UNIVERSIDADE FEDERAL DE VIÇOSA

FELIPE PEDERSOLI BORGES

FRACTIONATION METHODS OF EUCALYPTUS KRAFT LIGNIN FOR APPLICATION IN BIOREFINERY

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

Orientadora: Ana Marcia M. Ladeira Carvalho

Coorientadores: Iara Fontes Demuner
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Orientadora

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“The story of lignin is very similar to the story of the blind men and the elephant. Depending on which part of the elephant is touched, a different truth can be concluded about what an elephant is. Depending on which part of lignin you study, you can say it's aromatic, or aliphatic, or a polyphenol, and it's all true. What's critical is that we need to see not just a piece of the lignin, but the whole elephant.”

(Mikhail Balakshin, in a lecture at the IVSWPB 2020)

RESUMO

BORGES, F. P., M.Sc., Universidade Federal de Viçosa, julho de 2022. **Métodos de Fracionamento da Lignina Kraft de Eucalipto para Aplicação em Biorrefinaria.** Orientadora: Ana Marcia Macedo Ladeira Carvalho. Coorientadores: Iara Fontes Demuner e Fernando José Borges Gomes.

Lignina é o segundo biopolímero mais abundante na Terra, sendo o principal composto orgânico presente nos licores residuais de processos químicos de obtenção da celulose. Ainda que quase a totalidade dessa lignina seja atualmente queimada no ciclo de recuperação do processo kraft, aplicações em biorrefinaria tem sido cada vez mais estudadas, em virtude da riqueza de grupos funcionais presentes nesse polímero. Contudo, uma larga aplicação industrial ainda requer superar sua difícil trabalhabilidade, uma vez que possui grande polidispersividade e baixa reatividade. Dessa forma, esse estudo objetivou a obtenção de frações mais homogêneas e puras de lignina a partir da aplicação de métodos de fracionamento por estágio único e sequencial utilizando solventes orgânicos e por precipitação ácida. Os solventes orgânicos utilizados foram acetato de etila, etanol, metanol e acetona. Os pHs testados foram 9, 7, 5, 3 e 1 a partir da adição de ácido clorídrico. As frações foram caracterizadas quanto aos teores de lignina solúvel em ácido e insolúvel, carboidratos e cinzas, bem como por análise elementar. Razões S/G foram determinadas por Pi-CG-EM. Todas as frações obtidas em ambos os métodos de fracionamento apresentaram maiores teores de carbono, maior pureza e menor razão S/G que os materiais iniciais (lignina kraft de eucalipto e licor preto kraft de eucalipto), características muito favoráveis à aplicação em biorrefinaria. Frações solúvel em acetona (sequencial) e precipitada em pH 1 (estágio único) são as mais apropriadas para a produção de fibra de carbono. Frações solúvel em acetato de etila (estágio único) e insolúveis em pHs 3 e 1 (sequenciais) aparentam serem as mais adequadas para aplicações que requerem boas propriedades oxidativas. Já as frações solúveis em etanol (estágio único), metanol (estágio único), acetona (estágio único) e precipitadas em pH 9 (estágio único) e pH 5 (sequencial) são as que possibilitam melhor substituição química na obtenção por bioprodutos. Frações solúvel em etanol (sequencial) e precipitadas em pHs 5 e 1 (sequenciais) não apresentam interesse comercial em virtude do baixo rendimento.

Palavras-chave: Biorrefinaria. Lignina. Solventes orgânicos. Efeito do pH. Eucalipto.

ABSTRACT

BORGES, F. P., M.Sc., Universidade Federal de Viçosa, July, 2022. **Fractionation Methods of Eucalyptus Kraft Lignin for Application in Biorefinery.** Adviser: Ana Marcia Macedo Ladeira Carvalho. Co-advisers: Iara Fontes Demuner and Fernando José Borges Gomes.

Lignin is the second most abundant biopolymer on Earth, being the main organic compound present in residual liquors from chemical processes to obtain cellulose. Although almost all of this lignin is currently burned in the recovery cycle of the kraft process, applications in biorefinery have been increasingly studied, due to the richness of functional groups present in this polymer. However, a large industrial application still requires overcoming its difficult workability, since it has high polydispersity and low reactivity. Thus, this study aimed to obtain more homogeneous and pure lignin fractions from the application of one-step and sequential fractionation methods using organic solvents and acid precipitation. The organic solvents used were ethyl acetate, ethanol, methanol and acetone. The pHs tested were 9, 7, 5, 3 and 1, by adding hydrochloric acid. The fractions were characterized in terms of acid-soluble and insoluble lignin, carbohydrates and ashes, as well as by elemental analysis. S/G ratios were determined by Py-GC-MS. All fractions obtained in both fractionation methods showed higher carbon contents, higher purity and lower S/G ratio than the corresponding initial materials (eucalypt kraft lignin and eucalypt kraft black liquor), characteristics that are very favorable for application in biorefinery. Acetone-soluble (sequential) and pH 1 (one-step) precipitated fractions are the most suitable for carbon fiber production. Fractions soluble in ethyl acetate (one-step) and insoluble at pH 3 and 1 (sequential) appear to be the most appropriate for applications that require good oxidative properties. The fractions soluble in ethanol (one-step), methanol (one-step), acetone (one-step) and precipitated at pH 9 (one-step) and pH 5 (sequential) are the ones that allow better chemical substitution in obtaining bioproducts. Fractions soluble in ethanol (sequential) and precipitated at pHs 5 and 1 (sequential) are not of commercial interest due to their low yield.

Keywords: Biorefinery. Lignin. Organic Solvents. pH Effect. Eucalyptus.

LISTA DE ILUSTRAÇÕES

LISTA DE TABELAS

LISTA DE ABREVIATURAS E SIGLAS

H		P-hidroxifenila	*P-hydroxyphenil lignin*
G		Guaiacila	*Guaiacyl lignin*
S		Siringila	*Syringyl lignin*
Na_2S		Sulfeto de sódio	*Sodium sulfide*
Na_2CO_3		Carbonato de sódio	*Sodium carbonate*
$Ca(OH)_2$		Hidróxido de cálcio	*Calcium hydroxide*
NaOH		Hidróxido de sódio	*Sodium hydroxide*
CO_2		Dióxido de carbono	*Carbon dioxide*
O_2		Gás oxigênio	*Oxygen gas*
IPD	PDI	Índice de polidispersividade	*Polydispersity index*
Mp	Mw	Massa molar média ponderada	*Average molecular weight*
KL		Lignina Kraft	*Kraft Lignin*
KL1		Fração solúvel em acetato de etila para fracionamento de uma etapa	*Ethyl acetate soluble fraction for one-step fractionation*
KL2		Fração solúvel em etanol para fracionamento de uma etapa	*Ethanol soluble fraction for one-step fractionation*
KL3		Fração solúvel em metanol para fracionamento de uma etapa	*Methanol soluble fraction for one-step fractionation*
KL4		Fração solúvel em acetona para fracionamento de uma etapa	*Acetone soluble fraction for one-step fractionation*
KLS1		Fração solúvel em acetato de etila para fracionamento sequencial	*Ethyl acetate soluble fraction sequential fractionation*
KLS2		Fração solúvel em etanol para fracionamento sequencial	*Ethanol soluble fraction for sequential fractionation*
KLS3		Fração solúvel em metanol para fracionamento sequencial	*Methanol soluble fraction for sequential fractionation*
KLS4		Fração solúvel em acetona para fracionamento sequencial	*Acetone soluble fraction for sequential fractionation*
KLS5		Fração insolúvel para fracionamento sequencial	*Insoluble fraction for sequential fractionation*
BL		Licor preto	*Black liquor*
BL9		Fração obtida em pH9 no fracionamento de uma etapa	*Fraction obtained at pH9 in one-step fractionation*
BL7		Fração obtida em pH7 no fracionamento de uma etapa	*Fraction obtained at pH7 in one-step fractionation*
BL5		Fração obtida em pH5 no fracionamento de uma etapa	*Fraction obtained at pH5 in one-step fractionation*
BL3		Fração obtida em pH3 no fracionamento de uma etapa	*Fraction obtained at pH3 in one-step fractionation*
BL1		Fração obtida em pH1 no fracionamento de uma etapa	*Fraction obtained at pH1 in one-step fractionation*
BLS9		Fração obtida em pH9 no fracionamento sequencial	*Fraction obtained at pH9 in sequential fractionation*
BLS7		Fração obtida em pH7 no fracionamento sequencial	*Fraction obtained at pH7 in sequential fractionation*
BLS5		Fração obtida em pH5 no fracionamento sequencial	*Fraction obtained at pH5 in sequential fractionation*
BLS3		Fração obtida em pH3 no fracionamento sequencial	*Fraction obtained at pH3 in sequential fractionation*
BLS1		Fração obtida em pH1 no fracionamento sequencial	*Fraction obtained at pH1 in sequential fractionation*
RMN	NMR	Ressonância magnética nuclear	*Nuclear magnetic resonance*
Pi-CG-EM	Py-GC-MS	Pirólise acoplada à espectrometria de massa por cromatografia em fase gasosa	*Pyrolysis gas chromatography mass spectrometry*

SUMÁRIO

1. INTRODUCTION

Lignin is the second most plentiful biopolymer on Earth (DUVAL et al., 2016) and is by far the most available renewable source of aromatic units in nature (RAGAUSKAS et al., 2014; NORGREN and EDLUNG, 2014; LI et al., 2015). It is the main organic compound present in the residual liquors of the pulping processes (TAGAMI et al., 2019), but only 2% is used to generate products with higher added value, such as the lignosulfonates produced by the sulfite process (CAO et al., 2018). The remaining 98% are incinerated for power generation in the kraft mills (GELLERSTEDT et al., 2012; MANDLEKAR et al., 2018; HU et al., 2018). This generated energy is 60% higher than necessary to supply the internal demands of the manufacturing units (SANNIGRAHI et al, 2010).

The burning process also allows the recovery of chemical pulping reagents in the Kraft process, as mentioned by Duval et al. (2016) and Tagami et al. (2019). However, according to Luo and Abu-Omar (2017), this utilization as a fuel is not economically coherent, once the money equivalent of lignin used to generate energy is only $0.08 per kg. Furthermore, when used in chemical conversions, it can reach up to $1.08 per kg (VISHTAL and KRASLAWSKI, 2011).

During the kraft pulping process, which uses sodium hydroxide and sodium sulfide as main components of the white cooking liquor, a series of reactions occur in both carbohydrates and lignin. Among the reactions of lignin, the breakdown of ether bonds of type β-O-4 stands out, with small lignin fragments and free phenolic groups as products (DUVAL et al., 2016). The other etherified and condensed bonds of the lignin polymer also undergo cleavages, resulting in different structures as a product of the reaction. This means that the reactions of the kraft process result in a lignin with a much higher degree of heterogeneity than that of protolignin, which is already naturally polydisperse (TAGAMI et al., 2019). This degraded lignin is mixed in a solution called black liquor, which also contains pulping chemicals, carboxylic acids and non-processable wood elements (CARDOSO et al., 2009; KEVLICH et al., 2017). For a good extraction of Kraft lignin from black liquor, isolation techniques must be applied.

Studies have shown kraft lignin to be a potential supply pool of aromatics in chemical industries, being already applied in the production of lignosulfonates, dispersants, adhesives, technical carbons, transportation fuels and more (AZADI et al., 2013; DOMENEK et al., 2013; ARO and FATEHI, 2017; IBRAHIM et al., 2013; NORGREN and EDLUNG, 2014). Given its high availability, considering a kraft lignin-based biorefinery is also a logical proposal. However, because of its heterogeneity and polydispersity, complex and amorphous structure, low solvent solubility and uncertain reactivity, the use of kraft lignin for wide-scale applications is still commercially limited (VISHTAL and KRASLAWSKI, 2011; PARK et al., 2018; THELIANDER, 2008; NOWAK et al., 2018; TAGAMI et al., 2019).

The main techniques used to increase the uniformity of the molecular weight of the lignin polymer and reduce its polydispersity are the fractionation techniques. It is most commonly applied from the application of organic solvents by one-step or sequential fractionation (WANG and CHEN, 2013; LI et al., 2012; DUVAL et al., 2016; DOMÍNGUEZ-ROBLES et al., 2017; JÄÄSKELÄINEN et al., 2017; KIM et al., 2017; SAMENI et al., 2017; PARK et al., 2018; TAGAMI et al., 2019), pH effect precipitation (HELANDER et al., 2013; LOURENÇON et al., 2015; SEWRING et al., 2019; JARDIM et al., 2020) and membrane ultrafiltration (TOLEDANO et al., 2010). These methods aim to separate lignin into different fractions, allowing each of them to have a lower variability in molecular weight. As these techniques make it possible to obtain more homogeneous fractions of lignin, they turn it easier to be worked on the generation of bioproducts (JÄÄSKELÄINEN et al., 2017).

In addition to improving homogeneity, structural modifications of lignin to increase reactivity are also being studied (DAI et al., 2016; GAO et al., 2019), which can be carried out from demethylation, oxidation, hydrolysis, reduction, phenolation and hydroxymethylation reactions (INWOOD, 2014; ZULUAGA et al., 2018). It is important to mention that, for hardwoods, the S/G lignin ratio is of great relevance for the success of chemical replacements. Unlike the Kraft process, where higher amounts of lignin S are desirable, for biorefinery, there is a necessity for active sites, which means more free positions for substitution in the lignin molecule. Therefore, higher levels of lignin G and H are preferred.

Another technique to increase reactivity is the heat treatment of black liquor, carried out in order to demethylate and demethoxylate the eucalypt kraft lignin, later extracted from the liquor (LEPPÄVUORI et al., 2017). In this way, the fractionation of an already chemically modified lignin can induce an advance in the lignin biorefinery, in order to obtain a homogeneous fraction with greater reactivity.

In this context, the main objective of this research was to carry out the fractionation of eucalypt kraft lignin (KL) and kraft black liquor (BL) by the application of an eluotropic series of organic solvents and precipitation by the effect of pH, respectively, and to characterize each fraction obtained, identifying those with greater commercial potential based on the yields and chemical characteristics presented.

2. OBJECTIVES

Use kraft lignin and eucalypt black liquor for one-step fractionation and sequential fractionation from the application of an eluotropic series of organic solvents and also by the gradual pH acidification.

2.1. Specific Objectives

i. Obtain a pH range that provides a higher yield of the insoluble lignin fraction after black liquor precipitation;
ii. Carry out the fractionation of lignin from black liquor using the sequential pH technique;
iii. Perform a screening of industrial solvents for application in kraft lignin fractionation;
iv. Carry out the sequential fractionation of kraft lignin from an eluotropic series of organic solvents;
v. Check the behavior of the solubility of kraft lignin in a homologous series of alcohols;
vi. Characterize the extracted lignin fractions from Py-GC/MS analysis;
vii. Chemically characterize the lignin fractions, verifying the degree of purity of each material obtained;
viii. Identify the fractions of greatest commercial interest.

3. LITERATURE REVIEW

3.1. Protolignin

Protolignin, or *in situ* lignin, is the name given to lignin in its natural form, as it is present in plant cells. It is a complex, heterogeneous and amorphous macromolecule. This compound has as its main natural function the mechanical support of plants, in addition to reducing the permeability of water in the plant cell walls (DONALDSON, 2001; GOSSELINK, 2011). Lignin represents around 20-25% of the composition of hardwoods and approximately 30% of softwoods (CALVO-FLORES et al., 2010).

This polymer is composed of three basic phenylpropane units, so-called guaiacyl (G), syringyl (S) and p-hydroxyphenyl (H). These structures vary according to the degree of methoxylation of its aromatic ring (Figure 1). The S units have two methoxylic groups, G units have only one at carbon 3 (C3) and H has both carbons C3 and C5 free for substitution (SJÖSTRÖM, 1993).

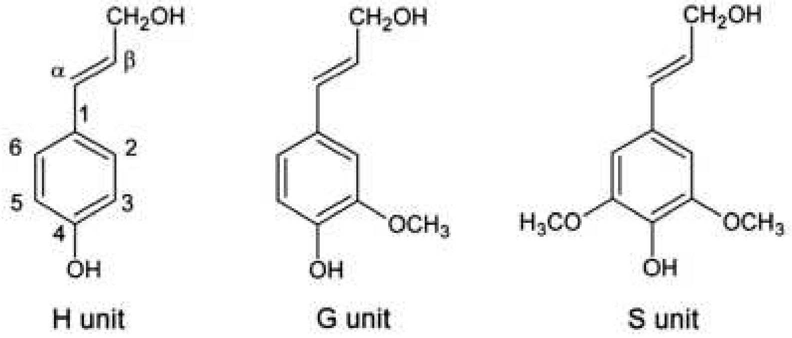

Figure 1. Main aromatic structures that make up the lignin macromolecule (DUVAL and LAWOKO, 2014).

The relative amounts of G, S and H vary according to the plant species, the section of the plant or even between different clones. Conifers contain more expressive amounts of G, as they have no S lignin, while hardwoods have both G and S prominently and a few H units. On the other hand, grasses may have all the three units in significant quantities when compared to wood species (VANHOLME et al., 2010). These phenylpropane units repeat themselves countless times, linking to each other by carbon-carbon or ether bonds, finally originating the large lignin macromolecule (Figure 2).

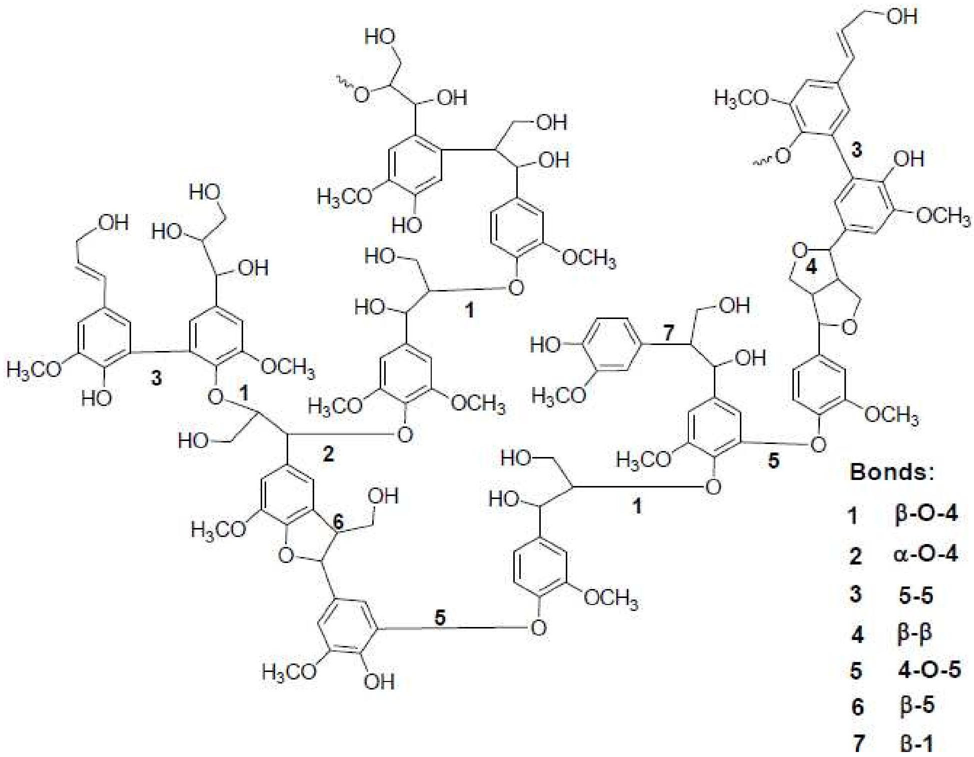

Figure 2. Main existing bonds in the conifer lignin polymer (DEMUNER et al., 2019).

It should be emphasized that there are still great doubts and controversies regarding the real structure of lignin, since it is not possible to isolate it from the plant cells without any modifications. As mentioned by Ralph et al. (2019), lignin H levels, for example, are commonly oversized, since other phenolic compounds, such as p-coumarate and p-hydroxybenzoate, are often erroneously counted as lignin derivatives when applying NMR spectroscopy.

Lignin contains several functional groups, whose main ones are hydroxyl (phenolic and aliphatic), methoxyl, carbonyl and carboxyl (EL MANSOURI et al., 2007). The availability of these groups will dictate the reactivity of this polymer against industrial processes, as well as its solubility in alkaline conditions (GOSSELINK, 2011).

Lignin biosynthesis can be divided into three acts, which occur in two different parts of the plant cells: the biosynthesis of the lignin monomers in the cytoplasm, the transportation of these monomers to the cell walls and finally the polymerization, which is an irreversible process (LIU et al., 2018; TERASHIMA et al., 2002).

As mentioned by Liu et al. (2018), lignin content, as well as its structure, can be modified by the advent of genetic modification. The suppression or induction of some specific genes' expressions may corroborate with the reduction of lignin levels. This mitigation is positive for the pulp industry, as well as modifying the lignin polymerization metabolic pathway, inducing the formation of a less condensed and more reactive lignin (WAGNER et al., 2009; GUO et al., 2017).

3.2. Kraft Process – An Industrial Route for Lignin Removal

Chemical processes for deconstructing lignocellulosic biomass dominate the pulp production scenario all around the globe. The main industrial methods for extracting lignin from wood are the kraft, sulphite, soda and Organosolv processes, with the kraft process being widely recognized as the most successful one (DOHERTY et al., 2011; DE LA TORRE et al., 2013; ALMEIDA and GOMIDE, 2013; SANTOS et al., 2016; ARO and FATEHI, 2017; DEMUNER et al., 2019). All these methods aim to break the lignin polymer into lower molecular weight compounds, which increases its heterogeneity and leads to different physicochemical properties according to the reagents and process conditions used (DOHERTY et al., 2011). Therefore, processed lignin is expected to be even more heterogeneous and more difficult to work with than the *in situ* lignin.

For pulp production, lignin does not represent a gain in yield. On the contrary, it is a compound to be removed in this process. The simplest use of processed lignin is burning for energy generation during the recovery cycle of cooking chemicals. Given the amount of liquor that is burnt in the recovery boilers, currently the energy production is surplus in the main factories, allowing its sale to distribution centers (SAARI et al., 2021). However, lignin can also be worked on to obtain products with higher added values.

Kraft pulping separates lignin from cellulose fibers by cooking wood chips in a solution of sodium sulfide and sodium hydroxide, namely white liquor, at a temperature of approximately 170°C (LORA, 2008). During this process, lignin is fragmented into fractions of lower molecular weights, which are soluble in strongly alkaline conditions (CHAKAR and RAGAUSKAS, 2004). The main reactions that occur with lignin are the hydrolysis of carbon-oxygen bonds, mainly the β-O-4 ones, since they represent about 40-60% of the bonds existing in the polymer and are the easiest to be cleaved (COLODETTE et al., 2015).

During the β-O-4 hydrolysis reaction, the free phenolic structure is ionized to phenolate, being converted into quinone-methide, which preferentially reacts with disulfide ions. There is, therefore, the generation of episulfides and lignin degradation products, according to the mechanism shown in Figure 3 (GIERER, 1980).

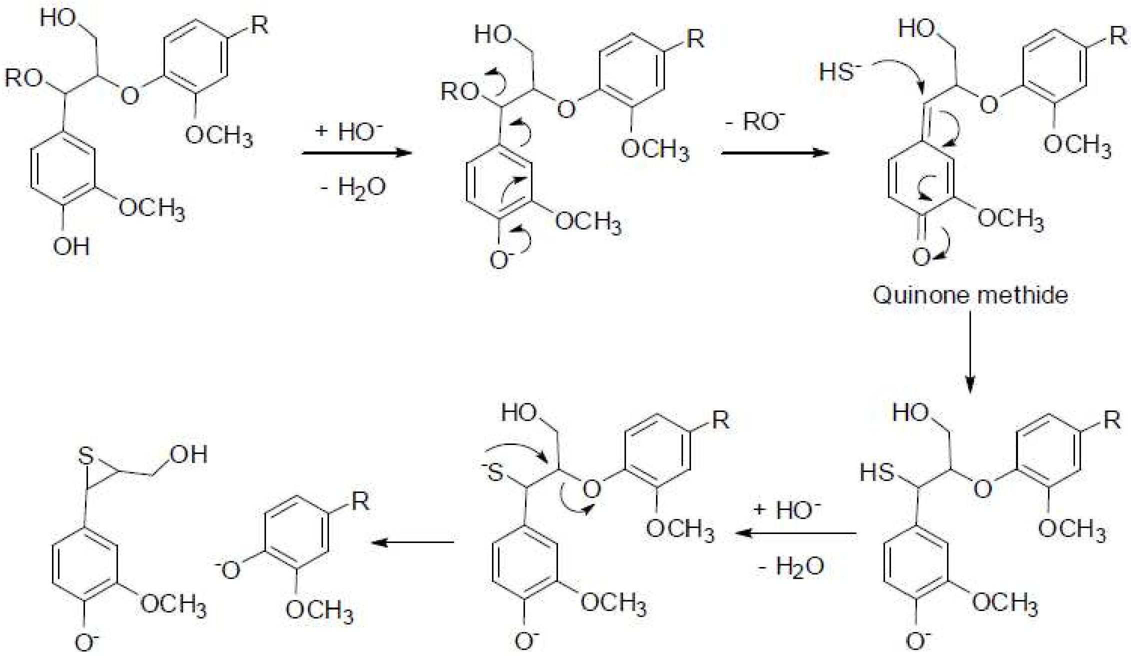

Figure 3. Reaction route of β-O-4 hydrolysis in kraft process (DEMUNER et al., 2019)

In an alternative route, there is the release of a terminal methoxylic group, generating formaldehyde as a reaction product. Etherified structures only undergo hydrolysis if there is a hydroxyl group on the alpha carbon of the aliphatic carbon chain (GIERER, 1980). So, non-phenolic units are very less reactive than the phenolic ones (EVSTIGNEYEV et al., 2020).

The reaction process is not only selective for lignin. In this way, there is also a loss of fibers in the kraft cooking, which reaches an average of 50 to 58% yield (GOMIDE and COLODETTE, 2006).

The black liquor generated in the Kraft process contains lignin, extractives, inorganic substances from wood, fibers leached from the process and cooking chemicals. This liquor is submitted to the recovery process, which burns organic matter and makes-up the chemicals from the process. In summary, the Kraft process recovery cycle comprises the following steps: concentration of weak black liquor by water evaporation; burning of strong black liquor to recover the inorganic compounds in the form of Na_2S and Na_2CO_3, as well as generating energy; preparation of cooking liquor, by reacting Na_2CO_3 and $Ca(OH)_2$ to produce NaOH; recovery of byproducts like tall oil, dregs and grits; and regeneration of lime (BAJPAI, 2018).

3.2.1. Technical Lignin

Technical lignin is defined as a form of lignin obtained after a series of processes that changes its natural form (LAURICHESSE and AVÉROUS, 2014). Technical lignin can be divided as kraft lignin, produced in the kraft process; lignosulfonates, obtained in the sulfite cooking; soda lignin, from the soda pulping; and hydrolysis lignin, produced in cellulosic ethanol plants as a by-product of enzymatic hydrolysis processes (DEMUNER et al., 2019).

Depending on the extraction method and raw material of origin, technical lignin can largely vary regarding molecular structure and molar weight, factors that determine its future applications.

Lignin obtained in the enzymatic hydrolysis process, for example, has better properties due to its mild conditions (CHEN, 2015). Kraft pulping, on the other hand, degrades and solubilizes lignin, causing a reduction of native lignin linkages and increase of phenolic groups (LANCEFIELD et al., 2018; GIUMMARELLA et al., 2019).

3.3. Isolation of Kraft Lignin

Lignin can be isolated from the black liquor by two methods: acidification and ultrafiltration membrane techniques. The yield and efficiency of the isolation process is essential for the use in biorefinery, since lignin with a high content of contaminants, mainly the ash content present in black liquor, have low commercial value (ZHU et al., 2014).

Kraft lignin is soluble only at high pH values due to ionized functional groups, such as phenyl and carboxyl. However, when the pH decreases, these groups are protonated, mitigating the repulsion forces between the lignin molecules. This makes them more aggregated and, therefore, less hydrophilic (LORA, 2008; SUNDIN, 2000).

There are two main commercial processes that use the precipitation by pH decrease to obtain purified kraft lignin from the black liquor: the LignoBoost and LignoForce processes. Differently, the membrane technology is carried out using a semi-permeable membrane which has pores of different sizes that retain lignin with similar molecular weight.

3.3.1. LignoBoost

The LignoBoost process was created by the research organization Innventia

(TOMANI, 2010) and its main purpose is reducing costs in the kraft process since it allows a decrease in the boiler demand and a further utilization of purified lignin in the obtaining of value-added products (TOMANI, 2010; KLET, 2017). This process provides a high lignin yield and a good degree of purity, with low ash and carbohydrate content, characteristics that turns the isolated lignin more attractive for further utilizations.

The process starts by taking out concentrated black liquor (30-45% dissolved solids) from evaporators of the kraft process recovery section. This black liquor is lightly acidificated with CO_2 until it reaches pH 9 to 10. The obtained slurry is filtered with a chamber press filter and re-suspended in water and sulfuric acid to obtain a pH 2.5 approximately. The resuspension goes on a second filtration step with acid water (TOMANI, 2010). The wet lignin is then crushed and dried to obtain lignin in a form of powder (FATEHI and CHEN, 2016). The process is summarized in the scheme of Figure 4.

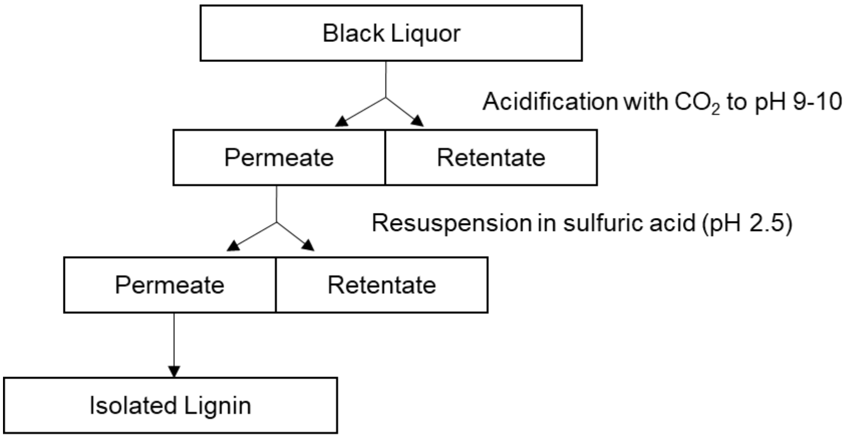

Figure 4. Simplified step-by-step of the Lignoboost process.

3.3.2. Lignoforce

The Lignoforce process was developed by FPInnovations and Noram to settle the problem associated with the production of totally reduced sulfur (TRS) compounds and other volatile sulfuric molecules, which are known to cause negative effects on human health (KOUISNI et al., 2016; JARDIM et al., 2020).

The first step and more important feature of this process is the black liquor's oxidation with O_2 to convert reduced sulfur species to non-odors compounds and also safe for health. After that, there is an acidification to pH 9 by CO_2 injection (HUBBE et al., 2019). Then, the resulting liquor goes to a coagulation step to form agglomerates that are filtered and washed with acid water. The cake formed by precipitated lignin is finally air dried. The process is summarized in the scheme of Figure 5.

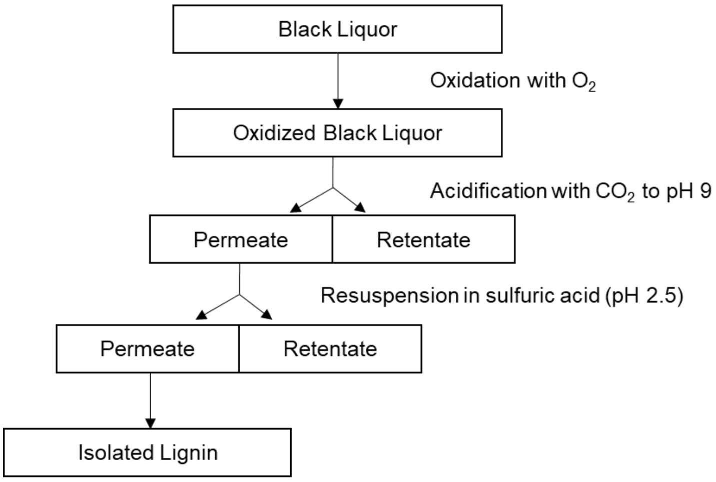

Figure 5. Simplified step-by-step of the Lignoforce process.

Kouisni et al. (2012) show how crucial is the oxidation to improve the filterability of the lignin during the filtration step. Since oxidation and acid/base reaction are exotherms, the temperature after oxidation and acidification increases. At these conditions, charged lignin groups associate easily, generating lignin clusters that can be readily filtered.

3.3.3. Membrane technology

Numerous studies have been carried out to investigate the feasibility of membrane technology to recover lignin from black liquor (TOLEDANO et al., 2010; HUMPERT et al., 2016; SEVASTYANOVA et al., 2014; ARKELL et al., 2014). This technique is based on the liquid separation components related to the size of the particles and molecules. The membrane cut-off (pore diameter) will define the technique as it follows: reverse osmosis, < 1 nm; nanofiltration, 1 to 5 nm; ultrafiltration, 2 to 100 nm, and microfiltration 100 to 2000 nm (KHULBE et al., 2008). It consists in a simple process that only requires a pump to apply pressure and membranes, usually polymeric and ceramic ones (KLETT, 2017).

It is well known that ultrafiltration is the best membrane technique to retain lignin and allow the free passage of the other liquor components as inorganics, water and monomeric compounds (SEVASTYANOVA et al., 2014; TOLEDANO et al., 2010). It also allows the control of the molecular mass distribution due to the choice of different membrane cut-offs. On the other hand, there are two relevant drawbacks on this process. Firstly, the flux of permeate components is likely to decrease due to the fouling phenomena, like pore plugging and cake formation. Secondly, the process gets harder to control as the concentration of the retained component starts to grow. (HUBBE et al., 2019).

3.4. Fractionation techniques

The application of technical lignin in high value-added products still presents itself as a great challenge due to the high degree of heterogeneity of this polymer. Therefore, methods to obtain a lignin with specific ranges of molecular weights and polydispersity are necessary (TAGAMI et al., 2019). A way to ensure this homogeneity is using lignin fractionation techniques.

Among the fractionation techniques, it must be cited the ultrafiltration, acid precipitation and extraction using organic solvents (TAGAMI et al., 2019; DUVAL et al. 2016; LOURENÇON et al., 2015).

The use of membrane filtration was initially employed in kraft industries as a wastewater treatment technology (THOMPSON et al., 2001). As the interest in lignin valorization grew up, ultrafiltration has also been studied as a way of obtaining fractions with low polydispersity and well-defined physicochemical characteristics (TOLEDANO et al., 2010, HELANDER et al., 2013).

Ultrafiltration appears to be an efficient method for obtaining predetermined molecular weight ranges due to the choice of membranes with specific mesh values. Furthermore, the biggest advantage of this process concerns the possibility of applying it directly to the cooking liquor without carrying out pH or temperature adjustments (SEVASTYANOVA et al. 2014).

On the other hand, the fractionation techniques by pH effect (acid precipitation) and extraction with organic solvents are less expensive, easier to control and present good performance in the separation of fractions.

3.4.1. Fractionation of Lignin by Organic Solvents

One alternative that has been studied to reduce lignin polydispersity is the fractionation of the polymer in more homogeneous parts by using different organic solvents.

This technique assumes that some industrial solvents are able to partially solubilize kraft lignin, so that each solvent will present a soluble fraction of exclusive polydispersity. Several solvents in sequence allow the soluble fractions to present unique properties according to the structural characteristics of what is extracted (DUVAL et al., 2016, TAGAMI et al., 2019).

Mörck et al. (1986) showed that lignin successive solvent extractions give different ranges of molar masses that are more homogeneous, which make it easier to define their features. They used dichloromethane, isopropanol, methanol and a mixture of methanol and dichloromethane to extract fractions with increasing molecular weights. Furthermore, other studies have applied the same technique, but using other solvent options, as hexane (WANG and CHEN, 2013; CUI et al. 2014), acetone (LI et al. 2012; CUI et al. 2014; TAGAMI et al., 2019) and diethyl ether (YUAN et al., 2009). When using this method, it is important to note that any changes, whether in the characteristic of the lignin present in the liquor, in the form of processing or in the conditions and amounts of solvent used, provide fractions with different characteristics. Regarding the various applications in biorefinery, studies are also required to identify the most viable fraction for each application.

In the last decade, Duval et al. (2016) used common industrial solvents (ethyl acetate, ethanol, methanol and acetone) to extract softwood kraft lignin sequentially. This study excluded chlorinated compounds, ethers and aromatics for environmental and safety reasons. Moreover, these selected solvents have low boiling points, which means that less energy is needed to recover the fractions by evaporation, without causing thermal lignin modifications. This study demonstrated that, for a homologous series of primary alcohols, the higher the carbonic chain, the lower the yield of the soluble fraction. It was also noticed that, for solvents of the same chain size, ketones lead to higher yields than alcohols.

Among the solvents selected for sequential fractionation, the following increasing order of yield of the soluble fraction was obtained: ethyl acetate, ethanol, methanol and acetone. It was also noticed that, within this sequence, for one-step fractionation, the higher the yield, the higher the polydispersity index (PDI) of the soluble fraction. This order, therefore, was adopted to obtain fractions in sequence, starting with the solvent with the lowest performance and ending with the one that best acts in the fractionation of a single step. Duval's good results meant that this eluotropic series was later used in other similar studies.

The highest yields obtained by Duval for kraft softwood lignin were those of the soluble fraction in ethyl acetate and the final insoluble fraction. Contrary to what was observed during one-step fractionation, sequential fractionation showed a drop in yield with each subsequent fraction, so that the application of acetone, the final stage, is not industrially viable as it results in too low amounts of lignin. Likewise, the polydispersity index also acted inversely in the sequential fractionation. This means that ethyl acetate had the highest PDI fraction, while acetone had the lowest PDI soluble fraction. Obviously, the initial and final insoluble fractions are disregarded, which have PDI higher than any others. For sequential fractionation, molecular weight (Mw) and PDI behaved inversely, with the fraction with the lowest PDI being the one with the highest Mw.

In general, all soluble fractions showed PDI more than 3 times lower than the initial technical lignin, demonstrating the great efficiency of the method. The study also demonstrated that fractionation is efficient in purifying lignin, drastically reducing the amount of carbohydrates in the soluble fractions. At each stage of fractionation, the amount of Klason lignin also increased. Duval noted that the most interesting fraction at the first moment could be the one obtained by using ethyl acetate, which was free from sugar and showed high yields with good polydispersity values.

Tagami et al. (2019) also studied the same eluotropic sequence proposed by Duval. In a complementary way, he worked with softwood and hardwood kraft lignin. For both forest species, Tagami et al. (2019) obtained higher-than-expected ethanol fraction yields in sequential fractionation, which was justified by the removal of low average molecular weight (Mw) lignins in the initial ethyl acetate step. According to the authors, this removal allows greater solvent permeability in the subsequent step.

Like Duval, Tagami noticed the presence of lower Mw lignin in the first fractionation step, increasing with each subsequent fraction. When comparing the behavior of different species in the same solvent, fractions of lower Mw were always obtained for hardwood than for softwood. It should be emphasized, however, that the softwood initial material had a Mw 3 times bigger than the one for hardwood.

From the study of the functional groups of each fraction by application of the NMR technique, Tagami verified that the fraction in ethyl acetate is the one that presents the greatest amount of total phenolic groups. This result is compatible with the statements that this fraction has the highest amount of acid-soluble lignin and also the lowest Mw constituents. It should be remembered that the main desired reaction of the kraft process, the breaking of β-O-4 bonds, is responsible for the increase of free phenolic groups in the technical lignin, as well as the creation of small lignin fragments.

Tagami et al. (2019) showed that the fractions with the highest Mw – especially the insoluble one – are those with the highest carbohydrate contents. This greater presence of sugars is attributed to the lignin-carbohydrate complexes, which cause greater deposition in lignins of higher molecular weight. Once again, the ethyl acetate soluble fraction proved to be quite interesting for general industrial applications, since it presented the lowest PDI values, lowest Mw, low carbohydrate content and good yield.

Park et al. (2018) studied the fractionation of lignin by using another sequential solvent option, which consisted in ethyl acetate, 2-butanone, methanol, acetone and dioxane/water. Milled wood lignin and Organosolv lignin from yellow poplar were used. In this research, the properties of the obtained fractions were studied and, once again, it was noticed that lower molecular weight fractions had more phenolic hydroxyl groups, as well as methoxyl groups. These groups content decreased in each subsequent step of the fractionation.

It is important to highlight that the presence of larger amounts of functional groups have a main role in lignin applications. The antioxidant ability of lignin is related to its free phenolic hydroxyl group content, as well as aliphatic hydroxyl group and methoxyl group (LI et al., 2012). That sort of fraction can be interesting for a use as natural antioxidant additives in cosmetics, polymers and pet food, for example (TAGAMI et al., 2019).

3.4.2. Fractionation of Lignin by the pH Effect

Much research has been done focusing on the precipitation and characterization of lignin as a function of the pH decrease. Evstigneev (2010) showed that the solubility of lignin in aqueous NaOH solution is reduced as the pH decreases and it also depends on the pKa of acid groups in the lignin polymer. In the kraft process, once the pH of black liquor is very high, lignin remains soluble due to its ionized phenolic groups, which interacts with sodium ions from the process liquor and behaves as an electrolyte (PASSINEN, 1968; HELANDER et al., 2013). As the pH of black liquor decreases, protonation of these groups occurs and lignin starts do precipitate (DEMUNER et al., 2019).

García et al. (2009) studied soda lignin precipitation by decreasing the pH of black liquor from 12.64 to 0.72 using sulfuric acid. At the highest pH value, only 2.74% of the total dissolved solids in the black liquor sample precipitated after centrifugation, while at the lowest one, 52.36% yield was achieved. The authors used *Miscanthus sinensis* as the lignocellulosic material for pulping in this research.

The acid applied in the precipitation plays an important role in the yield of the process and in the quality of the precipitated lignin. The comparison between sulfuric and hydrochloric acid showed that, although the lignin precipitated with both acids presented similar polydispersity (PDI) at the same pH, the material precipitated with HCl had higher purity, which means less inorganic and sugar content (SANTOS et al., 2014).

As a way of obtaining well-defined lignin fractions with relatively high yields, Lourençon et al. (2015) performed a simple acid precipitation of kraft hardwood and softwood black liquors in a sequential way. In this study, lignin was consecutively precipitated at five different pHs (9, 7, 5, 3 and 1). Specifically, hydrochloric acid was initially used to reduce the pH of the black liquor to 9, followed by centrifugation. Then, the precipitated fraction was recovered, while the supernatant got acidified again to the next pre-defined pH. Additionally, the authors reported that at pH 3, ashless lignin fractions were obtained for both hardwood and softwood, being, therefore, a product of interest for high added value applications. In both cases, at lower pHs, lignin presented lower Mw.

Helander et al. (2013) also studied the effect of acid precipitation on softwood black liquor, supplied by a Swedish pulp and paper industry. However, this study focused on obtaining only low molecular weight fractions, such as phenolic structures, given their great economic importance. In addition to the application in the synthesis of several chemicals, Norberg (2002) also highlights the capabilities of phenolic groups as antioxidant chemicals and softening agents. To ensure that all fractions of lignin obtained by acid precipitation had low Mw, the authors previously applied the crossflow ultrafiltration technique, using TiO_2 and ZrO_2 ceramic membranes of 1000 Da. The permeates were then sent for fractionation. The fractions obtained showed higher purity levels than the initial lignin. The authors also observed that filtration was already sufficient to guarantee excellent levels of purity, even without acidification. In fact, the ultrafiltration reduced the polydispersity of the material, being an additional gain to the fractionation by the pH effect. Since the permeate contains a large amount of material with low Mw and low polydispersity, a considerable increase in the sulfur contents when comparing with the initial material was also observed. This is justified by the cleavage mechanism of lignin β-O-4 bonds in the kraft process, in which episulfides are formed (GIERER, 1980; HELANDER et al., 2013).

3.5. Bioproducts obtained from lignin

The versatility of the chemical structure of lignin allows obtaining many bioproducts with different characteristics and applications (WELKER et al., 2015; BAJWA et al., 2019). Obviously, a wilder commercial utilization has as its main bottleneck the operational difficulties of lignin, which have been studied and overlapped over the last few years and continue as a great challenge for the academic laboratories and industries.

Considering that about 60% more kraft lignin is generated than is necessary to meet the internal energy consumption of the mills, its use for other purposes becomes an opportunity for optimization and greater profit generation. In addition, the abundance of aromatic structures in this polymer and, therefore, the high availability of carbon, puts it in the spotlight of several researchers focused on second-generation biorefineries (RAGAUSKAS et al. 2014; SANNIGRAHI et al., 2010; GOSSELINK, 2011). In this sense, the production of high value-added products using kraft lignin as raw material, such as biofuels (AZADI et al., 2013), adhesives (GOSSELINK, 2011), carbon fibers (NORGREN and EDLUND, 2014) and activated carbon, among others, (DUVAL et al., 2014) are very promising. Furthermore, the production of lignosulfonates from kraft lignin has also been studied in view of the limited production of this substance by the sulfite process (ARO and FATEHI, 2017).

The similarity of the structure of lignin with that of phenol-formaldehyde (PF) resins, as well as the fundamental characteristic of this biopolymer of gluing plant cell walls, makes it very interesting for the production of binders (GOSSELINK, 2011). In a mechanism proposed by Baekeland (1909), the synthesis of PF consists of polycondensing phenolic structures in excess of formaldehyde, either in the presence of acid or basic resins. This material can be used as adhesives on wood panels, varnishes, particle boards and plywood, for example (GOSSELINK, 2011; DONGRE et al., 2015; DEMUNER et al., 2019). However, the trend to reduce the use of fossil fuels in industry appears as a great motivator to mitigate the production of synthetic resins and replace them with materials produced from renewable sources (SOLT et al., 2018a). Another unfavorable factor is the market's dependence on oil price variations (ZHANG et al., 2013).

Since lignin is proposed as a replacement material for PF, it is desirable to have a large amount of phenolic groups in the initial material. This makes lignin fractions with lower molecular weights preferable, since they tend to have higher phenolic lignin contents. On the other hand, if Mw is too low, the polymerization process can also be impaired (LORA, 2002; TEJADO et al., 2007). To obtain a more homogeneous initial material and with a lower Mw, fractionation by organic solvents may be an important alternative (SOLT et al., 2018b). It should be noted, however, that the reactivity of kraft lignin with formaldehyde is lower than that of phenol, which has motivated several studies to increase reactivity through chemical modifications (HU et al., 2011; GHORBANI et al., 2018). Since chemical substitutions may be necessary, kraft hardwood lignins with lower S/G ratio and kraft softwood lignins will be favorable.

Lignin can also be used as a precursor material for the production of carbon fibers (KADLA and KUBO, 2002; BAKER et al., 2012). Following the same trend as adhesives, the use of lignin for carbon fibers (CFs) has as one of its motivations the search on reducing the use of fossil fuels, since the most used synthetic precursor is a petroleum-based polymer (DEMUNER et al., 2019). There are advantages and drawbacks in using lignin for this purpose. It is a material of high availability, low cost, high carbon content and origin from a renewable source. On the other hand, it is much more heterogeneous than polyacrylonitrile (PAN), which impairs the physical-mechanical properties of the carbon fiber produced (LI et al., 2017; BERLIN and BALAKSHIN, 2014). Once again, fractionation techniques may be interesting to mitigate the adverse effects of polydispersity in the application of lignin. Another way to improve the characteristics of the final product and reduce the use of PAN in the production of CFs is the copolymerization between lignin and precursors of fossil origin (MARADUR et al., 2012).

There are still other important factors for producing carbon fiber with suitable characteristics that refers to lignin’s structure and chemical composition. The carbon content of the feedstock needs to be high and its ash content should be less than 0.025% (MAINKA et al., 2015). Furthermore, it is known that more condensed lignins facilitate the thermostabilization after the spinning process in the carbon fiber production, making hardwood lignins with lower S/G ratios, and certainly softwood lignins, more favorable (HOSSEINAEI et al., 2016).

The basic structure of lignin, composed of phenylpropane units, makes this polymer the only renewable source existing in sufficient quantities to meet the industrial demand for the synthesis of aromatic compounds (GOSSELINK, 2011; LI and TAKKELLAPATI, 2018). Since oxygenated functional groups, as methoxylic ones, are problematic in the synthesis process, higher levels of lignin G are again preferred.

Although the amount produced worldwide is still low, lignosulfonates correspond almost entirely to the small percentage of lignin commercially sold, while the by-product of the kraft process is mostly incinerated (LAURICHESSE and AVÉROUS, 2014). Lignosulfonate corresponds to the by-product resulting from sulfite pulping. Sulfite pulping can be performed using an aqueous solution of sulfite or bisulfite of sodium, magnesium, calcium or ammonium, and the pH value is determined by the solubility and dissociation of the chosen salt (LORA, 2008; EKIELSKI and MISHIRA, 2020). During this process, lignin undergoes acid hydrolysis and sulfonation reactions of the aliphatic side chain (predominantly in the α position) which provide its solubilization in the aqueous solution (KUN and PUKÁNSZKY, 2017). In this context, it is also worth mentioning that the conditions under which delignification occurs will generate lignosulfonates with different physicochemical properties, as cited by Aro and Fatehi (2017).

Lignosulfonates have similar or higher molecular weights when compared to kraft lignin. The most abundant bond present in native lignin (β-O-4 bond) reacts to a lesser extent during sulfite pulping and, therefore, guarantees a less decomposed molecular structure when compared to the kraft one (KUN and PUKÁNSZKY, 2017). Lignosulfonates can be used in animal feed, as pesticides, surfactants, stabilizers in colloidal suspensions, dispersants for concrete mixtures, adsorbents and other applications (ARO and FATEHI, 2017; LORA, 2008; INWOOD, 2014).

3.6.Final remarks

For a long time, lignin remained hidden from industrial interests because it was considered way too difficult to work with. As studies progressed in terms of knowledge of the lignin structure and the possibilities of improving the reactivity and homogeneity of the molecule, commercial interest began to grow in the same proportion. Nowadays, there are several studies related to lignin and this polymer starts to assume the leading role that cellulose reached in the second half of the last century. However, there are still obstacles to be overcome and the effort of researchers is necessary to advance more further in the studies. It can be mentioned, for example, the still low yields of some techniques applied to technical lignin, or the difficulty in guaranteeing equal fractions of material for each batch of treatment, since the initial material is heterogeneous and will be obtained under different conditions every time that the clone or process parameters are changed. Another important issue to be addressed in order to make it commercially viable is the reduction of costs in the processes for obtaining lignin bioproducts. It is important to consider, however, that some techniques, such as the sequential fractionation, are simple and provide a cheap solution for mitigating the heterogeneity and polydispersity issues.

The kraft process is very well established in terms of closing its cycle and disposing of its by-products. Convincing managers that the bioutilization of lignin is more interesting than burning it in the boiler is a task that requires good arguments. However, it is undeniable that research advances are exponential in the hunt of this industrial and economic viability for lignin, and the future looks very promising.

4. MATERIAL AND METHODS

4.1. Material

This study used eucalypt kraft lignin (KL) and kraft black liquor with 51.1% of solids content (BL) provided by a Brazilian pulp mill. KL was used as the initial material for the fractionation by organic solvents, while BL was the initial material for the fractionation by acid precipitation. In both cases, one-step fractionation and sequential fractionation were performed.

The soluble fractions obtained by organic solvents were numerically named from the eluotropic sequence, starting from the one with the lowest solubilization power. Thus, KL1, KL2, KL3 and KL4 refer to the fractions soluble in ethyl acetate, ethanol, methanol and acetone respectively. For fractions obtained from sequential fractionation, an S was added, thus having KLS1, KLS2, KLS3 and KLS4. KLS5 refers to the insoluble fraction of sequential fractionation.

The fractions obtained by acid precipitation (also called precipitation by the pH effect) were named in reference to the pH reached. Thus, BL9, BL7, BL5, BL3 and BL1 are the fractions separated at each of the corresponding pHs. In a similar way to that performed for organic solvents, the fractions corresponding to the sequential fractionation have an S in their nomenclature, thus obtaining BLS9, BLS7, BLS5, BLS3 and BLS1.

The flowchart described in Figure 6 summarizes all the steps performed in this work.

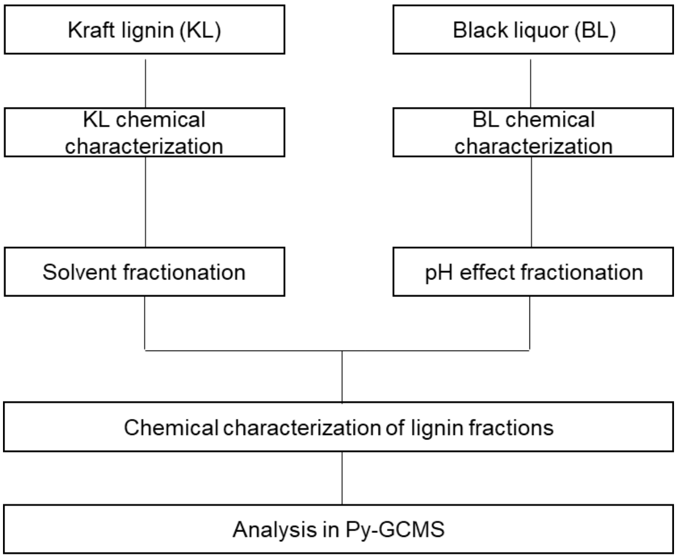

Figure 6. Flowchart of the experimental steps performed

4.2. Chemical Characterization of Kraft Lignin

The standards used for the chemical characterization of kraft lignin and liquor, as well as lignin fractions, are stated in Table 1.

Table 1. Analytical procedures used in the kraft lignin chemical characterization

Parameters	Procedures
Soluble lignin	TAPPI UM 250
Insoluble lignin	TAPPI T 222 om-02
Carbohydrates	SCAN-CM 71:09
Ashes	TAPPI 211 om-93

The elemental composition of lignin was determined using a CHNS-O equipment, of the LECO line. The TruSpec CHNS Micro module made it possible to measure the percentages of carbon, hydrogen, nitrogen and sulfur. The percentage of oxygen was identified by the TruSpec Oxygen Add-On module.

4.3. Organic solvent fractionation

4.3.1. One-step fractionation (solvent screening)

The screening of solvents was carried out in order to identify the one that allows obtaining a greater soluble fraction of kraft lignin. Methanol, ethanol, acetone and ethyl acetate were the solvents used. The choice for these chemicals is due to the low boiling point, which facilitates their recovery in the extraction stage of the soluble fraction and also prevents thermal degradation of the fractionated lignin. Furthermore, they are preferable to aromatic and chlorinated solvents for safety reasons. Propanol was also tested to verify the behavior of the homologous series of alcohols.

An amount of 2.0 g of oven-dried lignin kraft (KL) was added into an erlenmeyer flask with 20.0 mL of the tested solvent. The flask was closed with a lid and stirred for 2 hours at 140 rpm rotation and at room temperature. After stirring, the suspensions were filtered through a Buchner funnel with filter paper grade 4, which dry masses were previously determined. The retained fractions were subjected to drying in an oven at 105 ºC for 5 hours to obtain the masses of the insoluble lignin fraction, as well as its yield, by gravimetry, based on the total mass of the material. The soluble fraction was determined by difference.

The soluble fraction was isolated by the method of solvent recovery in a heating mantle, and reserved for further analysis (BORGES et al., 2021). This method also allows the reuse of the solvent in new replications of the fractionation, requiring only a make-up to compensate for the losses, as shown in Figure 7.

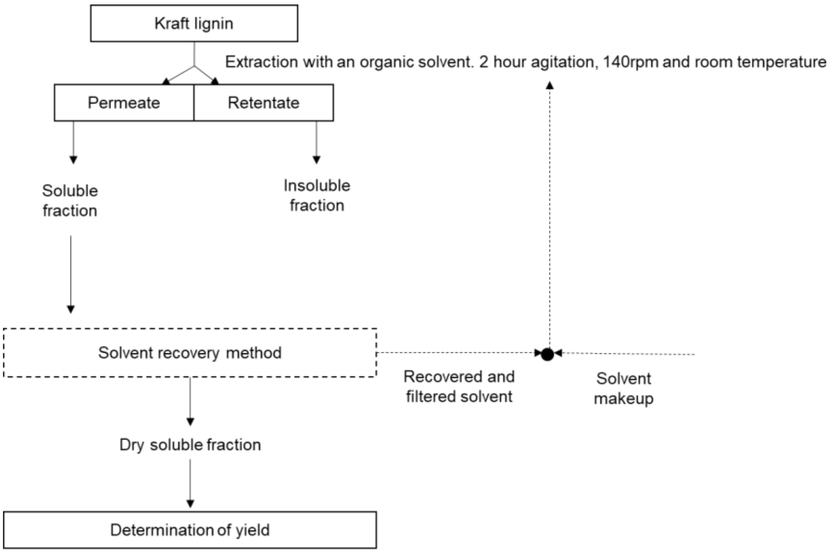

Figure 7. Solvent recovery method for fractionation with organic solvents (BORGES et al., 2021).

4.3.2. Sequential fractionation

Sequential fractionation of solvents was performed with 10.0 grams of kraft lignin at room temperature. The sequence of solvents followed the order proposed by Duval et al. (2016): ethyl acetate, ethanol, methanol and acetone. In each extraction, the system was gently shaken for 2 hours at 140 rpm, similarly to the screening procedure.

The soluble and insoluble fractions were separated by filtration in a Buchner funnel with filter paper grade 4. The soluble fraction was obtained by the solvent recovery method and its yield was calculated from the initial mass of the material. The insoluble part was recovered for a new solubilization in the following solvent. The amount of solvent added to the system was always enough to maintain the concentration at 100.0 g L-1, starting with 100 mL of ethyl acetate and 10.0 g of lignin, as proposed by Duval et al. (2016). The insoluble fraction was always dried at 40ºC for 24 hours before the next fractionation step.

The flowchart described in Figure 8 demonstrates all the steps performed in the sequential fractionation method by eluotropic series of organic solvents for kraft lignin.

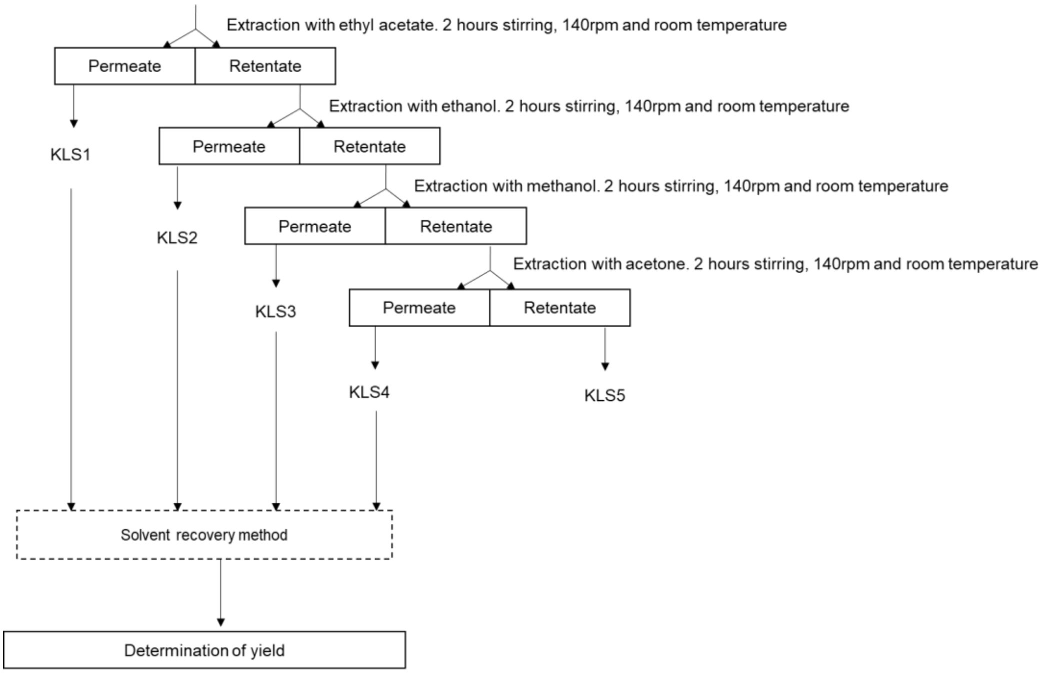

Figure 8. Flowchart of the proposed experimental design for sequential fractionation by eluotropic series of organic solvents for kraft lignin, based on Duval et al. (2016).

4.4. Acid precipitation

4.4.1. One-step fractionation (pH screening)

During one-step fractionation, 10.0mL of black liquor (BL) was used for acid precipitation. The pHs tested were 9.0, 7.0, 5.0, 3.0 and 1.0.

Initially, the liquor was at a pH close to 13.0, corresponding to the final pH of the kraft pulping process. To carry out the acidification of the medium, 1.0N and 0.1N hydrochloric acid were used.

The acid was added until the pH of interest was reached, always with constant stirring. Then, the acidified liquor was left to rest for 10 minutes for its maturation, which consists of the formation of lignin conglomerates. After the maturation process, the mixture was centrifuged at 2700rpm for 15 minutes.

Finally, the supernatant was separated from the precipitate. The precipitate was taken to drying in an oven at 105ºC, weighed to determine the yield and kept for further chemical characterization. The supernatant was discarded.

4.4.2. Sequential fractionation

As in the pH screening, 10mL of black liquor was used. Initially, with the addition of hydrochloric acid, the pH was lowered to 9.0, always keeping the system under agitation. Once again, maturation was carried out for 10 minutes, followed by centrifugation for 15 minutes at 2700rpm. Supernatant and precipitate were separated, with the insoluble fraction being taken to an oven at 105ºC until completely dry. However, this time, the supernatant is not discarded, which is again acidified to obtain the subsequent fraction. The process was repeated at pHs 7.0, 5.0, 3.0 and 1.0, as illustrated in Figure 9.

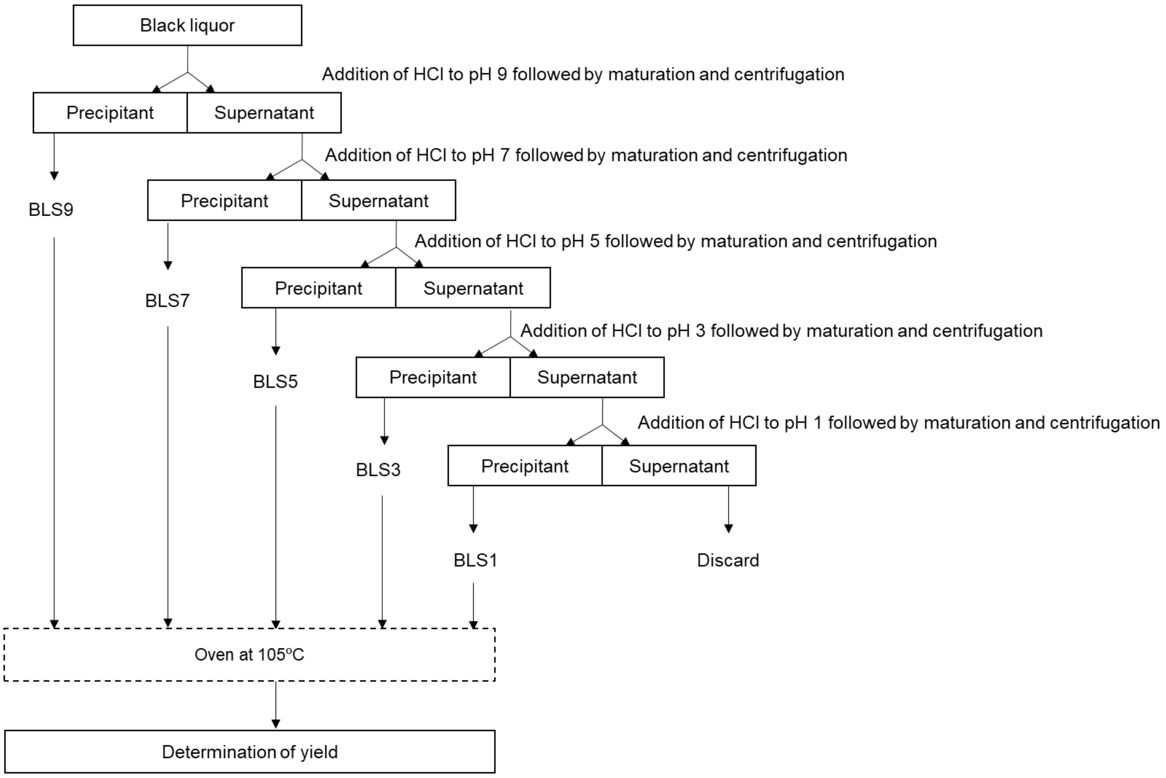

Figure 9. Flowchart of the proposed experimental design for sequential fractionation by acid precipitation for black liquor, based on Lourençon et al. (2015).

4.5. Characterization of Lignin Fractions by Py-GC/MS

Pyrolysis of the samples was performed in duplicate with a pyrolyser micro-oven (Frontier Laboratories Ltd., Fukushima, Japan) coupled to a Shimadzu GC-MS device (model PQ5050A), using an Ultra-ALLOY® column (UA5, 30 m × 0.25 mm ID, 0.25 µm film thickness), which acts similarly to a fused silica capillary column, but with greater heat resistance.

A sample of fractionated lignin (100 µg) was deposited in a small platinum beaker inserted into a quartz tube (2 x 40 mm) placed in the pyrolysis chamber. Pyrolysis was performed at 550 °C for 10s, as proposed in previous works (DEL RÍO et al., 2005; SCHORR et al., 2014; DEMUNER et al., 2021a; DEMUNER et al., 2021b).

The pyrolysis chamber was maintained at 250 °C and purged with helium to transfer the pyrolysis products to the GC column without loss. The chromatographic oven was heated from 45 °C to 240 °C at a rate of 4 °C min-1, with the final temperature being maintained for 10 minutes. The temperatures of the injector, detector and GC-MS interface were 100, 250 and 290 ºC concomitantly. The MS module was operated in the 50-350 mass scan range and 70 eV ionization. The identification of compounds was made by comparing the mass spectra with the GC-MS spectral library (Willey and NIST), mass fragmentography and by comparison with literature data (DEL RÍO et al., 2005; FERNÁNDEZ-RODRÍGUEZ et al., 2020; DEMUNER et al., 2021a; DEMUNER et al., 2021b).

The S/G ratio was calculated from the sum of the lignin S derivatives and the sum of the lignin G derivatives.

5. RESULTS AND DISCUSSION

5.1. Fractionation by organic solvents

5.1.1. Yields and elemental composition

The results of the soluble fraction of lignin (yield) obtained by one-step (direct) fractionation in each of the organic solvents used, as well as their elemental composition, are shown in Table 2.

Table 2. Yield and elemental composition for each lignin fraction in the one-step fractionation with organic solvents

Lignin	Yield, %	Elemental Composition, %				
		C	H	N	S	O
KL Initial	-	62.3	4.6	0.1	2.1	30.7
KL1 EtOAc	17.87	64.4	5.3	0.1	2.1	28.1
KL2 EtOH	47.12	64.2	5.4	0.1	2.4	27.9
KL3 MeOH	80.31	63.5	5.4	0.1	2.6	28.4
KL4 Acetone	81.66	64.3	5.2	0.1	2.4	28.0

The elemental analysis for unfractionated lignin showed values of carbon (62.3%), hydrogen (4.6%) and oxygen (30.7%) similar to those obtained by Tagami et al. (2019) and Dou et al. (2020). The sulfur values (2.1%) are also within the expected range for eucalypt kraft lignin which, according to Doherty et al. (2011), should be between 1 and 3%. Ethyl acetate (KL1) and acetone (KL4) were the solvents with the highest carbon content, presenting 64.4% and 64.3% respectively. It should also be noted that all fractions resulted in an increase in the carbon content when compared to KL, which is an indicator of lignin purification and consequent reduction of ash and carbohydrate contents (Table 4). In none of the cases there was a significant variation in the sulfur contents.

Ethyl acetate (KL1) is the solvent that has the lowest yield among those tested, justifying its choice to start the eluotropic series of sequential fractionation, as already proven by Duval et al. (2016).

Comparing the alcohols, methanol (KL3) has a higher soluble fraction than ethanol (KL2), as expected. In a homologous series of solvents, the longer the carbon chain, the lower the solubility of lignin in the solvent. For confirming this tendency, a one-step fractionation was also performed using propanol as solvent. The results can be observed in the Figure 10.

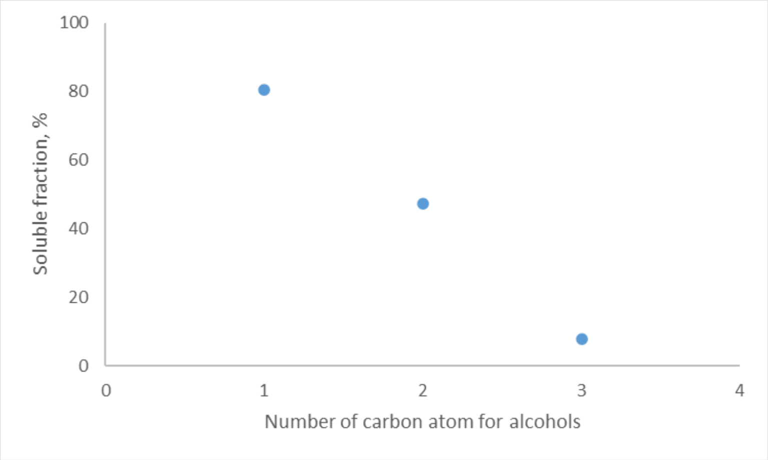

Figure 10. Yields of the soluble fraction for alcohols with different solvent chain length.

The sequential series used acetone (KL4) as the final stage, since this solvent tends to present the fraction with the highest Mw (average molecular weight) and highest PDI (polydispersity index) among the solvents involved in the study (DUVAL et al., 2016; TAGAMI et al., 2019). Obviously, the order of fractionation must also obey the solubilization force that each solvent presents.

The results for the sequential fractionation with organic solvents, as well as the elemental compositions, are shown in Table 3. Once again, as in the one-step fractionation, ethyl acetate and acetone were the solvents with the highest carbon content (64.4% and 64.7% respectively) and the general gain in carbon means that all solvents succeeded in purifying lignin.

Table 3. Yield and elemental composition for each lignin fraction in the sequential fractionation with organic solvents

Lignin	**Yield, %**	**Elemental Composition, %**				
		C	**H**	**N**	**S**	**O**
KL Initial	-	62.3	4.6	0.1	2.1	30.7
KLS1 EtOAc	17.87	64.4	5.3	0.1	2.1	28.1
KLS2 EtOH	8.82	63.5	5.2	0.2	2.6	28.5
KLS3 MeOH	31.58	63.4	5.2	0.2	2.6	28.6
KLS4 Acetone	12.26	64.7	5.5	0.2	2.3	27.3
KLS5 Insoluble	29.47	-	-	-	-	-

The results obtained do not follow the same trend of growth and fall between stages as in the study performed by Tagami et al. (2019) also with eucalypt kraft lignin. Tagami had subsequent yield drops from KLS1 (35.2% yield) to KLS4 (6.1% yield). However, in this study, KLS2 shows a sharp drop in yield when compared to KLS1, growing again in KLS3. The divergences are in general attributed to differences in methodologies and initial characteristics of the technical lignin used. It can be cited, for example, the same works by Tagami et al. (2019) and Duval et al. (2016), but now regarding softwood: while Duval showed subsequent yield drops from the beginning to the end of the eluotropic series, Tagami noticed a greater yield of KLS4 than that of KLS3. These discrepant behaviors are difficult to justify without further studies regarding the molecular structure of each fraction.

It is notable that any subtle changes, whether in the method, in the degree of purity of the chemicals, in the initial weighed masses, or in the chemical characterization of the technical lignin, lead to considerable changes in yield in the lignin fractionation. Differences in the initial lignin can be caused by variances in the wood of origin, in the type of industrial process used or even in the different conditions of the process.

As proposed by Duval et al., (2016), the predicted yield of each fraction (KLS) was calculated from the one-step fractionation yields, as it follows:

$$KLS1 = KL1$$

$$KLS2 = KL2 - KL1$$

$$KLS3 = KL3 - KL2$$

$$KLS4 = KL4 - KL3$$

$$KLS5 = 100 - KL4$$

The predicted results and the experimental results obtained from sequential fractionation were then compared, as shown in the Figure 11.

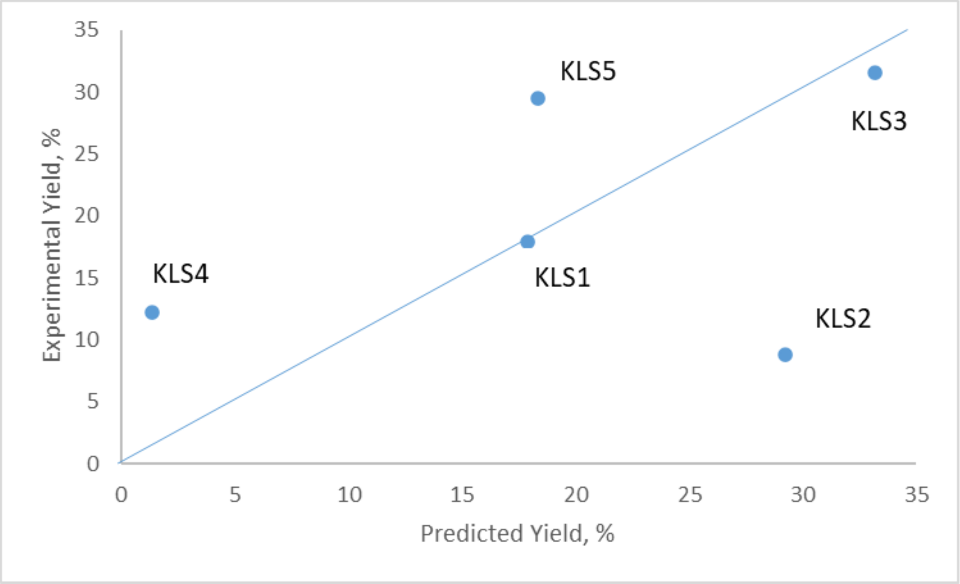

Figure 11. Experimental yields vs predicted yields obtained by sequential organic solvent fractionation

It can be seen that the two alcohols performed below the predicted values, and ethanol was the one that showed the greatest difference between predicted and experimental results. This negative behavior can be explained by the low yield also of the fraction soluble in ethyl acetate, which opens the eluotropic series. The ethyl acetate soluble fraction is the one that presents lower average molecular weights (Mw) for industrial hardwood kraft lignin when comparing the tested solvents (DUVAL et al., 2016; TAGAMI et al., 2019). Although all fractions are able to solubilize fragments of low Mw, Duval et al. (2016) demonstrated that ethyl acetate is the most selective solvent for these compounds. Since the efficiency in removing this fraction was low, the access of ethanol to medium Mw lignins may have been directly affected.

The insoluble fraction (KLS5) also showed high yields. The greater the insoluble fraction, the smaller the gain obtained by the sequential fractionation process, since this final fraction tends to be the most polydisperse one. Tagami et al. (2019) obtained a PDI of 4.8 for KLS5 in hardwood, which is more than twice bigger than the most polydisperse soluble fraction (2.0 for KLS4). For softwood, Duval et al. (2016) also found a PDI for KLS5 bigger than any soluble fraction and Tagami et al. (2019), working with spruce, obtained an insoluble fraction even more polydisperse than the initial material (KL).

It should also be mentioned that there is no preference for higher yields of a specific soluble fraction if there is no predetermined product application. Different fractions can be better or worse depending on the final product deserved from this material. However, when applying this sequence to this technical lignin, the fraction in ethanol presented yields below 10%, and is therefore less attractive for industrial applications, no matter how good their behavior and chemical characteristics can be.

5.1.2. Chemical characterization

The chemical characterization for each soluble fraction obtained, as well as the initial lignin, is presented in Table 4. For unfractionated lignin (KL), a total of 95.3% lignin, 2.5% sugars and 2.2% inorganic compounds were observed. Such values are, on average, close to those obtained in other studies with eucalypt kraft lignin (ZHOU et al., 2014; DIESTE et al., 2016; TAGAMI et al., 2019; GORDOBIL et al., 2016). It is important to mention that the quality of the initial material directly influences the performance of the fractions, as well as the subsequent application to obtain bioproducts. The highest possible degree of purity is desirable for the use in biorefinery, so lignins with low ash and carbohydrate contents are preferable. Therefore, the process of isolating and purifying lignin from liquor plays an important role that affects all following processes.

Table 4. Chemical characterization of the lignin fractions

Sample	Sol Lig, %	Insol Lig, %	Total lig, %	Carbohidrates Composition, %					Ashes, %
				Ara	Gal	Gly	Xyl	Man	
KL	9.8	85.5	95.3	0.1	0.2	0.9	1.3	0.0	2.2
KL1	9.3	88.9	98.2	0.0	0.0	0.5	0.1	0.0	1.2
KL2	6.6	91.1	97.7	0.0	0.1	0.7	0.1	0.0	1.4
KL3	8.2	90.2	98.4	0.0	0.1	0.4	0,2	0.0	0.9
KL4	6.5	91.4	97.9	0.0	0.1	0.6	0.1	0.0	1.3
KLS1	9.3	88.9	98.2	0.0	0.0	0.5	0.1	0.0	1.2
KLS2	9.1	89.0	98.1	0.0	0.1	0.6	0.1	0.0	1.1
KLS3	6.9	91.0	97.9	0.0	0.1	0.3	0.2	0.0	1.5
KLS4	4.8	92.4	97.2	0.0	0.1	0.6	0.1	0.0	2.0

Ara (arabinans); Gal (galactans); Gly (glycans); Xyl (xylans); Man (manans).

Fractionation by organic solvents, either direct or sequential, was selective for lignin, reducing the ash and carbohydrate content in all soluble fractions obtained. This means that, in addition to obtaining fractions with defined molecular weights and lower polydispersity, the use of organic solvents also helps to purify the isolated lignin.

The sum of sugars in each fraction remained relatively constant, varying between 0.6 and 0.9%, and always much lower than the sum of unfractionated kraft lignin. Attention must be paid to the behavior of xylans. In the paper-grade pulp kraft mill, cellulose and hemicelluloses represent yield gains. However, since the delignification process is not strictly selective, carbohydrate cleavage reactions also occur, especially the hydrolysis of acetyl groups in hemicelluloses, hydrolysis of β-glycosidic bonds and terminal depolymerization of the carbohydrate chain – also called peeling reaction (COLODETTE et al., 2015; FEARON et al., 2020). Due to their molecular structures, hemicelluloses are more susceptible to undesired reactions with white liquor than cellulose. Since the most common hemicelluloses in eucalypt are of the o-acetyl-4-o-methylglucuronoxylan type, the greater presence of xylans in the liquor and isolated lignin is justified (FUNDADOR et al., 2012). However, it was noticed that the organic solvents were quite selective with such structures, resulting in soluble fractions practically free of xylans, which were leached to the insoluble fraction. The same drastic behavior was not noticed for the glycans.

The fact that the most carbohydrates were leached to the final insoluble fraction is in agreement with what was predicted by Sevastyanova et al. (2014), who cited the greater presence of carbohydrate accumulations in lignin with higher Mw.

During the sequential fractionation, at each step, the ratio between insoluble and soluble lignin increased, as shown in Figure 12. This trend follows the expected growth order for Mw, as presented by Duval et al. (2016) and Tagami et al. (2019). Thus, the most selective fraction for low Mw is the one with the largest amount of acid-soluble lignin (KSL1 EtOAc), while the last soluble fraction of the sequential fractionation (KSL4 Acetone) has the highest Mw and, consequently, greater amount of insoluble lignin.

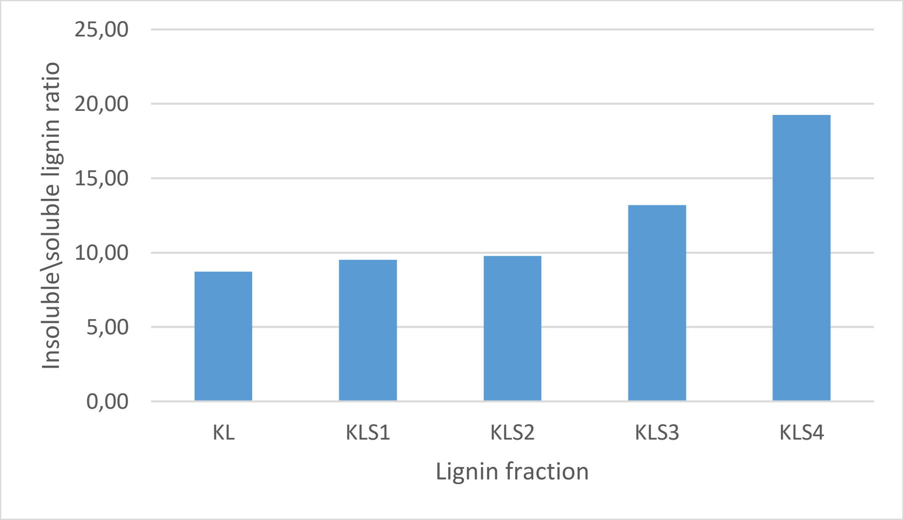

Figure 12. Insoluble and soluble lignin ration for each of the soluble fractions obtained by the sequential fractionation

Disregarding a greater reactivity analysis and considering only gravimetric aspects, the KSL3 fraction, obtained sequentially from methanol, presents itself as the most interesting for industrial applications, since the degree of purity is high and yield is the highest among the soluble fractions.

5.1.3. Py-GC/MS results

The results obtained from the Py-GC/MS analysis for each fraction in organic solvents, whether from one-step or sequential fractionation, as well as the calculated S/G ratios, are shown in Table 5. A S/G ratio of 3.10 was obtained for the starting material (KL). The value is consistent with expectations, as S-lignin is preferentially cleaved during eucalypt kraft cooking and woods with higher S/G ratio are generally preferred for the use in the process. This result is slightly superior to the starting materials used by Tagami et al. (2019) and Cassales et al. (2020), which obtained S/G ratios of 2.5 and 2.86 respectively, also measured by the pyrolysis gas chromatography mass spectrometry technique.

All lignin fractions obtained from organic solvents, whether sequentially or not, showed S/G ratios lower than the starting material. According to Demuner et al. (2019), the lower the percentage of lignin S, the more favorable is the material for application in biorefinery. C5 carbon is of paramount importance both for kraft cooking and for later applications of lignin. At the same time that the presence of methoxylic groups in this position prevents the formation of condensed bonds and, consequently, more difficult to be cleaved in the process conditions, they also reduce the amount of active sites for the production of new products, negatively interfering with the reactivity of the material.

The highest S/G ratio among the sequential fractions was obtained for ethyl acetate (KLS1), in agreement with the results of insoluble and acid-soluble lignin previously presented. According to Guerra et al. (2006) and Tagami et al. (2019), the presence of derivatives with methoxylic groups in lignin increases its antioxidant activity. Therefore, based on this principle, the KLS1 fraction would be interesting for application in products that require high antioxidant properties. However, it would be less suitable for applications that require chemical substitutions, such as sulfomethylation to produce lignosulfonates. The opposite applies to the KLS4 (acetone; sequential) fraction, which has the lowest S/G ratio among those sequentially obtained and, consequently, freer C5 carbons. However, the biggest disadvantage of this fraction is its lower purity when compared to the others.

Table 5. Py-GC/MS results for lignin fractionated by organic solvents

Compound	**Origin**	**Area percentage (%)**						
		KL1/KLS1	**KL2**	**KL3**	**KL4**	**KLS2**	**KLS3**	**KLS4**
Phenol	H	0.44	1.26	2.41	1.54	-	-	-
p-Creosol	H	-	1.03	2.04	1.55	-	0.33	0.36
o-Creosol	H	0.22	1.22	2.14	1.58	0.30	0.27	0.36
2,4-Dimethylphenol	H	0.11	0.88	1.81	1.39	-	-	0.20
2,5-Dimethylphenol	H	-	-	0.32	-	-	-	-
2,6-Dimethylphenol	H	-	0.44	1.04	0.54	-	-	-
TOTAL H		0.77	4.83	9.75	6.59	0.30	0.60	0.92
Catechol	Ca	0.82	2.33	3.37	2.81	1.36	1.25	1.40
3-Methoxycatechol	Ca	4.44	10.18	11.60	11.75	5.97	5.80	6.07
4-Methylcatechol	Ca	1.46	1.26	1.61	1.56	1.84	1.78	2.22
4-Ethylcatechol	Ca	-	0.60	-	0.64	-	-	-
1,2,3-Benzenetriol	Ca	-	-	-	-	-	-	-
TOTAL Ca		6.72	14.36	16.57	16.75	9.17	8.82	9.69
Guaiacol	G	2.17	4.67	3.61	5.28	3.46	3.46	3.38
3-Methylguaiacol	G	0.46	1.25	1.39	1.27	0.65	0.69	0.70
4-Methylguaiacol	G	2.44	4.05	3.50	4.62	2.75	2.96	3.46
4-Vinylguaiacol	G	-	-	-	-	-	-	-
4-Ethylguaiacol	G	1.19	2.66	2.82	3.04	1.29	1.37	1.56
4-Propenylguaiacol / Isoeugenol	G	0.60	0.41	0.94	0.70	0.25	0.28	0.47
Vanilin	G	1.65	1.62	-	1.32	1.48	1.69	1.79
4-Acetylguaiacol	G	1.23	1.13	-	1.03	1.11	1.05	1.01
Guaiacyl acetone	G	0.40	0.41	-	0.46	0.57	0.66	0.69
4-Propylguaiacol	G	-	-	-	-	-	-	0.22
TOTAL G		10.13	16.18	12.25	17.70	11.56	12.14	13.27
Syringol	S	10.24	14.50	13.07	16.63	13.62	13.22	11.57
4-Vinylsyringol	S	-	-	-	-	-	-	-
4-Methylsyringol	S	-	-	-	-	-	-	-
4-Propylsyringol	S	-	-	-	-	-	-	-
4-Acetylsyringol	S	6.08	0.21	1.22	0.37	4.64	4.13	3.35
Syringaldehyde	S	6.03	0.81	1.22	0.69	2.96	5.06	3.27
Syringylacetone	S	-	0.64	-	1.03	-	-	-
4-Propenylsyringol	S	2.44	2.44	0.97	2.57	2.57	2.81	3.66
3,4-Dimethoxyphenol	S	1.94	-	-	-	0.37	2.53	2.72
TOTAL S		26.73	18.60	16.48	21.29	24.16	27.74	24.56
Lignin S/G ratio	-	2.64	1.15	1.34	1.20	2.09	2.29	1.85

It is also notable that the non-sequential fractionation affects the S/G more radically, so that all fractions in direct fractionation presented S/G ratios drastically lower than the corresponding ones in the sequential process. For the production of lignosulfonates, KL4 (acetone; one-step) proves to be an interesting fraction, as it has a S/G of 1.20, a yield above

80% and uses only acetone, which is an inexpensive solvent with good possibilities for recovery and reuse.

5.2. Fractionation by the pH effect

5.2.1. Yields and elemental composition

The results of each fraction of lignin obtained by one-step (direct) fractionation in acid precipitation, as well as their elemental composition, are shown in Table 6.

Table 6. Yield and elemental composition for each lignin fraction in the one-step fractionation by acid precipitation

Lignin	**Yield, %**	**Elemental Composition, %**				
		C	**H**	**N**	**S**	**O**
BL	-	36.7	3.0	0.1	3.4	40.0
BL9	21.40	46.1	3.8	0.1	2.8	28.8
BL7	21.46	48.9	4.1	0.2	4.0	26.4
BL5	33.98	49.2	4.1	0.1	4.1	26.1
BL3	37.45	51.4	4.3	0.1	4.2	24.2
BL1	42.53	52.2	4.3	0.1	4.5	22.6

The carbon (36.7%), nitrogen (0.1%) and hydrogen (3.0%) contents obtained for the unfractionated kraft black liquor (BL) are relatively close to those cited by Frederick (1997), Casademont et al. (2020) and Cardoso et al. (2009), also with eucalypt kraft black liquor. Sulfur (3.4%) also fits the results obtained by Cardoso et al. (2009). However, 40.0% for oxygen is higher than that reported by all the other authors previously mentioned, which may be related to the process conditions and the added alkali charge, since this increase in oxygen certainly leads to a decline in the sum of inorganic substances, especially sodium, to close the mass balance.

One of the great advantages of using acid precipitation for lignin fractionation is the possibility of obtaining fractions with specific characteristics without using expensive chemicals and energetically unfavorable processes. It exclusively takes advantage of the intrinsic characteristic of kraft lignin to precipitate at acidic pHs, which is also the principle of the main techniques for isolating kraft lignin present in black liquor, such as the Lignoboost process.

The expected behavior is that the lower the pH of the medium due to the addition of a strong acid, the greater must be the fraction of precipitated kraft lignin. This behavior was confirmed in the screening, in which the lowest yield fraction was precipitated at pH 9 (BL9), while the highest yield was obtained in the most drastic pH condition (BL1).

There was no linear behavior of yield gain as a function of pH decrease. It is noticed that there is practically no gain when reducing the pH from 9 to 7, however, the highest percentage gain is obtained precisely from pH 7 to 5.

The results for the sequential fractionation by acid precipitation are shown in Table 7. Unlike the data treatment performed for sequential fractionation using organic solvents, here it is chosen to close the mass balance disregarding the soluble fraction of the last step, which corresponds to the discard of the process, as proposed by Lourençon et al. (2015). This justifies the divergence of yields between BL9 and BLS9, both corresponding to fractionations at the pH 9.

Table 7. Yield and elemental composition for each lignin fraction in the sequential fractionation by acid precipitation

Lignin	**Yield, %**	**Elemental Composition, %**				
		C	**H**	**N**	**S**	**O**
BL	-	36.7	3.0	0.1	3.4	40.0
BLS9	59.38	46.1	3.8	0.1	2.8	28.8
BLS7	11.94	45.6	3.7	0.2	4.7	27.0
BLS5	8.41	48.5	4.0	0.1	2.5	25.9
BLS3	18.60	49.7	4.0	0.2	2.7	25.2
BLS1	1.67	-	-	-	-	-

Similar to what was observed by Lourençon et al. (2015), the highest yield was obtained at the highest pH of sequential fractionation (BLS9) and the lowest yield was attributed to the last stage, corresponding to the most acidic pH (BLS1). The decrease, however, was not gradual, with growth between pHs 5 to 3. BLS1 yield is extremely low, meaning that this fraction can already be disregarded for any commercial applications. This is the reason why this fraction did not have its elemental composition determined.

Differently from what was observed in kraft lignin, there are much lower levels of carbon for liquors, whether in the unfractionated or acidified material. This is due to the composition of the initial lignin, which contains a large amount of ashed from the cooking liquor, corresponding to almost half of its mass. Since the liquor was obtained after the evaporation stage and before the burning step, it is expected that large amounts of sodium hydroxide and sulfide will be present, in addition to other sodium compounds as sulfates and carbonates in smaller quantities (CARDOSO et al., 2009; DEMUNER et al., 2021b).

As verified by Lourençon et al. (2015), the carbon contents showed a tendency to increase, while oxygen showed a decrease as the fraction becomes more acid, either in one-step fractionation (Table 6) or in sequential fractionation (Table 7). Therefore, the more acidic the fraction, the better its application for products that require higher carbon contents, such as carbon fibers, for example (ROBERTS et al., 1996; KADLA and KUBO, 2002; BAKER et al., 2012). At the same time, it should be kept in mind that some acidic fractions in sequential fractionation, while more favorable for this application, will have lower yields. If the yield is too low, the cost of production does not outweigh the benefits of the starting material for obtaining other products.

5.2.2. Chemical characterization

The chemical characterization for each fraction obtained, as well as the initial liquor, is presented in Table 8. Once again, it was decided not to characterize the last sequential fraction (BLS1), since its negligible yield is industrially impracticable, no matter that the fraction proves to be extremely superior to the others in its chemical composition.

Table 8. Chemical characterization of the liquor fractions

Sample	Sol Lig, %	Insol Lig, %	Total lig, %	Carbohidrates Composition, %					Ashes, %
				Ara	Gal	Gly	Xyl	Man	
BL	14.5	29.2	43.7	0.2	0.4	0.8	0.7	0.1	49.3
BL9	7.0	58.8	65.8	0.1	0.4	0.7	0.8	0.0	28.7
BL7	6.7	60.2	66.9	0.1	0.3	0.7	1.2	0.0	28.3
BL5	7.1	64.7	71.8	0.1	0.3	0.6	1.0	0.0	24.9
BL3	8.0	67.0	75.0	0.1	0.3	0.7	1.2	0.0	22.0
BL1	7.3	69.8	77.1	0.1	0.2	0.5	0.5	0.0	20.4
BLS9	7.0	58.8	65.8	0.1	0.4	0.7	0.8	0.0	28.7
BLS7	7.2	62.7	69.9	0.1	0.3	0.6	0.8	0.0	28.3
BLS5	5.4	69.4	74.8	0.1	0.3	0.6	0.7	0.0	23.2
BLS3	7.6	67.1	74.6	0.1	0.3	0.7	1.0	0.0	22.4

A total 50.7% of the kraft black liquor used (BL) is made of organic compounds, while 49.3% refers to the inorganic fraction, composed of cooking reagents and non-processable inorganic compounds present in the process chemicals and in the wood itself. Therefore, the process conditions, alkali charge, purity of the process reagents and wood quality are some of the factors that influence the final inorganic content in the liquor (HUBBE et al., 2019). The lignin contents obtained are higher than those achieved by Cardoso et al. (2009), also for eucalypt black liquor. It is important to note, however, that the lignin and carbohydrate contents will vary according to the final kappa number of the process, which is an indicative of residual lignin in the pulp. Therefore, the lower the final kappa number, the lower the lignin content in the pulp and, consequently, the higher the lignin content in the kraft liquor (COLODETTE et al., 2013). The carbohydrate content in the liquor, which is a consequence of degradation in the process (DEMUNER et al., 2019), also tends to be higher under more aggressive process conditions, such as, for example, at lower kappa numbers.

It can be noted that the mass balance for the liquors, whether in the starting material or in the fractions, does not total 100%, due to the presence of unmeasured compounds, such as acetic acid, formic acid, methanol and other degradation products (BAJPAI, 2018; HUBBE et al., 2019). However, it can be seen that the sum of lignin, carbohydrates and ash increases throughout the process from 95.2 in BL to approximately 99% in the final step of sequential fractionation (BLS1), indicating that the lower the pH of the medium, the lower the amount of these by-products in the fraction obtained.

The ash contents, in general, either in the one-step fractionation or in the sequential fractionation, showed to be lower as the pH decreased. Consequently, the total lignin contents present an inverse behavior, increasing with each pH reduction. Therefore, the lower the pH reached, the purer the lignin obtained (HELANDER et al., 2013; LOURENÇON et al., 2015; JARDIM et al., 2020).

As observed in Table 7, the yield obtained in BLS5 (8.41%) was very low, with an increase in BLS3 (18.60%) and then again, a drop in the final fraction (1.67%), a behavior different from what Lourençon et al. (2015) achieved. In the aforementioned research, with each decrease in pH, there was always a reduction in the yield in sequential fractionation for hardwood kraft liquor. This behavior is also reflected in the chemical characterization, as shown in Table 8, in which BLS5 differs considerably from the other fractions in terms of soluble and insoluble lignin contents.

Based on these results, it is estimated that the BLS5 fraction is made up of more condensed lignin and, consequently, of high molecular weight (GOMES et al., 2015). This finding is contrary to expectations based on previous works in the literature, in which, for hardwood liquor, the lower the pH, the lower the molecular weight of the fraction. In fact, in this study, the reduction of pH 7.0 to 5.0 does not seem to have been sufficient to precipitate the smaller lignin fragments, being able only to act on those fragments still with high Mw that passed unscathed by the more alkaline pHs, justifying the low content of soluble lignin, as well as the yield below expectations.

Another evidence that could help to justify this behavior of BLS5 is the elemental sulfur content, as shown in Table 7. Helander et al. (2013) indicate that the lignin fractions with lower Mw are the ones that contribute more to the elemental sulfur content, due to the delignification reaction mechanism in the kraft process. During the hydrolysis of the β-O-4 bonds, the phenolic structures are ionized, with a nucleophilic attack on the etherified bond that culminates in the formation of an episulfide, in addition to degradation products, justifying the increase in the sulfur rate (GIERER, 1980). In fact, for one-step fractionation, an increase in S content was observed with each pH reduction. On the other hand, in the sequential fractionation, BLS7 presented a sulfur content of 4.7%, while BLS5 had a sudden drop to 2.5%, not following the trend. However, a new elevation in BLS3 should be observed, which did not happen in this study.

High molecular weight lignins have lower solubility, in addition to weak acid groups (NORGREN et al., 2001). This means that there are not enough repulsive forces to keep the structure stable at more basic pHs, causing its early precipitation (LOURENÇON et al., 2015). On the other hand, lignins full of carboxylic and phenolic groups show strong interactions due to the negative character of these groups, remaining soluble. Clearly, with the addition of acid, the repulsion forces gradually decrease, resulting in the precipitation of the once-stable structures (NORGEN et al., 2001; LOURENÇON et al., 2015).

If the addition of acid still was not able to neutralize these charges on the lignin and cause precipitation, it is possible that there are contaminants in the liquor consuming the acid for another secondary purpose. Another theory would be that the starting material (BL) has a very high Mw and, at the same time, a very low PDI, which, for eucalypt kraft liquor, is not possible due to the wide variety of reactions in the process.

5.2.3. Py-GC/MS results

The results obtained from the Py-GC/MS analysis for each fraction in acid precipitation, whether from one-step or sequential fractionation, as well as the calculated S/G ratios, are shown in Table 9.

Table 9. Py-GC/MS results for lignin fractionated by acid precipitation

Compound	Origin	Area percentage (%)								
		BL9 / BLS9	**BL7**	**BL5**	**BL3**	**BL1**	**BLS7**	**BLS5**	**BLS3**	**BLS1**
Phenol	H	0.81	0.64	0.49	0.64	0.65	0.58	0.73	0.81	0.96
p-Creosol	H	0.57	0.42	0.40	0.48	0.53	0.35	0.47	0.60	0.65
o-Creosol	H	0.65	0.49	0.59	0.54	0.52	0.46	0.54	0.65	0.51
2,4-Dimethylphenol	H	0.27	-	-	-	0.13	-	-	0.12	-
2,5-Dimethylphenol	H	0.19	-	-	-	-	-	-	-	-
2,6-Dimethylphenol	H	0.20	0.14	0.14	0.11	0.12	-	0.09	0.14	-
TOTAL H		2.68	1.69	1.63	1.77	1.95	1.40	1.84	2.32	2.12
Catechol	Ca	-	0.65	0.72	1.14	1.46	0.64	0.78	1.15	0.81
3-Methoxycatechol	Ca	2.10	4.27	5.11	6.45	6.92	4.91	5.26	6.47	6.45
4-Methylcatechol	Ca	2.02	1.62	1.73	1.82	2.01	1.61	1.90	1.82	1.28
4-Ethylcatechol	Ca	-	-	0.23	-	-	-	-	-	-
1,2,3-Benzenetriol	Ca	-	-	-	-	-	-	-	-	-
TOTAL Ca		4.12	6.54	7.78	9.42	10.39	7.15	7.94	9.44	8.54
Guaiacol	G	10.51	9.78	10.49	9.86	8.03	10.47	9.58	9.09	5.74
3-Methylguaiacol	G	1.04	0.87	0.94	0.88	0.85	0.87	0.80	0.84	0.43
4-Methylguaiacol	G	1.33	1.46	1.63	2.20	2.70	1.44	1.55	1.88	1.95
4-Vinylguaiacol	G	5.00	4.11	4.70	-	-	4.71	4.34	-	-
4-Ethylguaiacol	G	1.23	0.91	1.07	1.21	1.24	1.01	0.97	1.12	0.97
4-Propenylguaiacol / Isoeugenol	G	0.21	0.23	0.30	0.69	0.67	1.61	0.64	0.61	0.28
Vanilin	G	0.66	0.99	0.70	0.60	0.44	0.71	0.58	0.49	0.65
4-Acetylguaiacol	G	0.75	1.52	1.22	0.76	0.93	0.85	1.73	0.78	1.42
Guaiacyl acetone	G	0.44	0.51	0.55	0.46	0.64	0.44	0.40	0.42	0.36
4-Propylguaiacol	G	0.28	0.17	-	0.21	0.44	0.24	0.19	-	-
TOTAL G		21.47	20.55	21.60	16.87	15.93	22.34	20.78	15.23	11.80
Syringol	S	30.25	33.12	34.68	31.36	26.53	33.34	31.44	29.05	17.41
4-Vinylsyringol	S	-	-	-	-	-	-	-	-	-
4-Methylsyringol	S	-	-	-	-	-	-	-	-	-
4-Propylsyringol	S	-	-	-	-	0.62	-	-	-	-
4-Acetylsyringol	S	1.84	1.69	1.70	1.21	1.27	1.65	-	1.27	3.71
Syringaldehyde	S	0.83	1.33	1.45	1.02	0.81	0.89	1.80	1.06	2.28
Syringylacetone	S	-	-	-	-	-	-	-	-	-
4-Propenylsyringol	S	2.14	2.24	2.58	-	3.22	2.39	2.00	2.22	2.23
3,4-Dimethoxyphenol	S	0.64	1.13	1.49	2.09	2.40	1.64	1.61	2.00	1.98
TOTAL S		35.70	39.52	41.90	35.67	34.84	39.90	36.84	35.60	27.60
Lignin S/G ratio	-	1.66	1.92	1.94	2.11	2.19	1.79	1.77	2.34	2.34

For one-step fractionation, the lower the pH, the higher the S/G ratio of the fraction, a result that is in agreement with the expectation of obtaining fractions with lower Mw the more acidic the pH. This behavior was also observed in the sequential fractionation, except between pHs 7.0 and 5.0, where there was a drop in the S/G ratio, a result that was already expected due to the anomalous chemical characteristic previously presented for BLS5.

Once the S/G ratio of 2.92 was obtained for the unfractionated kraft liquor (BL), it is noted once again that fractionation by acid precipitation, as well as by organic solvents, is favorable for applications that require chemical substitutions, since the S/G ratios of all fractions were always lower than the initial material (BL). The type of application itself must take into account other factors than simply the S/G ratio. Higher Mw lignins, such as BL9 and BLS9, are more interesting for the production of dispersants, while more acidic fractions, such as BL3, BLS3 and BL1, may be favorable for the production of adhesives, due to their low molecular weight – always bearing in mind that LS1 is being disregarded due to the derisory yield (TOLEDANO et al., 2010). It is a setback, however, that lower Mw fractions will also be those with higher S/G ratio. So, for adhesives, one must know what wants to prioritize: higher content of phenolic groups or more groups for chemical substitution. If the answer is reactivity, so a smaller S/G ratio must be taken into account.

Catechol-type lignin showed a tendency of increasing as the pH was acidified, except for the BLS1 fraction. Li et al. (2018) cites the importance of catechol as an intermediate in chemical conversions of lignin that occur through biological pathways, resulting in more energetically efficient metabolic processes.

6. CONCLUSION

It was possible to obtain different fractions of lignin both in the fractionation by organic solvents and by acid precipitation. One-step fractionation and sequential fractionation also presented fractions with different behavior, either chemically or in terms of yield, allowing the choice of the best fraction according to the desired commercial application.

All fractions obtained in both fractionation methods showed higher carbon content, higher purity and lower S/G ratio than the corresponding initial materials (KL and BL), characteristics that are very favorable for application in biorefinery.

The fractions soluble in ethanol after sequential fractionation (KLS2), insoluble at pH 5 by the sequential method (BLS5) and insoluble at pH 1 also by the sequential method (BLS1) showed yields below 10%, being therefore less attractive for biorefinery from the economic point of view.

The fractions with the highest carbon content in each fractionation method and, therefore, more suitable for the production of carbon fibers, were the one using acetone by sequential fractionation (KLS4 with 64.7% carbon) and the one insoluble in pH 1 by one-step fractionation (BL1 with 52.2% carbon).

The fractions soluble in ethyl acetate by one-step fractionation (KL1) and insoluble at pH 3 and 1 by the sequential method (BLS3 and BLS1) were the fractions with the highest S/G ratio in each fractionation method, being the most suitable for application in products that require high oxidative properties.

The fractions KL2 (ethanol, one-step), KL3 (methanol, one-step), KL4 (acetone, one-step), BL9 (pH 9, one-step) and BLS5 (pH 5, sequential) have the lowest S/G ratios, being interesting for applications that require chemical substitutions, such as the production of lignosulfonates. For adhesives, BL3 (pH 3, one-step), BLS3 (pH 3, sequential) and BL1 (pH 1, one-step) lignins are favorable if the content of phenolic groups is prioritized over reactivity. On the contrary, the same criterion for lignosulphonates selection must be applied, where fractions with a higher content of lignin G are preferred.

7. RECOMMENDATIONS FOR FUTURE RESEARCH

Determine the molecular weight and polydispersity index (PDI) of lignin fractions using the gel permeation chromatography (GPC) technique;

Produce thermally modified lignin and verify the difference in behavior of fractions with unmodified material;

Test the methodology proposed in this study with different masses of the starting material and verify if there is a significant change in yields;

Apply the fractions produced to obtain bioproducts and compare the performance with commercial reference materials;

Carry out the economic feasibility study of the industrial application of fractionation methods to obtain more homogeneous lignin and later apply in biorefinery.

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