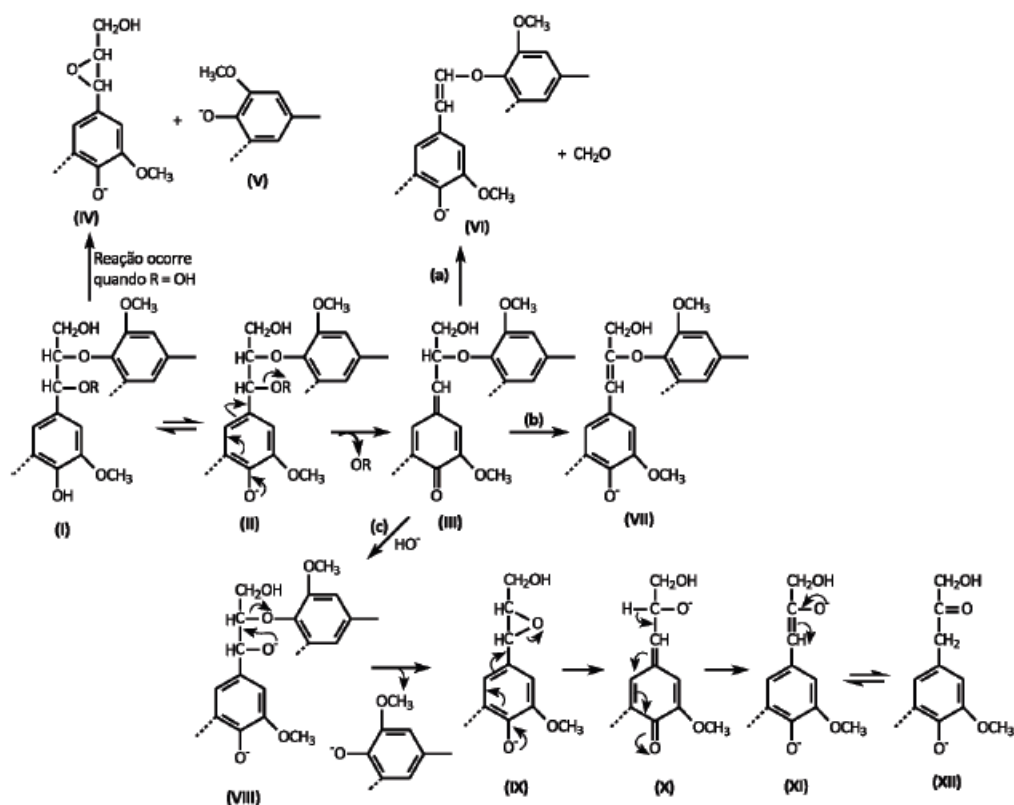
Figure 6.Lignin phenolic structure reactions in soda pulping. (GIERER, 1980).
(I) Phenolic structure; (II) Phenolate ion formation; (III) Methoxy quinone structure; (IV) reaction of formation of an epoxide; (V) phenolic group; (VI) Elimination of the hydroxymethyl terminal group to an aryl ether; (VII) Removal of proton β, resulting in a styryl ether; (VIII) Attack of the -OH on carbon α; (IX) Formation of an epoxide; (X, XI, XII) Disruption of epoxide.

1.1.4 Organosolv lignin

The biomass delignification in organosolv pulping takes place using a mixture of water and organic solvents. Lignin extracted by organosolv process may have high purity and chemical reactivity. It is also a sulfur free process and presents no toxicity for some applications such as pharmaceuticals, however it depends on the pretreatment condition from which it is obtained (KUMAR et al., 2019). It has a homogeneous structure, almost similar to native lignin, low molecular weight and polydispersity (KUMAR et al., 2019). The Figure 7 shows a possible mechanism of the delignification process on the organosolv pulping.

Some studies show that increased severity in organosolv processes leads to a reduction in molar mass of extracted lignin by 36 to 56%, compared to untreated lignin. In addition, reduction of aliphatic hydroxyl group contents, increase of syringyl phenolic units and condensed phenolic structures may be observed (YAÑEZ et al., 2014).
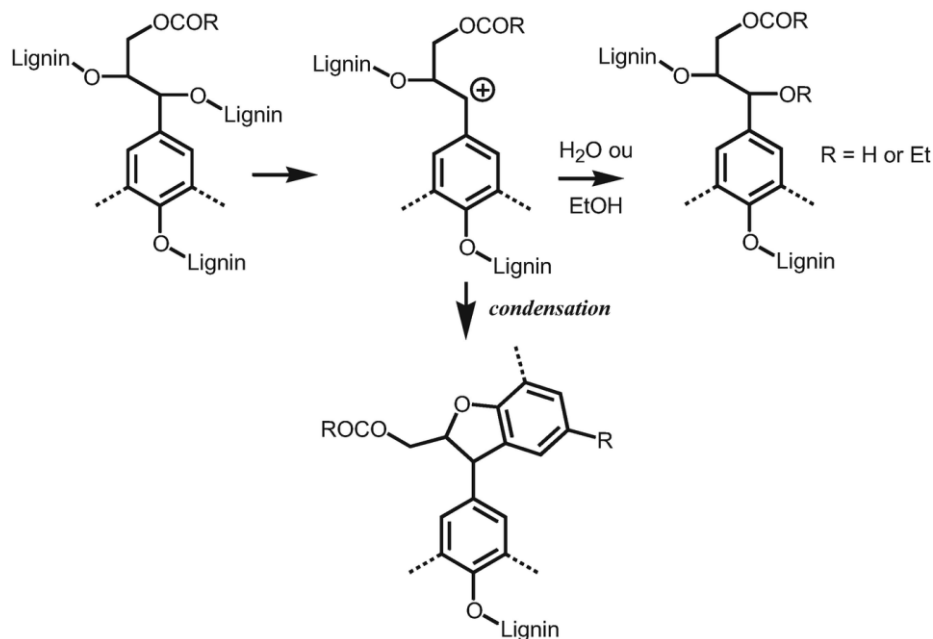
Figure 7. Organosolv lignin during the pulping process (BROSSE et al., 2017).

Organosolv lignin has high solubility in organic solvents and almost insoluble in water, because they are very hydrophobic. To recover organossolve lignin from the solvent, it must be precipitated, which typically involves adjust of concentration, pH and temperature (VÁZQUEZ et al., 1997).

2. INDUSTRIAL LIGNIN EXTRACTION

Lignin is one of the most abundant renewable carbon resources. It is widely available on earth, attracts much interest and can be obtained at relatively low cost (ALONSO et al., 2012). Lignin is the only renewable natural aromatic biopolymer that can be a candidate to replace phenol, an aromatic polymer which is obtained from fossil fuels, a non-renewable resource. It is a promissory compound for being an eco-friendly substitute for aromatic chemical from petroleum (ISIKGOR and BECER 2015).

Native lignin has been studied for decades and the challenger around the isolation process still unclear. Isolation and purification methods may cause structural modification in different levels, depending on the process used to it. In pulp and paper processes, many impurities are present in technical lignin and high condensed structures are formed, and it can hinder conversion process later (WANG et al., 2019).

Luong et al. (2012) point out that the lignin extraction process from black liquor is the first step for the use of lignin, as it aims to recover valuable organic materials from these materials. The acidification process has been considered as an efficient and economical process for the isolation of lignin from black liquor.

Among the processes of black liquor acidification for lignin extraction the LignoBoost, LignoForce are being the most used processes by the pulp mills (DESSBESELL et al., 2020). There are also some companies that have created their own process for isolating the lignin from the black liquor (RODRIGUES et al., 2018). In all these processes, lignin is precipitated by lowering the pH to about 9 to 10.5 by carbon dioxide (CO_2) treatment. Then, the precipitated lignin is filtered. The reduction of pH of black liquor can result in a hydrogen sulfide (H_2S) in the process. The precipitated lignin (slurry) is redispersed in a tank with acid filtrate which is generated at a subsequent stage of filtration. At this stage, the pH and temperature of the precipitation and mixing tanks are the same, but the acid concentration gradients in the wash (second filtration) stage are low. After the second stage of filtration, the precipitated lignin is crushed and dried to form lignin powder. In these processes, the change in lignin pH, ionic strength and solubility will occur in the slurry and not in the precipitates, which helps the properties of the precipitated lignin (FATEHI e CHEN, 2016).Precipitation yield can be increased with a greater decrease in pH, but would result in higher CO_2 consumption, which would increase the operational cost (ÖHMAN, 2006).

Problems related with conversion of lignin must be surmounted to achieve desirable products, including characterization of lignin and its derivatives, lignin depolymerization and product upgrading. Some authors have pointed that the isolated lignin structure is affected by the biomass sources, fractionation methods and fractionation severity (KIM et al., 2018).

According Wang (2019) depolymerization condition of lignin is high reactive and it leads to an uncontrollable side reaction, including repolymerization or condensation to form new structures. Technical lignin obtained by soda, sulfite or kraft pulping process are usually less reactive than native lignin, because the reactive β-O-4 ether linkages were replaced by recalcitrant C-C bonds due the acid or alkali treatment (LI et al., 2015).

2.1 Lignin Activation

Although lignin has a variety of functional groups (hydroxyl, methoxyl, carbonyl and carboxyl groups), its use is limited due to the presence of one or even two methoxyl groups in its structure, which makes it difficult to use in some products due to its low reactivity. To

circumvent this limitation, several studies have been done to increase lignin chemical reactivity by modifying its structure. These modifications consist of increasing the reactivity of hydroxyl groups or changing the nature of chemical active sites. For this, different pathways of chemical modification have been investigated to improve lignin reactivity (LAURICHESSE and AVÉROUS, 2014).

According to Ganewatta et al. (2019) for the chemical reaction of esterification, alkylation or etherification, hydroxypropylation with epoxides, urethanization *via* isocyanate or non-isocyanate routes, the presence of aliphatic hydroxyl groups and aromatic units facilitate the reactions. Phenolation is considerate one of the most promising modification methods to improve the lignin reactivity, by increasing the phenolic hydroxyl group, to increase reactive sites for aromatic substitution reactions (JIANG et al., 2018). In the aromatic units, chemical reaction as sulfomethylation, hydroalkylation, amination, and nitration can be an option to change lignin chemical reactivity. Understanding lignin behavior under different chemical treatments will help to obtain a lignin with desirable properties for specific applications. This has been a big challenge for many scientists (GANEWATTA et al., 2019). In the Figure 8, different pathways for lignin chemical pretreatment are presented.
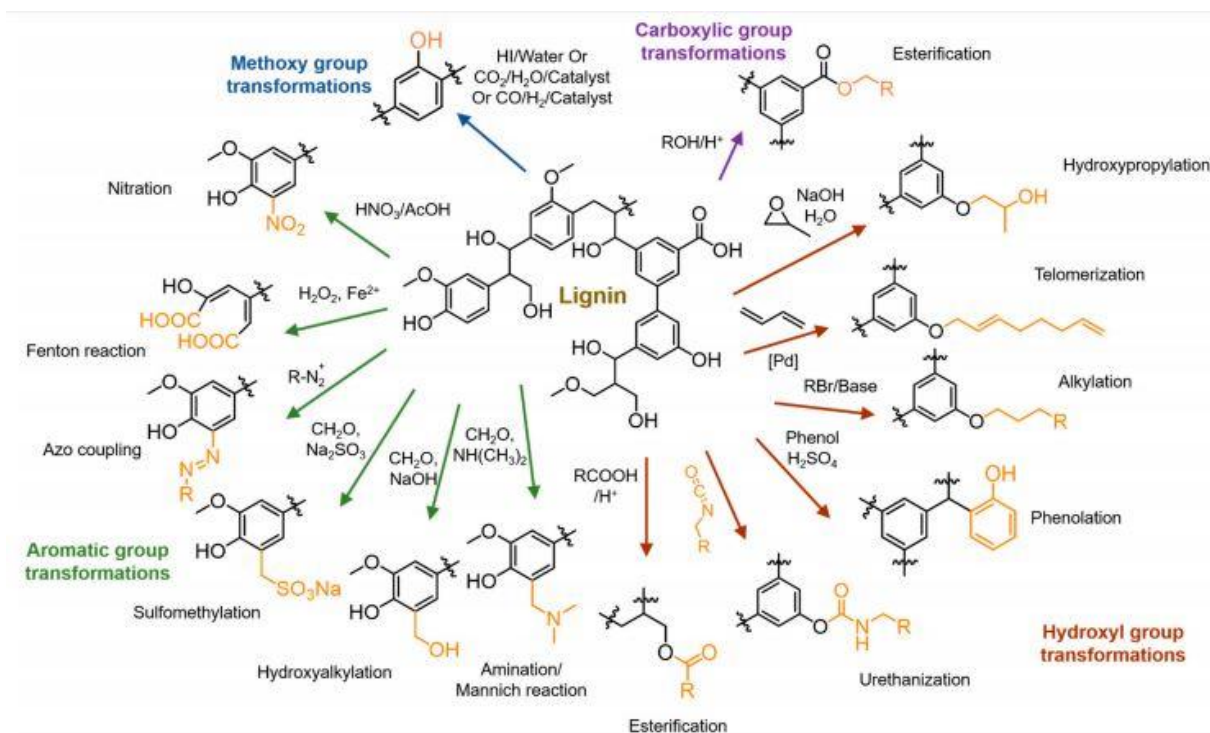
Figure 8. Different pathways for chemical treatment on lignin (GANEWATTA et al., 2019).

3. HIGH VALUE-ADDED PRODUCT FROM LIGNIN

Most of lignin produced in pulp mills as byproduct is burned for energy generation. Although energy power is necessary for industry, burning lignin in order to produce heat is not only harmful to the environment, but also a waste of resource (BRUIJNINCX; WECKHUYSEN, 2014).

Opportunities for lignin use for different purposes exist, but there are many challenges. According to Wang et al. (2019), the main valuable products potentially obtained from lignin are: polymers, mixed phenols, mixed aromatic alcohols, mixed organic acids, mixed hydrocarbons, mixed quinones, mixed benzylic aldehydes, aromatics pyrolysis oil, alkyl benzenes, carbon fibers and activated carbon. In order to get high added-value applications for these materials, lignin has been mixed with different types of polymers. However, its high complex structure and reactivity make it difficult. Monitoring its behavior and its miscibility with other polymers is crucial to figure out its compatibility and understand the structure property relationship (SEN et al., 2015).

Chemical modification of lignin is required to achieve better properties in lignin-polymer blend, such as: resins, polymers, surfactants, adsorbing agent, nucleating agent, thermal stabilizer, UV blocker, carbon fibers, supercapacitor for energy storage, biomedical and pharmaceutical applications, fire retardant and biocide (COLLINS et al., 2019).

3.1 Resins

Among most resin used in wood adhesive industry, phenol-formaldehyde is commonly used due to its good performance in water and weather resistance, and high mechanical strength. Phenol and formaldehyde are both from fossil fuels, so their prices vary with oil price. Moreover, phenol and formaldehyde are toxic and carcinogenic (FOYER et al., 2016).

As alternative, lignin-phenol-formaldehyde (LPF) can be synthesized, because lignin structure is similar to phenol structure. In this case, lignin is partially or completely used as substitute to phenol in the resin formulation (HUSSIN et al., 2017), as suggested in the Figure 9.
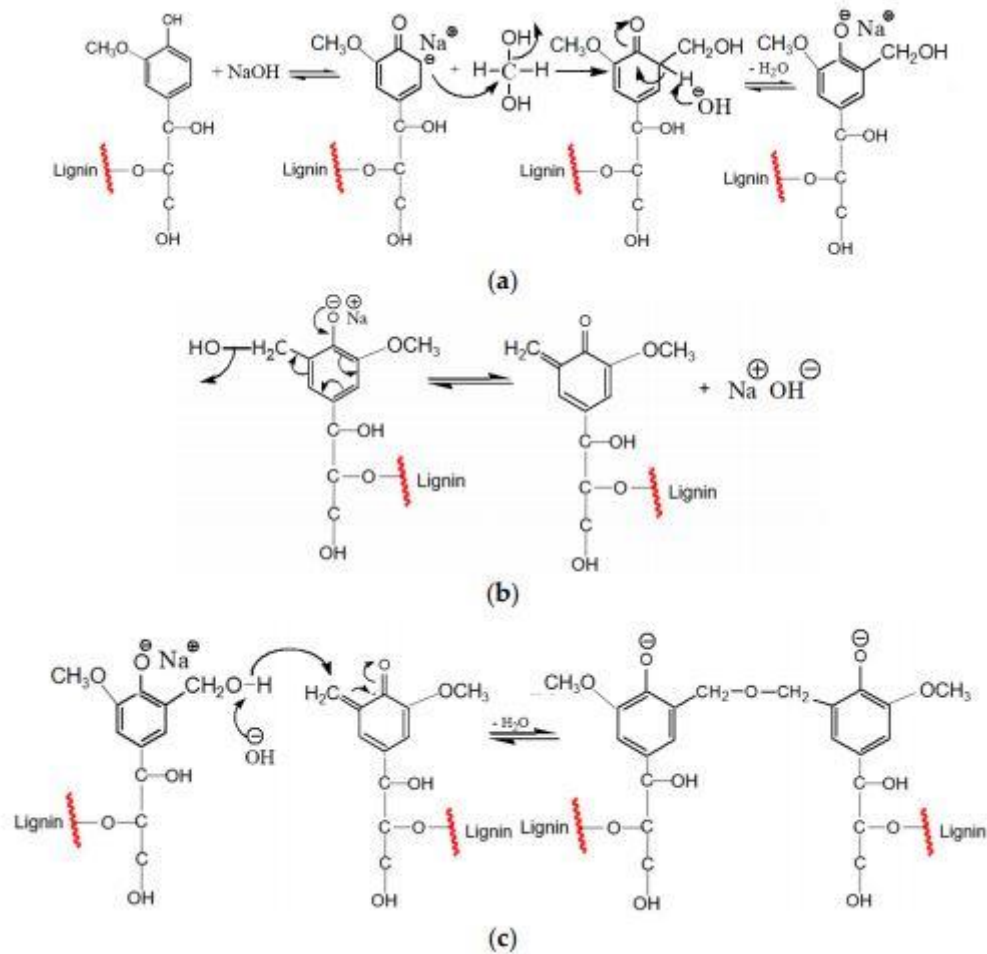
Figure 9. Scheme of the proposed reaction mechanism of lignin-based bio-phenol formaldehyde resin formation. (a) Formation of monosubstituted methylolated phenols through addition reaction. (b) Formation of quinone methide intermediates. (c) Formation of diphenyl-methylene (SIDDIQUI et al., 2017).

To make lignin appropriate to be used as adhesives for wood boards, several properties of lignin have to be considered. Its chemical heterogeneity is a limiting factor, because lignin is processed using different chemical processes, giving to it a significant influence on the adhesive properties of the synthesized phenol-formaldehyde adhesives (MAHENDRAN et al., 2013). Many researchers have done studies to synthesis LPF and its applicability. Ghorbani et al. (2018), preparing LPF adhesive substituting 40 wt% of phenol by pine kraft lignin, found good results in paper-based laminates for water absorption, thickness swelling and mechanical properties like flexural strength, elastic modulus and relative impact energy.

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3.2 Technical Carbon

Due to the fact that lignin presents high carbon content and aromatic structures, it has been studied as precursor for production of functional materials such as activated carbon, activated carbon fiber, carbon catalyst, electrodes for electrochemical applications. It can also be used to produce a range of structural carbon materials such as carbon fibers, carbon black among others (PUZIY et al., 2018).

Among all these applications, carbon fiber and activated carbon are very valuable product for technical lignin. The study for this application has been growing rapidly (GOSSELINK, 2011, DESSBESELL et al., 2020).

According to Grand View Research Inc. (2019) the USA market are expecting a boost of the demand for lightweight material, such as carbon fiber, which presents excellent mechanical properties, low weight, high thermal, able to conduct heat and electricity and shows chemical stability in the absence of oxidizing agents. This makes this material very attractive for transportation industry, sporting goods, and large structures as turbine blades (WITTEN et al., 2015; PUZIY et al., 2018). For instance, the use of carbon fiber in aircraft allows the manufacture of a lighter aircraft with high strength besides it can be used to produce multifunctional structural parts capable of de-icing or protect aircraft wings from thunder due to its property of good electrical conductivity (FORINTOS and CZIGANY, 2019).

Currently, about 90% of commercial carbon fiber production, polyacrylonitrile (PAN) is used as a precursor. The PAN is a synthetic polymer derived from petroleum that represents half the cost of producing carbon fiber, making this a cost-limitation for carbon fiber applications (BAKER and RIALS, 2013; FRANK et al., 2014). Lignin has an attractive attention to replace PAN in the carbon fiber manufacturing due to its high carbon content, as well as its bioavailability and low cost.

Another advantage to the lignin is the high carbon yield during carbonization and the absence of toxic gases during the carbonization of PAN (HUANG, 2009). The major challenge for this use is due to the intrinsic heterogeneity characteristic of lignin such as different molecular weight, diverse chemical linkages, and many functional groups making the lignin a heterogeneous polymer. It contributes to the poor mechanical performance of lignin-based carbon fiber (LI et al., 2017).

3.3 Lignin for chemical

The lignin is also a source to replace petrochemical considering aromatic monomers. Depolymerization process is a good method to obtain low-molecular-weight compound from lignin (SUN et al., 2018). For instance, the lignin depolymerization may be achieved using thermal or chemical routes such as pyrolysis, catalytic hydrogenolysis, solvent depolymerization, alkaline oxidation, supercritical water, alkaline hydrolysis (PANDEY and KIM 2011). Among the depolymerization technique, the feasibility of lignin depolymerization process depends on the technique and chemical composition of technical lignin (PONNUSAMY et al., 2019). Compounds such as vanillin, divanillin, ferulic acid, hydroxybenzaldehyde, syringaldehyde and guaiacol can be obtained from the depolymerization process (Figure 10) (GANEWATTA et al., 2019).

Figure 10. Lignin-derived renewable chemicals monomer precursors (GANEWATTA et al., 2019).

Among these monomers, vanillin has gained significant interest for its use as a precursor to polymer synthesis. It is produced from petrochemical source, but kraft lignin source may be more environment-friendly. For this, the challenge is to purify the kraft lignin for use in vanillin product, since it may be sold as natural aroma just if the base material and the processes are natural. Hence, numerous strategies are being developed to use biotechnology to produce vanillin using kraft lignin (FACHE et al., 2015).

3.4 Lignosulfonates

Kraft lignin is also being tested as coagulant and dispersants. Due to low solubility at neutral pH and limited charge density, kraft lignin has received chemical treatment to improve

it (COUGHLIN et al., 2013). Sulfonation process has been applied to lignin so it can be used as coagulant or dispersant. Gao et al. (2019) treat kraft lignin by phenolation followed sulfonation of sodium sulfite and sulfuric acid (Figure 11). In their experiment lignin presented good performance as coagulant for dye removal from their simulated solution. However, sodium sulfite lignin required higher dosage, because it has lower charge density than sulfuric acid lignin.
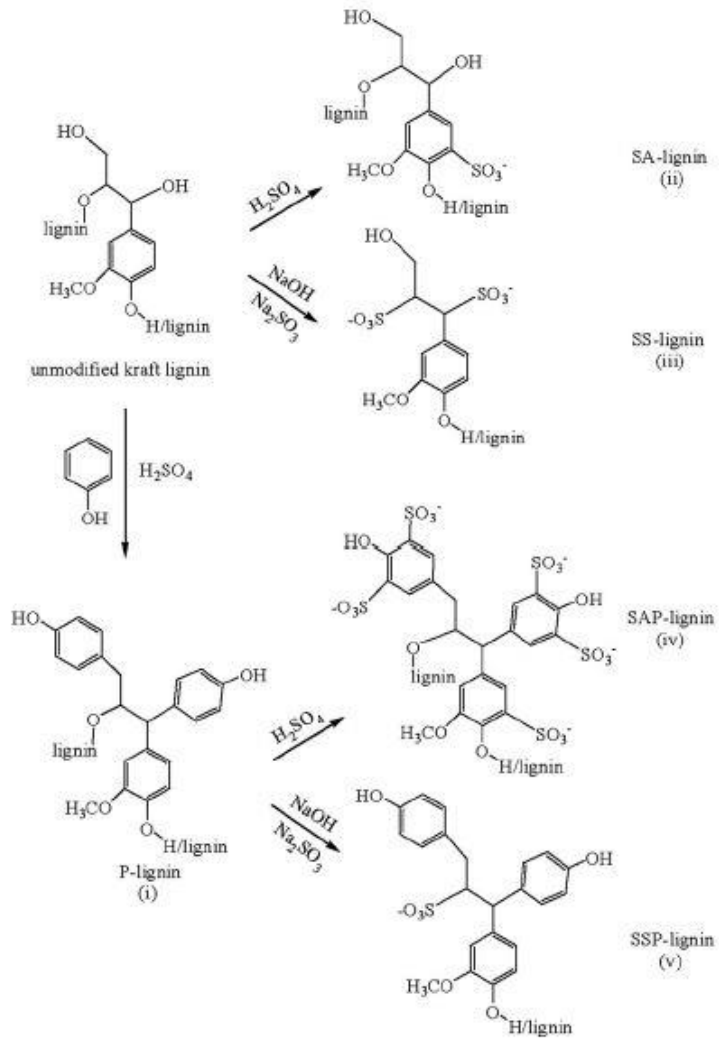
Figure 11. Reaction scheme for sulfonation of non-phenolated lignin and phenolated lignin. (GAO et al., 2019).

Inwood et al. (2018), in their study treating lignin chemically with sulfuric acid and sodium sulfite, improved its solubility across the range of pH when compared with non-treat lignin. According their results, they found favorable conditions to use modified lignin as dispersant.

CONCLUSIONS

Due to similarity in its structure, lignin has a great potential for phenol substitution, which is a non-renewable raw material source. The changes that lignin takes during manufacturing processes will interfere in its structure, which will directly imply in its application. Moreover, when lignin is chemically treated for future applications, it will change its structure according to the chemical treatment done.

Such behavior has led many researchers to understand what exactly lignin is. Therefore, many publications have been made about lignin in order to understand its real behavior under the conditions in which it is exposed and how-to tailor process of its treatment specifically for its application purpose.

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CHAPTER II:

LIGNIN-PHENOL-FORMALDEHYDE ADHESIVES SYNTHESIS

LIGNIN-PHENOL-FORMALDEHYDE ADHESIVES SYNTHESIS

ABSTRACT

Lignin is a material commonly obtained as a byproduct from forest-based industries such as pulp mills, as well as from the agrobusiness like sugar or second-generation ethanol. Due to its content of phenolic structures, lignin may be used as phenol replacement in phenolic adhesive formulation. Due to its content of phenolic structures, lignin may be used as phenol replacement in phenolic adhesive formulation. Because of low lignin reactivity, phenolation method may be used to increase its reactivity and make it more useful for various applications, mainly for lignin-phenol-formaldehyde resin synthesis. In this study, the phenol was partially replaced in the phenol-formaldehyde resin by using two kinds of lignin, one commercial eucalypt kraft lignin, and another one the commercial eucalypt kraft lignin phenolated in laboratory, which were evaluated for plywood production. Six lignin-phenol-formaldehyde adhesives were synthesized using non-phenolated and phenolated lignin in substitution proportions of 30%, 40% and 50% of the phenol; in addition, a control treatment in which there was no substitution of phenol by lignin was synthesized. The phenolation process increased the phenol content of kraft lignin by 14.7%. The use of lignin had effects on the properties of the synthesized adhesives, for both non-phenolated and phenolated lignin. The adhesive with 50% of phenolated lignin in replacement to phenol in the synthesis was considered the best resin due to higher percentage of replacement, and better adhesive performance regarding gel time and preservation of plywood strength property.

Key words: adhesives, eucalypt, kraft lignin, phenolation, plywood.

1 INTRODUCTION

Lignin is a natural biopolymer, which constitutes 15-35 % (w/w) of lignocellulosic biomasses, which is composed of amorphous aromatic polymer of three types of phenylpropanoid units: *p*-hydroxyphenyl (H unit), guaiacyl (G unit), and syringyl (S unit) (Machado et al., 2020; Terzioglu et al., 2020). Technical lignin is a byproduct mainly obtained from pulp mills, such as industries that use alkaline or sulfite pulping processes, and it is widely available (Chung & Washburn, 2016; Bajwa et al., 2019). This makes it an attractive biopolymer for being used as feedstock in a wide variety of potential industrial applications, such as high value added products like carbon fiber, dispersants, emulsifiers, among others (Kosiková et al., 2000; McCarthy & Islam, 2000; Chakar et al., 2004; Prado et al., 2012; Baker & Rials, 2013; Mainka et al., 2015). One of the most promisor application of the technical lignin from the kraft pulping process is to replace phenol, in phenol-formaldehyde adhesives, for instance, to produce wood panels such as plywood (Zhang et al., 2013; Yang et al., 2015). However, lignin structure may change drastically during its isolation process from the lignocellulosic biomass, resulting in a low reactivity material for many applications (Stewart, 2008; Pilato, 2010; Smolarski, 2012, Huang et al., 2019).

The application of technical lignin in the phenol-formaldehyde adhesives formulation requires longer pressing time and/or temperature for plywood manufacturing due to lower reactivity when directly applied as an adhesive (Danielson & Simonson, 1998; Sedliacik, 2010; Lu et al., 2011; Laurichesse & Averous, 2014; Solt et al., 2019). Therefore, efforts are needed to improve the lignin reactivity (Laurichesse & Averous, 2014). This could be done through lignin modifications increasing its reactivity in phenol-formaldehyde systems, such as methylolation, phenolation, demethylation/demethoxylation and others (Mankar et al., 2012; Xu et al., 2012; Jiang et al., 2018; Wang et al., 2019). Among these, phenolation has showed significant performance to increase lignin reactivity being one of the most promising modification methods. It can be done by increasing the phenolic hydroxyl groups and readily available reactive sites in technical lignin (Lu et al., 2011; Ghorbani et al., 2016; Jiang et al., 2018).

It is also particularly important to state that the industrial challenge is to develop not only an efficient lignin modification, but also a cost-efficient one. Based on that, this study aimed to evaluate the use of eucalypt kraft lignin in phenol formaldehyde adhesive formulation, as well as to evaluate a phenolation method available in the literature to improve kraft lignin reactivity to further application in the phenol-formaldehyde adhesive formulations.

2 MATERIAL AND METHODS

2.1 Material

For this study, a commercial eucalypt kraft lignin sample from Suzano Pulp and Paper was used. Lignin was precipitated from kraft black liquor at the industrial plant company itself using an own technology, which is unpublishable due to industrial secrecy. The plywood was prepared using ply veneer woods of *Ceiba pentandra* (L.) Gaertn (commonly called *Sumaúma* in Brazil) with a thickness average of 0.23 cm, which is commercially used for this purpose in Brazil.

2.2 Methods

2.2.1 Kraft Lignin Characterization

The kraft lignin was characterized regarding its content of insoluble lignin (Gomide & Demuner, 1986), soluble lignin (TAPPI UM 250), ash (TAPPI T-211 om 02), metal (SCAN-N 38:01), elemental analysis (CHNS-O), (TAPPI 211 om-93), carbohydrate (SCAN 71:09) and heating value (TAPPI T-684).

2.3 Lignin Phenolation

It was evaluated in this work a phenolation method to improve kraft lignin reactivity by adding phenol in its structure. In literature, some researchers have achieved about 30% till 50% of phenol incorporation, increasing its reactivity in kraft softwood lignin (Jiang et al, 2018; Chang et al. 2015, Du et al. 2014).

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The phenolation treatment (Figure 12) was developed based on Yang et al. (2014). The kraft lignin was phenolated under alkaline medium. Although, phenolation method may be performed in both alkaline and acid media. In this study, the alkaline phenolation method was chosen, because synthesis of adhesive phenol formaldehyde is performed in alkaline condition.

In the phenolation process, first, an amount of 1g of lignin and 2g of phenol were added to a two-neck flask, equipped with a reflux condenser and a mechanical stirrer. Then, the pH

value of the mixture was adjusted to 9-10 using a 30% sodium hydroxide solution. The temperature of the mixture was raised to 95ºC and kept constant for 1 h with under stirring. The mixture was poured in a diethyl ether/water solution (1:1 v/v) and the pH value of this mixture was adjusted to 2. The precipitated phenolated lignin was isolated by centrifuging and then thoroughly washed with ethyl ether. After that, phenolated lignin was dried at 103ºC till constant weight.
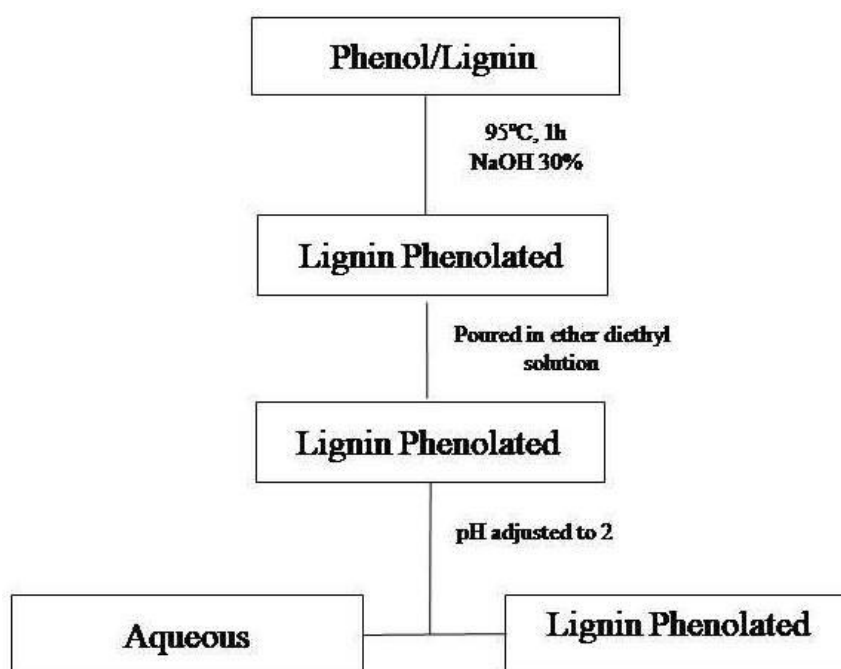
Figure 12. Phenolation process in alkaline condition.

2.4 Phenolic Hydroxyl Content by UV Spectrophotometry

The content of phenolic hydroxyl group was measured by UV spectroscopy based on the methodology described by Wexler (1964). A stock solution of lignin was prepared by dissolving 5 mg of lignin in 10 mL dioxane solution at 96%. Next, 1 mL of the solution was diluted 10 times with 50% dioxane solution to measure the absorbance of lignin by a UV spectrophotometer.

The reduced lignin was diluted 10 times with 50% dioxane solution and further acidified with a solution of 1 mol/L of HCl, drop by drop until pH 1 and taken to UV spectrophotometer to be measured. The ionized solution was prepared taken a sample of the stock solution, diluted

10 times with 50% dioxane solution. Then, a sample of the solution was alkalized with a solution of 1 mol/L of NaOH, drop by drop until pH 13. The spectra of ionized lignin were measured by UV spectrophotometer.

This UV spectroscopy techniques were applied for both the commercial (reference) and the phenolated kraft lignin. The calculations of free phenolic hydroxyl were based on the absorbance difference.

2.5 Preparation of phenol formaldehyde adhesive

A formulation of phenol formaldehyde adhesive based on Khan (2004) was synthesized to be used as a reference of the other adhesives evaluated in this study. Preparation of phenol formaldehyde adhesive, the molar ratio of formaldehyde and phenol were kept at 2:1. First, in a two-neck-flask equipped with a reflux condenser, thermometer and a mechanical stirrer, formaldehyde (37%), phenol and a solution of NaOH (50%) were mixed and heated up to 90ºC. These reagents were kept under that temperature for 2 hours under constant stirring. During the process, charges of a solution of NaOH (50%) were added into the two-neck flask for keeping the pH at 12. After two hours the two-neck flask was removed from the hot plate and the adhesive cooled until reaching a temperature of $\pm 25°C$. It was also used a commercial phenol-formaldehyde adhesive as a reference to the synthesized adhesive.

2.6 Preparation of lignin phenol formaldehyde adhesive

Lignin phenol formaldehyde adhesives were synthesized by replacing different amount of phenol by lignin. The amount of lignin replaced in this study were 30%, 40% and 50% as showed in the Table 1.

Table 1. Lignin phenol formaldehyde adhesive synthesized.

Treatment		Lignin	Lignin/Phenol (%)
T1	Phenol formaldehyde (commercial)	-	-
T2	Phenol formaldehyde (laboratorial)	-	-
T3	LPF 30%	Pure	30/70
T4	LPF 40%	Pure	40/60
T5	LPF 50%	Pure	50/50
T6	PLPF 30%	Phenolated	30/70
T7	PLPF 40%	Phenolated	40/60
T8	PLPF 50%	Phenolated	50/50

LPF- Lignin phenol formaldehyde; PLPF – Phenolated lignin phenol formaldehyde.

The six formulations of the lignin phenol formaldehyde adhesives were synthesized by adapting the procedure used for the synthesis of the phenol formaldehyde adhesive (reference), replacing the phenol component of the composition with the pure lignin or with phenolated lignin matching each treatment of the adhesive in the Table 1. In order to delay hydroxymethylation reactions during synthesis of the adhesive with lignin, 10 mL of methanol (p.a.) were added into the two-neck flask to adjust the viscosity of the final adhesive.

2.7 Characterization of phenol formaldehyde and lignin phenol formaldehyde adhesives

To evaluate all the adhesives synthesized in this study, the following procedures were taken: pH, solid content, gel time and viscosity. The pH obtained by direct measurement using a pHmeter at 25°C in approximately 100 mL samples, according to Bianche (2014). The solid content of the adhesives was determined according ASTM-D-1518-60. Samples of 1g of adhesive were weighted and oven-dried at 103°C till constant weight. The solid content fractions were calculated using the Equation 1.

$$\% \text{ Solid content} = \frac{Dried\ Weight}{Wet\ weight} \times 100 \qquad \text{Eq. 1}$$

Gel time was measured based on Pizzi & Mittal (2011). It was weighted about 10g of adhesive in a test tube, followed by addition of catalyst ($CaCO_3$), which was 2% of the solid content present in the sample in the test tube, it was immersed in a glycerin bath at 120°C. The time started to be counted immediately when the glass tube had been immersed in the hot bath.

The gel time is considered as the time when the resin formed a string around the glass rod when the glass rod was taken out from the resin.

Viscosity was determined by the Höppler Rheo-Viskometer (Firma Haake Medingen GmbH). For this, the glass tube of the Rheo-Viskometer was filled till the indicated mark as described by the manufacturer. The Rheo-Viskometer was adjusted according to the density of the adhesive that would be determined. Then, the viscosity of the adhesive was determined according to the Equation 2.

$$\eta = (T \times K) \times (M + A) \qquad\qquad \text{Eq. 2}$$

Where: η = viscosity (Cp); T = time (seconds); K = constant of the tube; M = weight placed in the plate (g); A = constant of the tube.

2.8 Plywood Preparation

At first, 10 parts of wheat flour was slowly mixed with 10 parts of water using a glass rod. Then, 280 g/m^2 of adhesive were added and mixed till a homogeneous mix. The ply laminates of moisture content 8% were used for plywood preparation. The adhesive was applied on both side of interface on 3 ply veneer wood sized 25cm x 25cm x 0.6cm. The ply veneer wood panels were pressed at 130°C and 32 kgf/cm^2 for 10 minutes. The panels were cooled at room-controlled temperature of 20°C and 65% of relative humidity.

For strength test, each plywood panel was cut into 8 samples measuring 15cm x 2.54cm x 0.6cm totalizing 64 samples. These samples were kept in the room-controlled temperature till constant weight before being used for testing. Shear strength of adhesives bonded plywood was measured according ABNT (1986) NBR ISO 12466-1 using a universal testing machine.

2.10 Data Analysis

The experiment was carried out following a completely randomized design, consisting of two lignin (commercial and phenolated) and three percentages of substitution (30%, 40% and 50%) of phenol by lignin in the synthesis of the adhesives. For the tests of the adhesives, three repetitions were performed for the characterization.

Data were subjected to Shapiro-Wilk test to evaluate the normality of the data and Bartlett test to assess for homogeneity of variances. Then, the analysis of variance (ANOVA) was performed and the treatments were compared among them by Scott-Knott test at 95% of

probability. Statistical analyzes were performed with the aid of the *R- Statistical* software.

3 RESULTS

3.1 Kraft Lignin Characterization

The first step of this study was the kraft lignin characterization, which was relevant for evaluating the sample purity, as well as the other main compounds that are present in the sample beside lignin. In the Table 2 the results of the lignin characterization are presented. Regarding the lignin content, in the kraft lignin sample evaluated this value was 94.0 %, being 87.9 % insoluble acid lignin and 6.1% soluble lignin. According to the literature these values are similar to those found by Magalhães et al. (2019) and Boschetti et al. (2019) for commercial kraft lignin. Still concerning the organic fraction in the kraft lignin, there is a certain amount of carbohydrate (1,9%), which are expected to come from the lignin carbohydrate complex, but generally this value is around 1% (Tarasov et al., 2018).

Regarding the inorganic fraction, the ash content of kraft lignin observed in this study was 2.6%. This value is according to those found by Boschetti et al. (2019), but higher than those found by Tomani (2010), who obtained 1% of ash content in kraft lignin. The inorganic content comes from the pulping process (wood, recovery system, water). Regarding the main metals content present in the kraft lignin, sodium is the highest one, as expected, since the kraft process applies sodium hydroxide and sodium sulphide as main reagents in the kraft process (Kouisni et al., 2012; Klett, 2017). The other metals found are in accordance with the literature (Wensley, 2004).

It was evaluated in this work the heating value from the kraft lignin for comparing it with lignin used commercially, since the thermal application has been the most applied to the lignin (Tomani, 2010; Sameni et al., 2013). It was observed that the high heating value (HHV) and low heating value (LHV) are 25.4 MJ/Kg and 24.5 MJ/Kg, respectively. These results are similar to those found by Tomani (2010) for the same type of feedstock.

It was also evaluated the lignin elemental composition (CHNSO), being observed that the kraft lignin consists of 65.2 % of carbon, 5.4% of hydrogen, 0.2% of nitrogen, 2.1 % of sulfur, and 25.5% of oxygen. These results indicate that the kraft lignin evaluated in this work is comparable to the technical lignin from the commercial plant as well as demonstration plants

(Ház et al., 2019).

Table 2. Kraft lignin composition and thermal characteristics.

Properties		Value
Soluble lignin, (%)		6.1
Insoluble lignin, (%)		87.9
Total lignin, (%)		94.0
	Glucans	0.43
	Xylans	0.29
Carbohydrate, (%)	Mannans	0.66
	Arabinans	0.23
	Galactans	0.25
Ash (%)		2.6
Metal (mg/kg) Fe/Ca/Cu/Mn/Mg/Na/K		143.4/ 1339.5/ 10.6/ 44.7/ 320.5/ 3632.7/ 421.6
LHV (MJ/kg)		24.5
HHV (MJ/kg)		25.4
Elemental analysis (%) (C/H/N/S/O)		65.2/5.4/ 0.2/ 2.1/ 25.5

3.2 Phenolated Lignin Characterization

It was evaluated a technique for improving lignin phenol content. A technique of phenolation was chosen for conducting the preparation of the based lignin-phenol-formaldehyde adhesives. The phenolation techniques were evaluated by UV spectrometry, and the results of phenolation were compared with the phenol content present in the kraft lignin (3.5%). In the Figure 13, it is presented the absorbance spectrum of the pure phenol. In the Figure 14, it is presented the absorbance spectrum of the non-phenolated and phenolated lignin. Regarding the lignin phenolation treatments evaluated in this study, it was possible to observe an increase of 14.7 % in phenolic hydroxyl groups in lignin structure. This corresponds to some phenolic groups attached in lignin structure, which are expected to increase its reactivity (Hu et al., 2011; Jiang et al., 2018; Zhang et al., 2018).
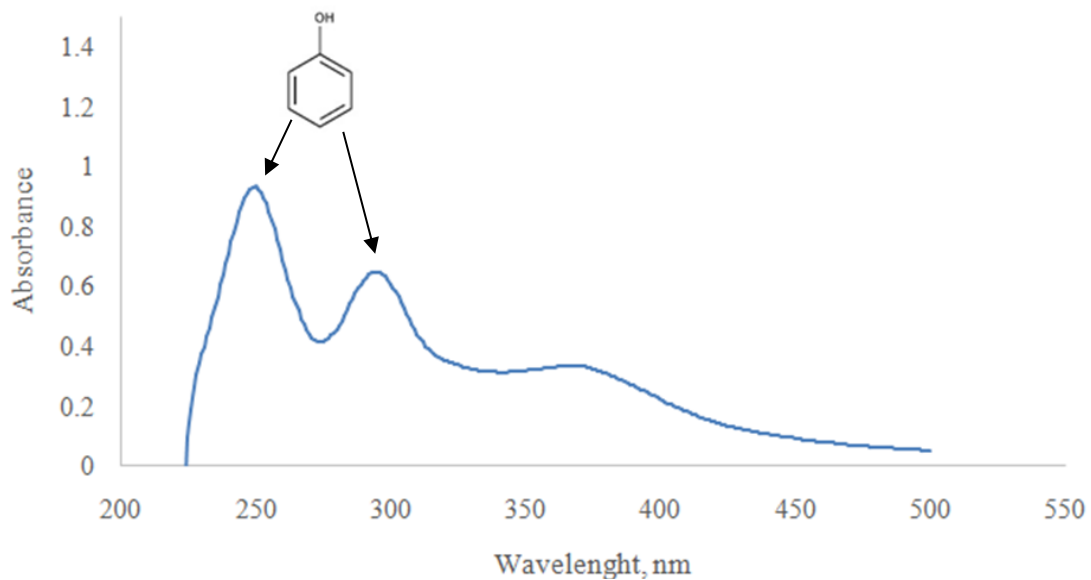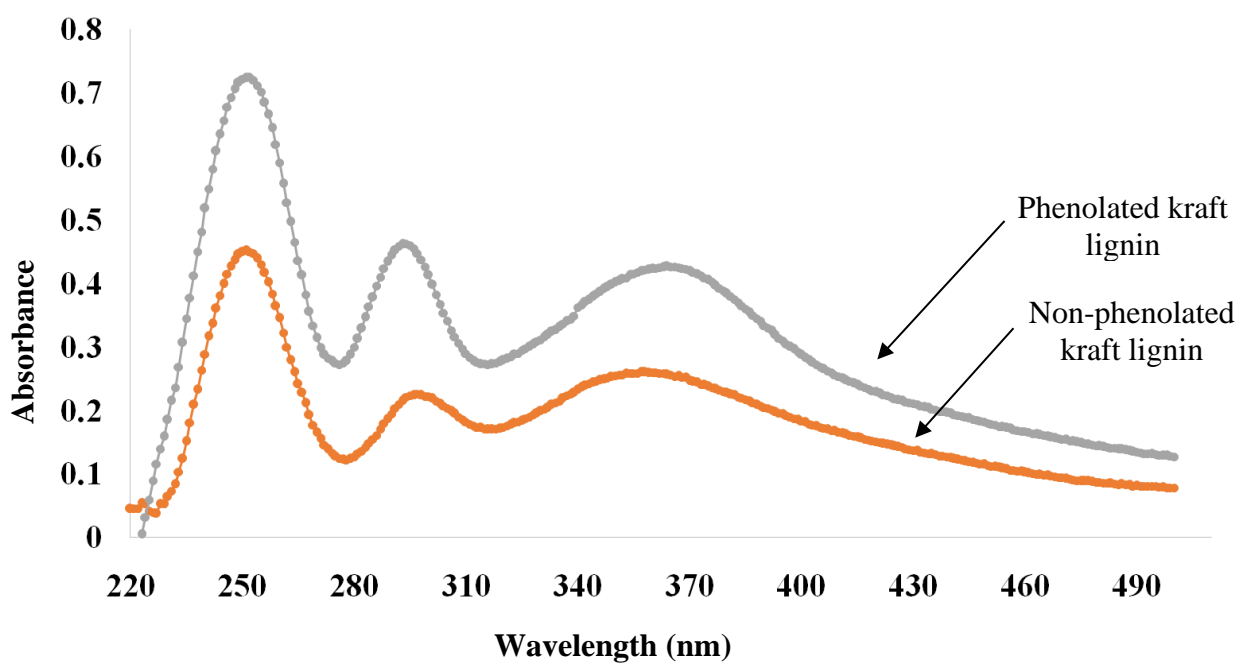
Figure 13. UV spectrum of phenol.

Figure 14. Differentiated UV spectrum of the non-phenolated kraft lignin and phenolated kraft lignin.

3.3 Adhesives based on lignin-phenol-formaldehyde

In this work it was investigated the phenol replacement in the phenol-formaldehyde adhesive by using commercial eucalypt kraft lignin. The references for the adhesives produced using lignin were a laboratorial and commercial phenol-formaldehyde adhesive. Both, laboratorial and commercial adhesives were characterized regarding their solids, pH, viscosity, and gel time (Table 3). The other adhesives were prepared replacing phenol by phenolated lignin as described in the methodology.

Table 3. Physical properties and characteristics of the adhesives.

Treatment	pH	Solid Content (%)	Gel Time (s)	Viscosity(cP)
T1	12.3	54.1	660	635.8
T2	12.5	51.4	452	706.7
T3	12.2	63.1	2900	475.9
T4	12.3	61.0	2313	628.2
T5	11.9	39.7	1595	908.1
T6	12.1	62.6	1085	526.4
T7	11.8	57.8	901	679.2
T8	11.3	39.3	837	1458.3

Where: T1-Commercial; T2-Synthesized; T3-LPF 30%; T4-LPF 40%; T5-LPF 50%; T6-PLPF 30%; T7-PLPF 40%; T8-PLPF 50%; LPF- Lignin phenol formaldehyde; PLPF – Phenolated lignin phenol formaldehyde.

It was found that all properties of the laboratorial phenol formaldehyde adhesive are according to the commercial phenol formaldehyde adhesive. The laboratorial phenol formaldehyde adhesive had a solid content around 51.4%, viscosity of 706.7 centPoise (cP) and gel time of 452 seconds.

The viscosity value obtained for the phenol formaldehyde adhesive meets the requirement for commercial formulations of this adhesive, which ranges from 600 to 800 cP (Pizzi & Mittal, 2003). It was observed that with the addition of lignin in the replacement phenol in the formulation of the adhesives, the viscosity of the synthesized adhesive was also increased. The higher amount of lignin added to the adhesive formulation, the higher the viscosity value of the adhesive. This behavior was observed for both lignin evaluated (non-phenolated and phenolated). Du (2018) studying adhesives based on lignin also observed higher viscosity in phenolated lignin-based samples than kraft lignin-based samples, and it is probably because of the higher reactivity of phenolated lignin towards formaldehydes.

Another pattern observed related to viscosity is that the adhesive synthesized with non-phenolated lignin compared to the adhesive synthesized with phenolated lignin, presented a

different viscosity, being phenolated lignin higher. The higher the amount of phenolated lignin used in replace to phenol in the synthesis of the adhesive, the higher the viscosity of the adhesive. This was mainly evidenced in the formulation which used 50% of phenolated lignin replacement. The viscosity of the adhesive was higher than the other ones, making it impossible to be used in the manufacture of wood panels. In order for the plywood to be made with this specific adhesive (T8), 30 mL of a solution of 30% NaOH were added to it aiming to decrease the adhesive viscosity, and then it could be applied to the surface of the wood. The values presented in Table 3 are the values recorded after the addition of sodium hydroxide solution into the adhesive.

Du (2018), Kalami et al. (2017), and Ghorbani et al. (2018) using lignin from different sources and processes also find the same behavior of the adhesives, with viscosity increasing due to the incorporation of lignin. Du (2018) explains that viscosity increases because of high lignin molecular weight, which increases sharply when condensation reaction takes place between lignin molecules or between lignin molecule and phenol formaldehyde.

It is important since viscosity affects the proper distribution of the adhesive on the wood surface. It plays a key role in the wetting functions on the wood surface. When a low viscosity adhesive is used, excessive penetration of the adhesive may occur through the porous structure of the wood, resulting in insufficient amount of adhesive in the glue line, which is called hungry glue line, compromising bonding efficient of woods. On the other hand, if the viscosity is above the desired values, under-penetration of the adhesive may occur, creating a thick glue line, which may also compromise some of the other strength properties and thus compromising an efficient bonding of woods too (Bianche et al., 2016).

For the results of the solids content an inverse behavior occurred with the addition of lignin. The solids decreased when lignin is added in the synthesis of the adhesive, as it can be seen in the Table 3. This behavior was observed for both evaluated treatments using kraft lignin, with non-phenolated lignin T3, T4 and T5 with 63.06%, 60.98% and 39.75% of solid contents, respectively; and with phenolated lignin in T6, T7 and T8 with the solid contents of 62.60%, 57.81% and 39.35%, respectively. According to the results of gel time in this study it was observed that the phenolated lignin had lower time in this test than the non-phenolated lignin. Even though, the gel time was above that suggested in the literature for phenol formaldehyde adhesive, the lignin phenolation treatment decreased the gel time of the adhesives.

3.3 Resin performance in the mechanical test

One of the most important parameters regarding plywood strength properties is the shear strength, which is related to the glue line resistance. In this study the values found to shear strength test of the evaluated plywood prepared with commercial, laboratorial, and lignin-based adhesives are presented in Table 4.

Table 4. Mean values of Shear Stress of plywood with adhesives formulated.

Treatments		Shear Strength (kgf/cm^2)
T1	Phenol formaldehyde (commercial)	12.23 a
T2	Phenol formaldehyde (laboratorial)	11.38 a
T5	LPF 50%	10.51 a
T7	PLPF 40%	10.29 a
T4	LPF 40%	10.24 a
T8	PLPF 50%	10.19 a
T6	PLPF 30%	09.19 b
T3	LPF 30%	07.81 b

Where: LPF- Lignin phenol formaldehyde; PLPF – Phenolated lignin phenol formaldehyde.
Means followed by the same letter in a column do not differ by the Scott-Knott test, at the 5% nominal significance level.

Statistically there was no significant difference among the shear strength of lignin-based adhesives compared to the commercial and the synthesized adhesives, except for both treatments with 30% of lignin (T3 e T6) replacement in the formulation. The shear strength of plywood samples with these adhesives were 7.81 kgf/cm^2 for the T3 and 9.19 kgf/cm^{2}for the T6. The Figure 15 shows the performance of all the treatments in the shear strength test, but indicating the minimum value required by the EN 314-2 (European Standard, 1993).
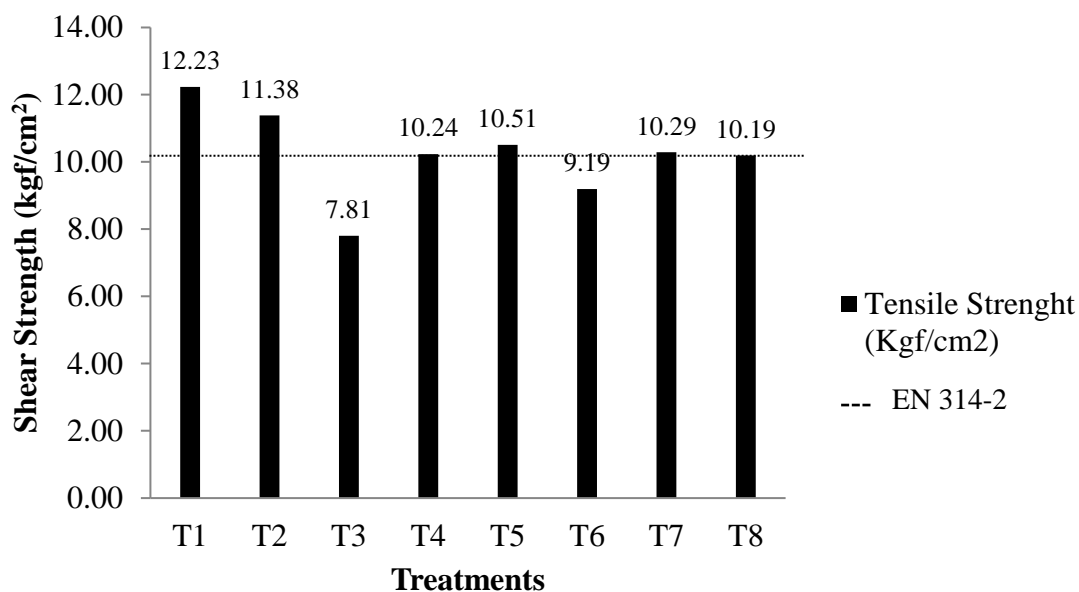
T1-Commercial; T2-Synthesized; T3-LPF 30%; T4-LPF 40%; T5-LPF 50%; T6-PLPF 30%; T7-PLPF 40%; T8-PLPF 50%; Where: LPF- Lignin phenol formaldehyde; PLPF – Phenolated lignin phenol formaldehyde.

Figure 15. Mean values of shear strength, in kgf/cm^2, of the specimens made from the synthesized adhesives with partial replacement of lignin.

The poor performance may be explained by the low viscosity of the adhesive, which may have led to the formation of a hungry glue line and thus compromising the joining of the wood blades. This may lead to low plywood strengths in the shear test. According to Pizzi and Mittal (2003) the ideal viscosity value for commercial formulations should range from 600 to 800 cP. The viscosity of the T3 was 475.9 cP and T6 was 526.4 cP, both were under the value stipulated by the authors. This may have been occurred due to the amount of methanol added to the reaction to retard hydroxymethylation reactions during synthesis. The amount used was previously fixed for all adhesive formulations, without considering the lignin content present in each of them.

The other treatments met the shear strength values stipulated by EN 314-2 (European Standard, 1993) which must be equals or higher than 10.2 kgf/cm^2 without any requiring of wood defects. There was no statistical difference among these treatments at the 95% probability level in the Skott-Knott test. The treatments with the highest shear strength resistance were the treatments T1 and T2. The other treatments (T4, T5, T7 and T8) which were partially replaced with lignin in the formulations showed shear strength values close to each other. The test showed values around 10.2 to 10.5 kgf/cm^2.

Many of the studies in the literature have shown that replacing up to 50% of phenol by lignin in adhesive synthesis has achieved satisfactory results, without compromising the shear strength properties of plywood. The values found in this study are consistent with those results found by Danielson & Simonson (1998) and Dias (2014), where the shear strength value in the glue line for synthesized adhesives with phenol formaldehyde and those adhesives with kraft lignin replacement up to 50% substitution showed similar values among the treatments. Santos et al. (2015) found similar behavior results of shear strength tests in wood particleboard using phenolated kraft lignin in the synthesis of adhesives. Values above 50% of replacement have shown poor performance in mechanical testing as reported by Yang et al. (2015), and Rinaldi et al. (2016).

Kalami et al. (2017) using lignin from dilute acid pretreatment and enzymatic hydrolysis of corn stover in the synthesis of phenol formaldehyde adhesives with 100% lignin replacement found higher shear strength values when compared to phenol formaldehyde adhesive in their work. It is important to observe that the lignin used in their work was derived from a grass that features a lignin with increased reactivity compared to the hardwood lignin due to carbon free position C3 and C5 in the aromatic ring which allowed greater affinity with formaldehyde during the synthesis of the adhesive (Ferdosian et al., 2017).

It is also important to observe that most of the studies with lignin-based adhesives found in the literature that replaces phenol by lignin during the synthesis of adhesives, used lignin from softwoods. This lignin, when compared to hardwood lignin, presents higher reactivity and consequently higher affinity with formaldehyde during adhesive synthesis, which may lead to a better performance of the wood panel to the strength properties in which they are submitted. In this study, it was used a kraft lignin from eucalypt (hardwood), which is less reactive than lignin from softwood and grasses; however, the results demonstrated that, despite its low reactivity, hardwood lignin proved to be a promising raw material for phenol replacement during adhesive synthesis.

3.4 Relative cost of the synthesized adhesives

One of the most relevant factors regarding use of lignin in the synthesis of adhesives, despite be considered a renewable and ecofriendly source, is that it must present a lower cost of obtaining when compared to phenol. According to Dessbesell et al. (2020) price of phenol is unstable, with price oscillating over time. As mentioned in their work, the average price per ton of phenol was around US$1304/ton. The same authors also mention that the price of lignin

obtained through a commercial technology is around US$600/ton, these values were also confirmed by the authors through the company that donated the kraft lignin. Considering the values of all feedstocks for preparing the adhesive, it was calculated the relative cost of producing lignin-phenol-formaldehyde adhesives by replacing lignin for phenol according to the treatments evaluated in this work. The adhesive, phenol formaldehyde was considered the reference (100%), as showed in the Table 5.

Table 5. Yield of the adhesives and relative costs.

	Treatments	Yield (%)	Relative Cost (%)
T1	Phenol formaldehyde (commercial)	-	-
T2	Phenol formaldehyde (laboratorial)	68.4	100
T3	LPF 30%	63.6	80.9
T4	LPF 40%	63.8	74.5
T5	LPF 50%	64.0	68.0
T6	PLPF 30%	63.6	80.9
T7	PLPF 40%	63.8	74.5
T8	PLPF 50%	64.0	68.0

Where: LPF- Lignin phenol formaldehyde; PLPF – Phenolated lignin phenol formaldehyde.

Considering the reagents consumption for preparing the adhesives, that one which 30% of the phenol was replaced by lignin, the relative cost of producing this adhesive would reduce to 80.9% of the total cost comparing to phenol formaldehyde adhesive reference. As for the adhesive that 40% replacement was made, this value reached 74.5% of the cost. The adhesive with 50% replacement, this value was 68% in relation to the cost of the phenol formaldehyde adhesive. These data show that, when the use of lignin is applied in the synthesis of the phenol formaldehyde adhesive, the production cost based on chemical consumption may be reduced for about 30%, showing that the use of this biopolymer may be profitable as well as ecofriendly.

CONCLUSION

Considering the commercial kraft lignin chemical characterization, it was observed a high purity of the evaluated sample, with 94% of lignin. The evaluated sample is comparable with the lignin samples described in demonstration plants as well as commercial scale plants.

The phenolation process increased 14.7% of phenolic hydroxyl in the kraft lignin structure, leading to a more reactive lignin. The lignin-phenol-formaldehyde adhesives synthesized with phenolated and non-phenolated lignin was possible. The plywood manufactured with the adhesives produced in this study attempted the minimum shear strength required by the European Standard EN 314-2 (1993). The adhesive with 50% of phenolated lignin in replacement to phenol in the synthesis was considered the best adhesive due to higher percentage of replacement, and faster gel time than the non-phenolated lignin.

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GENERAL CONCLUSIONS

The use of lignin as a raw material for the production of bioproducts is promising, mainly inserted in the concept of biorefineries associated to the pulp mills. 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, and the kraft lignin will be the most available source of commercial lignin, already available in large scale. On the other hand, for improving the different potential applications, some challenges remain, mainly in terms of the structure complexity, heterogeneous nature, and low reactivity of lignin depending on the lignin source (wood and nonwood, for example).

The phenolation process evaluated in this study increased 14.7% of phenolic hydroxyl in the kraft lignin structure, leading to a more reactive lignin. The lignin-phenol-formaldehyde adhesives synthesized with phenolated and non-phenolated lignin was possible. The plywood manufactured with the adhesives produced in this study attempted the minimum shear strength required by the European Standard EN 314-2 (1993). The adhesive with 50% of phenolated lignin in replacement to phenol in the synthesis was considered the best adhesive due to higher percentage of replacement, and faster gel time than the non-phenolated lignin.