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FRANCISCO PEREIRA MARQUES NETO

CRITICAL EVALUATION OF LIGNIN OBTAINED FROM DIFFERENT LIGNOCELLULOSIC BIOMASSES AND USING DIFFERENT DELIGNIFICATION PROCESSES

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Thesis presented to the Postgraduate Program in Chemistry, Federal University of Ceará, as a partial requirement for obtaining the title of PhD in Chemistry. Concentration area: Chemistry.

Supervisor: Morsyleide de Freitas Rosa
Co-supervisor: Renato Carrhá Leitão

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EXAMINATORS

Dr^a^. Morsyleide de Freitas Rosa

Universidade Federal do Ceará (UFC)

Dr. Diego Lomonaco Vasconcelos de Oliveira

Universidade Federal do Ceará (UFC)

Dr. Renato Carrhá Leitão

Embrapa Agroindústria Tropical (Embrapa)

Dr. Adriano Lincoln Albuquerque Mattos

Embrapa Agroindústria Tropical (Embrapa)

Dr. Francisco de Assis Avelino de Figueiredo Sobrinho

Instituto Federal de Educação, Ciência e Tecnologia do Ceará (IFCE)

Dedicated to my family, my dearest friends, and my beloved wife. Thank you all for the support and love. I love you all!

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The cosmos is within us. We are made of star-stuff.
We are a way for the universe to know itself.

(Carl Sagan)

ABSTRACT

Lignocellulosic biomasses are renewable, abundant, and low-cost resources that are generated from various industrial processes. They are mainly composed of cellulose, hemicellulose, and lignin. Lignin is an aromatic polymer complex that has attracted considerable attention in recent years due to its potential to replace phenols obtained from the petroleum-based industry for application in the most diverse areas. However, its complex structure makes its valorization difficult. The objective of this work was to evaluate the effects of steam explosion in the acetosolv process, to optimize the lignin extraction process by ethanosolv, as well as to provide a critical evaluation of the lignins characteristics from coconut fiber (CF), oil palm mesocarp fiber (OPMF), and sugarcane bagasse (SCB) towards of their potential applications. The chemical, structural, and thermal characteristics of the lignins were determined by klason lignin, 2D-HSQC, FTIR, GPC, TGA/dTG, and DSC. Biomasses were pretreated by steam explosion at 168 °C and reaction time of 10 min. Steam explosion followed by acetosolv increased lignin yield by approximately 15% and 17% in OPMF and SCB, respectively. Furthermore, the steam explosion reduced the reaction time of acetosolv in four-fold while maintaining the same extraction yield only for SCB. Our findings demonstrate that steam explosion is efficient in improving lignin yield and/or decreasing the severity of the extraction process. Furthermore, ethanosolv was optimized and lignin yield was maximized for all biomasses. Ethanol concentration and temperature have great significance in the delignification process. Under the conditions studied, the reaction time did not significantly influence and the shortest reaction time was enough to maximize the lignin yield. Regarding the characteristics of lignins, the processes used were able to extract lignins with high purity and high quality. Therefore, it can be concluded that the sugarcane bagasse lignins, especially the one extracted by ethanosolv, presented the best characteristics in general compared to the other lignins, due to the high extraction yield, high purity, high thermal stability, and higher content of reactive sites for polymerization reactions being the most suitable for technological applications. However, CF and OPMF lignins probably only need purification to be applied as building blocks.

Keywords: agrowaste; steam explosion; organosolv; optimization; characterization.

RESUMO

As biomassas lignocelulósicas são recursos renováveis, abundantes e de baixo custo que são geradas a partir de diversos processos industriais. São compostas principalmente por celulose, hemicelulose e lignina. A lignina é um complexo polímero aromático que tem atraído bastante atenção nos últimos anos pelo potencial em substituição aos fenóis obtidos da indústria petroquímica para aplicação nas mais diversas áreas. No entanto, a sua estrutura complexa dificulta a sua valorização. O objetivo deste trabalho foi avaliar os efeitos da explosão a vapor no processo acetosolv, otimizar o processo de extração de lignina por etanosolv, bem como realizar uma avaliação crítica das características das ligninas de fibra de coco verde (CF), fibra do mesocarpo de dendê (OPMF) e bagaço de cana-de-açúcar (SCB) no sentido das suas potenciais aplicações. As características químicas, estruturais e térmicas das ligninas foram determinadas por lignina klason, 2D-HSQC, FTIR, GPC, TGA/dTG e DSC. As biomassas foram pré-tratadas por explosão a vapor a 168 °C e tempo de reação de 10 min. A explosão a vapor seguida de acetosolv aumentou o rendimento de lignina em aproximadamente 15% e 17% em OPMF e SCB, respectivamente. Além disso, a explosão a vapor diminuiu o tempo de reação do acetosolv em quatro vezes mantendo o mesmo rendimento de extração apenas para SCB. Nossos achados demonstram que a explosão a vapor é eficiente em melhorar o rendimento de ligninas e/ou diminuir a severidade do processo de extração. Além disso, a etanosolv foi otimizada e o rendimento de lignina foi maximizado para todas as biomassas. A concentração de etanol e temperatura possuem grande significância no processo de deslignificação. Nas condições estudadas, o tempo de reação não influenciou significativamente e o menor tempo de reação foi suficiente para maximizar o rendimento de lignina. A respeito das características das ligninas, os processos utilizados foram capazes de extrair ligninas com alta pureza e alta qualidade. Portanto, conclui-se que as ligninas do bagaço de cana-de-açúcar, sobretudo a extraída por etanosolv, apresentaram as melhores características no geral comparadas as demais ligninas, devido ao alto rendimento de extração, alta pureza, alta estabilidade térmica e maior quantidade de sítios reativos para reações de polimerização sendo a mais indicada para aplicações tecnológicas. No entanto, as ligninas de CF e OPMF provavelmente precisam apenas de purificação para serem aplicadas como blocos de construção.

Palavras-chave: resíduo agroindustrial; explosão a vapor; organosolv; otimização; caracterização.

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LIST OF ABBREVIATIONS AND ACRONYMS

2D-HSQC	Two-dimensional heteronuclear single quantum coherence spectroscopy
BL	Black liquor
CCD	Central composite design
CF	Coconut fiber
DMSO-d6	Dimethyl sulfoxide deuterated
DSC	Differential scanning calorimetry
dTG	Derivative thermogravimetric analysis
EtOH	Ethanol
FA	Ferulate
FTIR	Fourier-transform infra-red spectroscopy
G	Guaiacyl
GPC	Del permeation chromatography
H	p-Hydrophenyl
HW	Hot water
HPLC	High performance liquid chromatography
MIBK	Methyl isobutyl ketone
MW	Microwave
NMR	Nuclear magnetic resonance
OFAT	One-factor-at-a-time
OPMF	Oil palm mesocarp fiber
PCA	p-Coumarate
S	Syringyl
S’	Oxidized syringyl
SCB	Sugarcane bagasse
SE	Steam explosion
TGA	Thermogravimetric analysis
THF	Tetrahydrofuran
USDA	United States Department of Agriculture Foreign Agricultural Service

LIST OF SYMBOLS

°C	Degrees Celsius
°C min^{-1}	Degrees Celsius per minute
g	Gram
g mol^{-1}	Gram per mol
h	Hour
kPa	Kilopascal
min	Minute
mL min^{-1}	Milliliter per minute
mM	Millimolar
MPa	Mega Pascal
N_2	Nitrogen gas
O_2	Oxygen gas
psi	Pound per square inch
wt%	Weight percent
µL	Microliter

SUMMARY

1 INTRODUCTION

The replacement of non-renewable resources, especially petroleum-based products, increased the renewable resources such as lignocellulosic biomass. Lignocellulosic biomass, or lignocellulose, are currently partially used as an energy source in industrial ovens. The use of these residues as fuels represents an underutilization, as they are rich in macromolecules with potential industrial interest, i.e., cellulose, hemicellulose, and lignin. Lignin is a macromolecule rich in phenols which can be used in the development of several new technologies and products with high added value (LAURICHESSE; AVÉROUS, 2014; UPTON; KASKO, 2016).

There is growing interested research in possibilities of lignin applications in commercial chemicals, materials, and fuel. The development of value-added lignin-derived co-product can help to make the second generation biorefineries and paper industry more profitable by valorizing their byproduct lignin (BAJWA et al., 2019). Unripe coconut fibers, oil palm mesocarp fibers, and sugarcane bagasse are an important source of lignin due to their high lignin content, availability, underutilization, and low cost.

The obtention of lignin from theses biomasses is estimated in 5.1×10^7 tons per year (MARQUES et al., 2021). Lignin can be used by the chemical industry as partial or total replacement of phenol from petrochemical industry or other high-added value products (LAURICHESSE; AVÉROUS, 2014; UPTON; KASKO, 2016). However, lignocellulosic biomass in general has a worldwide production estimated as approximately 1×10^{13} tons per year with lignin content of 15–40%. It is estimated a potential lignin production of at least 1.5×10^{12} tons per year from lignocellulose (CARVAJAL; GÓMEZ; CARDONA, 2016; ZOGHLAMI; PAËS, 2019). Brazil has an important vegetal biodiversity with potential to be explored in technological application, with the lignin as phenol source in substitution to fossil source.

Lignin is a three-dimensional polymer with complex and heterogeneous aromatic structure. It is found in plant wall cell linked together to cellulose and hemicellulose which provides impermeability, mechanical strength, and control of water transportation. Unfortunately, lignin is considered a residue or a low-added value subproduct, being mostly applied as boiler fuel in the paper pulping industry. Only, a small amount of lignin (2%) is used in commercial applications (CAO et al., 2018). The chemical structure of lignin varies depending on plant source, extraction process, process parameters, which turns it a challenger material (RAGAUSKAS et al., 2014).

Lignin is mostly composed by *p*-hydroxyphenyl (H), guaiacyl (G), and syringyl (S) units linked by C–C and ether linkages. These monomeric units or monolignols distinguish among themselves by the presence or absence of methoxyl groups in the *ortho* position in the aromatic ring. The methoxyl groups are absent in the H unit, G unit has one methoxyl group, and S unit has two methoxyl groups. Additionally, lignin can present more than 20 types of bonds between the monomeric units of lignin, mostly carbon–carbon and ether bonds (PANAMGAMA; PERAMUNE, 2018).

From lignin, it is possible to obtain a variety of new polymeric materials and chemical products with high-added value (LAURICHESSE; AVÉROUS, 2014; UPTON; KASKO, 2016). Therefore, it should be obtained as much information as possible about the lignin structure which it can be used in the best way possible supporting its further application. Lignin extraction methods can also modify its structure. Organosolv is an extraction process known to not generate significant changes in lignin structure. Organosolv lignin has high purity, low molecular weight, and less condensed structures (BROSSE; SANNIGRAHI; RAGAUSKAS, 2009).

In order to improve the delignification, pretreatment is often used. Biomass in general has rigid structure, due to lignin maintains the wall cell compact. This attribute granted by the lignin is called recalcitrance. Recalcitrance makes the lignin extraction a high-energy and chemical-consuming process. Physical and/or chemical pretreatments have been investigated for the improvement of energy efficiency, for decrease chemical use, and/or recalcitrance.

Steam explosion is the most widely employed physico-chemical pretreatment method for any lignocellulosic biomass because of its potential for disrupting crystallinity of cellulose, delignification, and easy hydrolysis of the hemicelluloses (SINGH; SUHAG; DHAKA, 2015). During steam explosion, an almost simultaneous depolymerization and repolymerization reactions takes place in the lignin due to the acidity created during the treatment (LI; HENRIKSSON; GELLERSTEDT, 2007). Carbonium ions are the common intermediate for both reactions routes which are originated from benzyl alcohol structures in the lignin aliphatic chain. The intermediate may break the ether bonds, leading to lignin depolymerization or may react with an electron-rich carbon in an adjacent aromatic ring, leading to a stable carbon–carbon linkages resulting in repolymerization. Only under extremely mild conditions of steam treatment can this reaction be suppressed (LI; HENRIKSSON; GELLERSTEDT, 2007).

Steam explosion increases the specific surface area of the biomass that occurs due acid-catalyzed hydrolysis followed by explosive decompression which takes place in the reactor. The increase of surface area promotes better contact of chemicals, i.e., solvent, catalyst, and water, in the lignocellulose, leading to improvement of lignin extraction. The effect of delignification process variables (temperature, reaction time, catalyst, solvent used, among others) on the lignin structure is not known for sure for all biomasses.

The main objectives of this thesis were to: (i) evaluate the effects of steam explosion on severity and lignin yield of the acetosolv delignification as well as the lignin characteristics; and (ii) optimize the ethanosolv delignification with the evaluation of obtained lignins. In order to achieve these goals, the thesis has been divided into three main chapters. Firstly, the chapter I, “State-of-the-art”, provides a short review about the lignocellulosic biomasses: coconut fiber, oil palm mesocarp fiber, and sugarcane bagasse; the characteristics of the lignin; the delignification process; and the optimization methods. Therefore, the chapter II, “Steam explosion pretreatment improves acetic acid organosolv delignification of oil palm mesocarp fibers and sugarcane bagasse”, reports the evaluation of the effect of low severity steam explosion followed by acetosolv in the lignin yield as well as the influence of the steam explosion in the subsequent process. Furthermore, the characteristics of exploded lignins were evaluated and compared to the raw ones by chemical, structural, and thermal characterization in order to understand their properties and potential applications.

However, acetosolv is an approach that applies more toxic and expensive chemical. Alternatively, ethanosolv is a very popular organosolv method, due to this process typically yields clean lignins with excellent retention of the high β-aryl ether content, high-purity, high-quality with low content of impurities besides to employ a less toxic and cheaper solvent compared to acetosolv. In addition, an optimization approach could improve the understanding of the lignin extraction behavior with the changes in the process parameters. Accordingly, the chapter III, “Optimization by response surface methodology of ethanosolv lignin extraction from coconut fiber, oil palm mesocarp fiber, and sugarcane bagasse”, reports the evaluation of the process variables of ethanosolv in the lignin yield and the effects of optimized ethanosolv in the lignin structure. Moreover, the characteristics of obtained lignins were evaluated by chemical, structural, and thermal characterization in order to provide insights in their further application.

Therefore, the aim of this work was the extraction of high-yield and high-quality lignins from Brazilian biomasses through three eco-friendly processes in order to contribute in the valorization of the agro-industrial chains. A critical evaluation of the potential application of those lignins was performed through a complete characterization (chemical, structural, and thermal) in order to provide insights of their application as alternative to petroleum-based compounds such as phenol.

2 STATE-OF-THE-ART

2.1 Lignocellulosic biomasses

Lignocellulosic biomasses or lignocellulose are the main sources of renewable organic matter obtained as waste from the forest, agriculture, and industry. They are mainly constituted cell wall polysaccharides, such as cellulose and hemicelluloses, and lignin, in addition to moisture, extractives, and inorganic compounds in low amounts. Particularly, lignin is found in the cell wall in quantities that vary widely depending on the type of plant, the part of the plant, and its age (SANCHEZ; SIERRA; J., 2011). Lignocellulosic materials have a very complex structure, in which cellulose and hemicelluloses are densely packed and enveloped by lignin, conferring recalcitrance to the biomass, making the vegetal cell wall mechanically and microbiologically resistant (PIN et al., 2019).

Since lignocellulosic biomasses are not digestible by humans, their use as a low-cost and abundant chemical raw material does not compete with food production, thus lignin, cellulose, and hemicellulose constitute a promising alternative to fossil petrochemical resources (GILLET et al., 2017). Lignocellulosic biomasses and waste products highlight as an interesting source of phenols building blocks. Biomass has a worldwide production estimated as approximately 1×10^{13} tons per year and the lignin content ranging from 15 to 40%. Therefore, it is estimated a potential lignin production of at least 1.5×10^{12} tons per year (CARVAJAL; GÓMEZ; CARDONA, 2016; ZOGHLAMI; PAËS, 2019).

Coconut fibers, oil palm mesocarp fibers, and sugarcane bagasse are three biomasses with great potential for application in lignin extraction, with lignin content ranging from 25% to 35%. These biomasses play a major role worldwide, mostly in Brazil, Malaysia, India, China, Indonesia, and the Philippines due to their abundance, underutilization, and being a renewable source of biopolymers of industrial interest, such as cellulose nanocrystals and lignin.

2.1.1 Coconut fiber

Coconut is an oilseed from the *Cocos nucifera* plant, known worldwide. Usually, it is processed in the final stage of maturation to produce oil and other products. Brazil is the fifth-largest producer of coconut in the world, with a production of around 2.33 million tons per year and a harvested area of 186.950 hectares (FAOSTAT, 2021). The largest coconut producers are

Indonesia, the Philippines, India, and Sri Lanka with a total of around 49.0 million tonnes of fruit in 2019 (FAOSTAT, 2021).

Unripe coconut is the immature fruit produced for the consumption of coconut water, which generates a large amount of solid waste such as unripe coconut fibers (FREIRE et al., 2017). Unripe coconut water is usually consumed directly from the fruit in coastal cities or bottled for sale. Adoption of healthy dietary habits by the Brazilian society has increased the consumption of coconut water (100-350 million liters/year), to become an environmental problem throughout the country (CABRAL et al., 2016).

Both processes generate large amounts of waste (**Figure 1**). In natural conditions, unripe coconut can take more than 8 years to decompose leading to environmental problems, reducing the life of sanitary landfills or causing pollution if not properly disposed (CABRAL et al., 2016; CARRIJO; LIZ; MAKISHIMA, 2002; NASCIMENTO et al., 2016). Unripe coconut fibers (CF) correspond to approximately 80% of fruit weight, however, the high humidity does not favor their application in processes usually used for ripe coconut as boiler fuel.

Figure 1 – Coconut waste disposed after extraction of coconut water.

Source: Personal archive of R. C. Leitão.

Another challenging aspect of coconut is that the CF and coconut fruits can float in ocean water without rotting for more than a month. CF is more resistant to attack by fungi and insects which is linked to higher amount of phenolic compounds such as tannin and lignin with lignin content around 35%; since coconut fiber contains more lignin as compared to other natural fibers, it is more durable (HASAN et al., 2021; NARCISO et al., 2021).

On the other hand, several research has been investigating the use of CF technological applications such as the production of cellulose nanocrystals and lignin (NASCIMENTO et al., 2016; ROSA et al., 2010), fiberboard production (ARAÚJO JÚNIOR et al., 2018; NARCISO et al., 2021), composites (HASAN et al., 2021; VALÁŠEK et al., 2018), and bioethanol (CABRAL et al., 2016). In addition, due to its lignin content around 35%, CF has the great potential to lignin extraction with further lignin application.

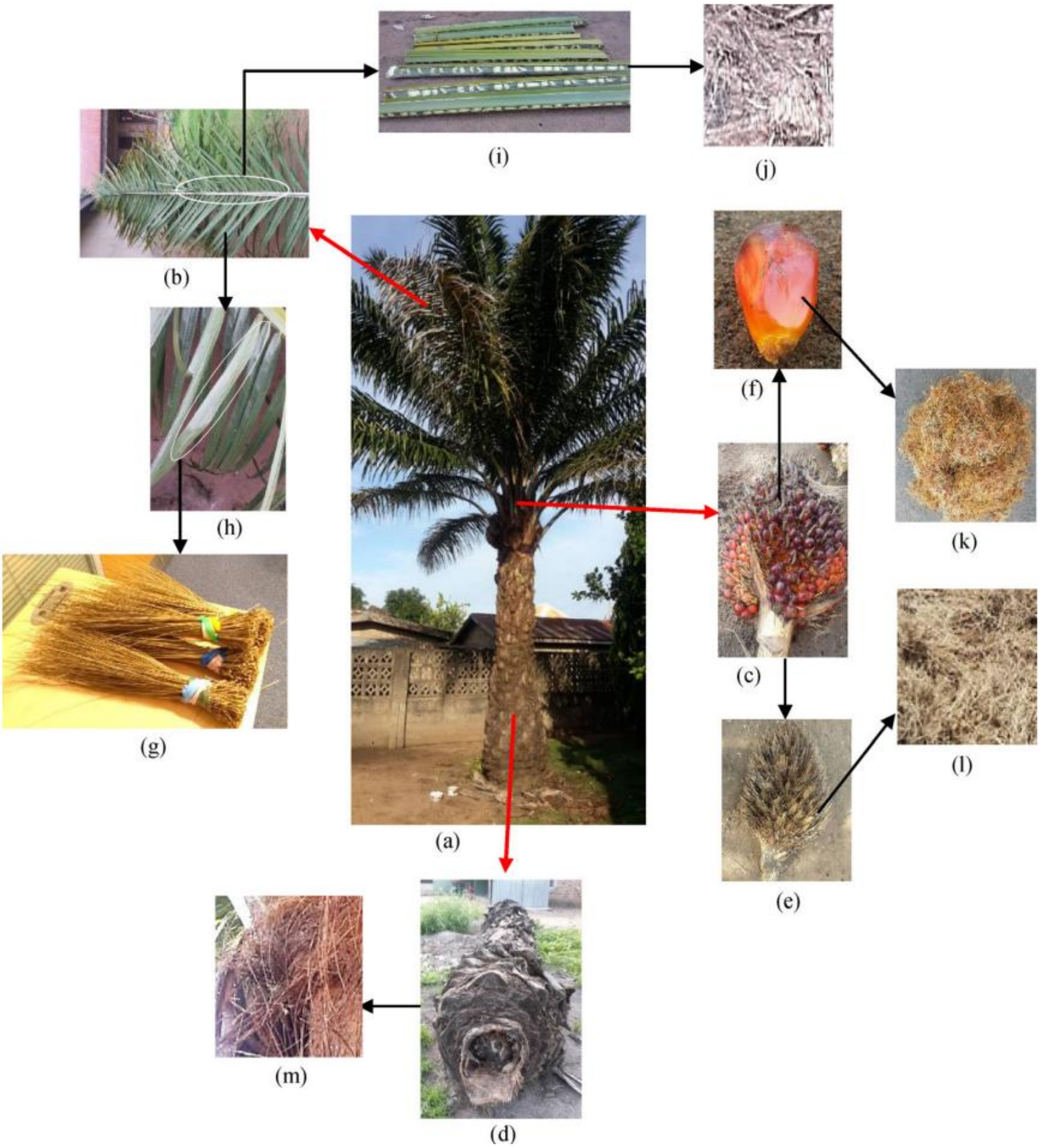
2.1.2 Oil palm mesocarp fiber

Oil palm (**Figure 2**) is a plant of African origin used in the palm oil production chain around the world. Palm oil (*Elaeis guineenses*) is obtained by pressing the oil palm fruit, and is considered one of the main world commodities. Among vegetable oils, palm oil is the most produced, imported, exported, and used for domestic consumption than any other oil in the world (USDA, 2021). It is the commercially cheapest oil, followed by corn, soybean, and cotton oil. It is also the most used as raw material for different areas in the oleochemical, pharmaceutical, soap, and cosmetic industries, however, its main use is in human food, responsible for absorbing 80% of world production.

Palm oil is one of the major ingredients in up to 50% of all daily-used products, everything from cosmetics, such as lipsticks, shampoo, and deodorants, to food ingredients, like margarine, chocolate, pastries, and baby food, including instant noodles, mentioned as either hydrogenated vegetable fats or plant fats (KANIAPAN et al., 2021). The industries of margarine, solid fats, cooking oil, mayonnaise, bread, milk, artificial chocolate, and fried foods are the main consumers of palm oil.

In 2019, there were a production of oil palm fruit around 410.7 million tons in approximately 28.3 million hectares (FAOSTAT, 2021). It is estimated that in the 2021/22 harvest 76.4 million tons of palm oil will be produced worldwide (USDA, 2021). Brazil produces around 275.000 tons of palm oil per year, while Indonesia, one of the largest producers, produces around 40 million tons. The national demand is around 500 thousand tons of oil, requiring the product to be imported. Indonesia and Malaysia are the largest producers of palm oil, which produce around 85% of global production. The palm oil industry generates an equally large amounts of solid waste, such as empty bunches, mesocarp fiber, and broken endocarps. Oil palm mesocarp fiber (OPMF) is a waste generated from pressing palm oil for oil extraction.

Figure 2 – Different types of oil palm fibers (OPF): (a) oil palm tree; (b) leaf; (c) fruit; (d) trunk; (e) empty fruit bunch; (f) dissected oil palm fruit; (g) oil palm broom fibers (OPBF); (h) oil palm leaflet; (i) oil palm frond; (j) oil palm frond fibers (OPFF); (k) oil palm mesocarp fibers (OPMF); (l) empty fruit bunch fibers (EFBF); (m) oil palm trunk fibers (OPTF).



Source: (MOMOH; OSOFERO, 2020).

Often, oil palm mesocarp fiber consists of fruit fibers, kernel, and broken shells, which are mostly used as fuel in ovens for the production of steam and heated water. The OPMF can be used in the production of composites (CAMPOS et al., 2018; SHINOJ et al., 2011; THEN et al., 2013), in composting (VAKILI et al., 2015), in the soil supplementation with the ash produced by its burning (ANYAOHA et al., 2018), extraction of cellulose and cellulose nanocrystals (CHIENG et al., 2017; PEREIRA et al., 2020; SOUZA et al., 2016), and glucose production (AL-MURAISY et al., 2017).

For every 1 ton of palm oil produced, approximately 1.74 tons of OPMF are produced (SINGH et al., 2011). Considering that the OPMF consists of approximately 35% of lignin, it is estimated that Brazil has the potential to produce around 167.500 tons of lignin from this residue per year. Therefore, the use of OPMF for the extraction of lignin in order to apply it in technologies that add value to the residue.

2.1.3 Sugarcane bagasse

Sugarcane bagasse (SCB, **Figure 3**) is a residue produced by pressing and milling sugarcane in which it comes from the sugar and ethanol production chain, that is low-cost and high available. Sugarcane production generates a huge amount of bagasse and straw, which are mainly burned in biomass boilers (especially bagasse) to maintain the plant's energy self-sufficiency and sometimes sell surplus energy as an alternative recipe (PIN et al., 2019). This surplus corresponds to 7% of the country's energy matrix (UNICA, 2018). However, even producing excess energy, only 50% of the bagasse is used for this purpose (CARDONA; QUINTERO; PAZ, 2010), and the remaining waste leads to environmental and storage problems (COSTA et al., 2014).

Brazil is the world's largest producer of sugarcane. It is estimated that the production will be 628.1 million tons of sugarcane produced in the 2021/22 harvest, 4% lower than 2020/21 harvest (CONAB, 2021). Considering that approximately 30% of sugarcane is converted into SCB containing approximately 25% of lignin, it is possible to estimate the generation of 47.1 million tons of lignin after the harvest (RAMOS, NACHILUK, 2017) (LEE; MARIATTI, 2008). SCB is made up of approximately 50% cellulose, 25% lignin and 25% hemicellulose, which makes it very attractive for biotechnological applications (PARAMESWARAN, 2009).

Figure 3 – Sugarcane bagasse.

Source: ASSESSORIA DE COMUNICAÇÃO DA ABIQUIM, 2013.

In addition to the energy production in the processing plant itself, SCB can also be used more efficiently, mainly in the production of second-generation ethanol (CARDONA; QUINTERO; PAZ, 2010; SARKAR et al., 2012). Studies showed other potential applications such as methane production (COSTA et al., 2014), production of phenolic resins (MOUBARIK et al., 2013; PINHEIRO et al., 2017), reinforcement agent in composites, and heavy metals adsorbent (KHOO; CHOW; ISMAIL, 2018; LOH et al., 2013).

2.2 Lignin

Lignin is an amorphous tridimensional polymer that is highly complex and heterogeneous. It is one of three major components in the plants and second in amount after cellulose. Lignin is the most abundant renewable aromatic resource with the potential to be the main resource of aromatic structures in a bio-based economy (GILLET et al., 2017; WANG et al., 2017). In plants, lignin provides a rigid network in the cell wall in combination with cellulose and hemicellulose which grants permeability control, microbiological, mechanical strength, and thus contributes to biomass recalcitrance.

Lignin is formed by dehydrogenative polymerization between three alcohols: *p*-coumaryl alcohol (*p*-hydroxyphenyl unit), coniferyl alcohol (guaiacyl unit) and sinapyl alcohol (syringyl lignin). These building blocks, also called monolignols, are linked together mostly by carbon-carbon and ether bonds forming a tridimensional structure. They differ in the amount of methoxy groups on the aromatic ring, which are usually denominated as H (*p*-hydroxyphenyl), G (guaiacyl), and S (syringyl) units.

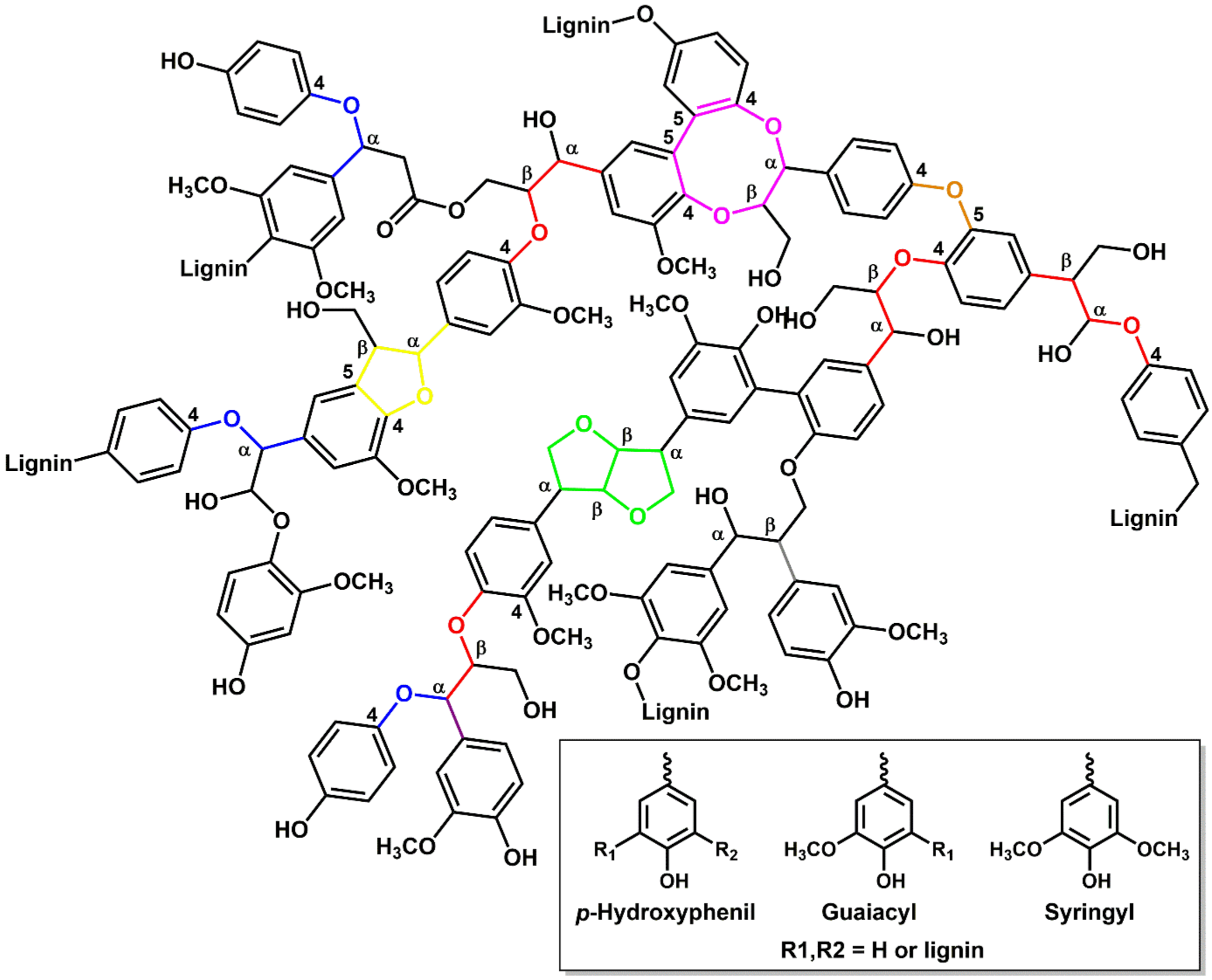
The monomeric proportion of lignin structure is strongly dependent of the plant species. Softwood lignin, such as pine and spruce, is almost formed exclusively by G units, with low content of S units. Hardwood lignin, such as poplar and eucalyptus, contains both G and S units. Herbaceous biomass produced lignin composed of all three monolignols, although the H-content is usually low (< 5%) (SCHUTYSER et al., 2018). Additionally, lignins can also present substantial amounts of other building blocks such as hydroxycinnamates (*p*-coumarate, ferulate, *p*-hydroxybenzoate, tricin, acetate, and other products from incomplete monolignol biosynthesis.

There are twenty types of C–C and C–O bonds in lignin structure, including $–OCH_3$, –COOH and –C=O, and several interunit bonds such as α–O–4, β–O–4, 4–O–5, β–β, β–1, β–5 e 5–5 (PANAMGAMA; PERAMUNE, 2018) (**Figure 4**). According the literature, the seven last bonds are the most common in lignin, however there are other bond types in minor amounts: β–6, α–β, α–O–γ, γ–O–γ, 1–O–4, 1–5 and 6–5 (PONNUSAMY et al., 2019). The β-O-4 linkage represents the most dominant linkage of all three (softwood, hardwood, and grasses) types of sources; however, their comparative content follows the order grasses > hardwood > softwood (EKIELSKI; MISHRA, 2021).

The whole structure of native lignin in biomass is not completely known, due the variation in lignin structure depending on the type of the plant and the modification that occurs during the extraction process. Nevertheless, it is known that C–O–C, α –O–4, and β–O–4 bonds are predominant. The **Table 1** shows the monolignol content and linkage proportions relate to the differences among lignin source from softwood, hardwood, and grass.

Only 2% of 1.5–1.8 billion tons of industrial lignin produced annually are used in commercial application, with the lignosulfonate being mainly used for producing specialty chemicals as an additive in building materials, dispersants, adhesives, surfactants and other value-added products (BAJWA et al., 2019; CAO et al., 2018). Most of the industrially produced lignin is used as fuel in boilers. However, several studies have been done in recent years to use lignin as a resource to replace phenols from the petrochemical industry (PONNUSAMY et al., 2019; RAGAUSKAS et al., 2014).

Figure 4 – General structure of lignin with monolignol and several types of substructures.



Note: blue: α –O–4; red: β–O–4; green: β– β; lilac: dibenzodioxocina (α –O–4, β–O–4, 5–5); yellow: β–5; gray: β–1.

Source: The author.

There is growing interested research in possibilities of lignin applications in commercial chemicals, materials, and fuel. The development of value-added lignin-derived co-product can help to make the second generation biorefineries and paper industry more profitable by valorizing their byproduct lignin (BAJWA et al., 2019). New biobased materials from lignin are highly dependent on its structure properties and purity. In order to elucidate the lignin structure and properties, several studies have been investigating the types of biomasses and process which lead to a suitable lignin for industrial application.

Despite extensive investigation, the complex and irregular structure of lignin is not completely understood (CAPANEMA; BALAKSHIN; KADLA, 2004). The most common methods of structural characterization are nuclear magnetic resonance spectroscopy (NMR), Fourier-transform infra-red spectroscopy (FTIR), and gel permeation chromatography (GPC).

Thermal features are usually obtained from thermogravimetry analysis (TGA), derivative thermogravimetry analysis (dTG), and differential scanning calorimetry (DSC). Klason lignin can provide the purity of lignin.

Table 1 – Monolignol content and linkage proportions in lignin molecule from softwood, hardwood, and grass.

			Percentage of total amounts (%)		
			Softwood	**Hardwood**	**Grass**
Monolignols	H unit	*p*-coumaryl alcohol	<5	0–8	5–33
	G unit	coniferyl alcohol	>95	25–50	33–80
	S unit	sinapyl alcohol	0	46–75	20–54
Linkages	C–O–C	β–O–4	43–50	50–65	74–84
		α–O–4	5–7	<1	n. d.
		4–O–5[a]	4	6–7	n. d.
	C–C	5–5	5–7	<1	n. d.
		β–β	2–6	3–12	1–7
		β–5	9–12	3–11	5–11
		β–1	1–9	1–7	n. d.
	Others		16	7–8	n. d.

Note: [a] Only present in the dibenzodioxocin moieties (5–5, α–O–4, β–O–4).

Source: (LIU et al., 2020).

Regarding structural characteristics, NMR spectroscopy has been shown to be a reliable and comprehensive method in the domain of wood chemistry which provides more precise and comprehensive information on qualitative and quantitative assays for the frequencies of linkages and the composition of H/G/S units in the lignin analysis (LU et al., 2017; WEN et al., 2013). Functional groups, H/G/S units, and the amount and the types of linkages can be qualitatively and quantitatively determined by NMR spectroscopy.

Heteronuclear Single-Quantum Coherence (HSQC) experiment, have taken over from the traditional 1D ^{1}H and ^{13}C experiments that suffered from insufficient resolution to distinguish subtle structural details, and are now widely employed for the investigation of lignin composition and structure (RINALDI et al., 2016). HSQC spectra attracted significant attention due to its versatility in indicating structural elucidation and transformations in lignin structure. 2D-HSQC correlates the ^{13}C–^{1}H signals in cross-peaks in which carbons are directly correlated with their attached protons, separating each component of lignin structure in the form "contour".

This technique is able to correlate a proton to a carbon that is two or three bonds away. It is a powerful experiment in that the connectivity of structural units can be identified (STARK; YELLE; AGARWAL, 2016). Despite the obvious value of the technique for lignin characterization, the information provided by HSQC should not be over-interpreted. The most important difficulty of HSQC is the limitation in perform quantitative analysis. Semi-quantitative determination of integral ratios is, however, possible when the ^{13}C– ^{1}H pairs are located in similar chemical environments, e.g., Cα-Hα signals for lignin sidechains or C_2–H_2/C_6–H_6 aromatic signals, because 1 JCH assumes similar values under this condition (RINALDI et al., 2016). Furthermore, HSQC characterization allows important information about the variable effects in the extraction process and the applied conditions on the lignin structure. Therefore, the elucidation of lignin structure also provides possibilities to lignin application and to perform chemical modifications.

2.2.1 Lignin as resin building block

Lignin is seen as a definitive alternative to replace petroleum-based compounds such as phenol. One of most popular application is in polymerization reaction in the aromatic ring. Phenolic resins mainly belong to the class of thermosetting resins, such as epoxies, bismaleimides, polyimines, cyanate esters, and polybenzoxazines.

Polymerization reactions during the synthesis of phenol-formaldehyde (PF) resins take place through electrophilic substitution of formaldehyde at a free position of the aromatic ring. In lignin, H- and G-type units have respectively two and one free C5 position (ortho to the phenolic hydroxyl) in the ring, susceptible of reacting with formaldehyde. While in S-type units both C3 and C5 positions are linked to a methoxy group, resulting in low reactivity with formaldehyde.

According to FROLLINI et al. (2013), lignin extracted from non-wood plants, such as CF, OPMF, and SCB, has more active centers towards formaldehyde than lignin extracted from wood due to the greater proportion of *p*-hydroxyphenyl units in aromatic rings. Electrophilic attacks can easily occur on the free ortho positions of these rings, which increases their reactivity. From this point of view, lignins with H and G groups as the principal structural units must be *a priori* more suitable for PF formulations (TEJADO et al., 2007).

MOUBARIK et al. (2013) successfully obtained plywood panels using soda sugarcane bagasse lignin with molecular weight similar to this study. As a proof of concept, bagasse lignin could be used to replace 30% of the PF resins used to bond plywood panels, without adversely affecting bond properties with lower formaldehyde emission levels compared to only phenol-formaldehyde ones (MOUBARIK et al., 2013). In order to improve reactivity, lignin phenolation is often applied. ZHAO et al. (2016) study the substitution of phenol for phenolated lignin. They were able to substitute in a range of 10–70% of phenol content in LPF. However, the main purpose to use lignin as substitute of phenol is apply a renewable source of phenolic compound rather a petroleum-based chemical. In this regard, lignin phenolation does not make much sense.

Additionally, the increase the reactivity of technical lignins toward formaldehyde can be done with biological pretreatment, ultrafiltration, demethylation, hydroxyalkylation, and depolymerization (GHAFFAR; FAN, 2014; ZULUAGA et al., 2018). The use of low molecular weight lignins as partial or total phenol substitute in phenol-formaldehyde resins is recommended because of their high reactivity in comparison with lignins with high molecular weight (TOLEDANO et al., 2010).

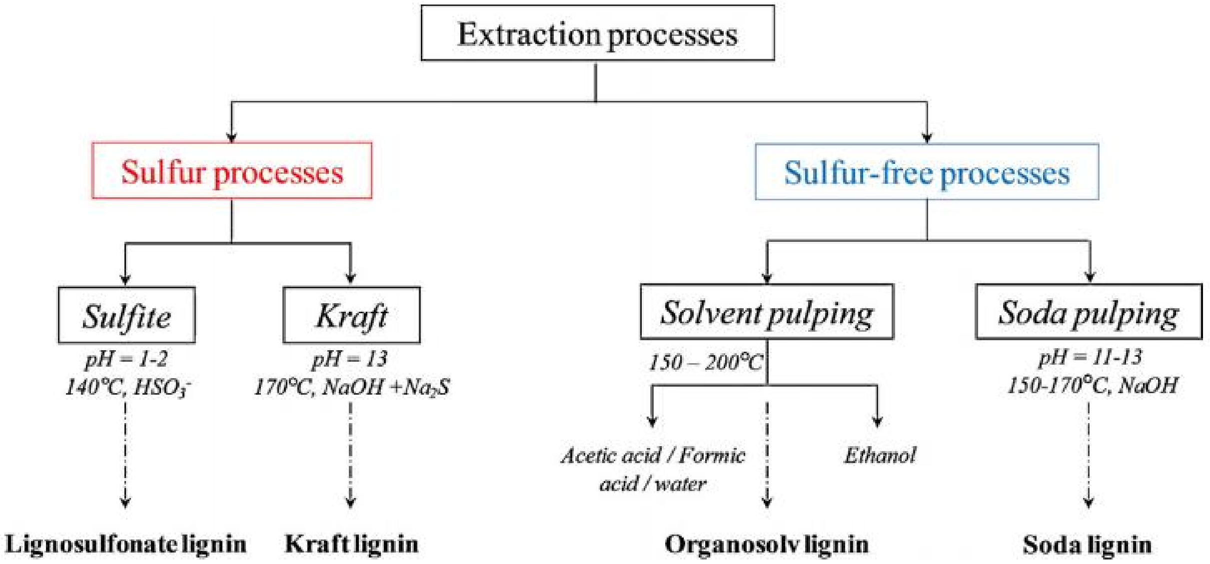
Benzoxazines are a type of phenolic resin that raised interest in the recent years due to their unique properties as low water absorption, low flammability (high char yield), high stiffness, and excellent dimensional stability which could be used as matrix for composites in aerospace applications. Benzoxazines are synthesized using phenol, formaldehyde and amine (aliphatic or aromatic) by employing solution or solventless methods The difference between benzoxazines and traditional phenolic resins is the connections between the phenolic moieties. Traditional phenolics are connected through methylene bridges, while benzoxazines are connected first through the formation of a cyclic structure from the phenolic hydroxyl to the ortho position (FROLLINI; SILVA; RAMIRES, 2013). Sulfur lignins from wood source usually have high contents of syringyl units and low concentrations of *p*-hydroxyphenyl units which hinder conversion into high density of benzoxazines and thus prohibit an extended polybenzoxazine formation (ABARRO et al., 2016). However, non-wood lignin has a better content of *p*-hydroxyphenyl units compare to wood lignin which could improve its application in the polybenzoxazine synthesis.

ABARRO et al. (2016) study the phenolation of lignin in synthesis of benzoxazines. They showed that *p*-hydroxyphenyl and guaiacyl units were successfully converted to benzoxazine units. However, the lignin was phenolated which would make the replacement of phenol unfeasible. SILVA et al. (2019) successfully obtained polybenzoxazine resin from SCB lignin applying only solvent fractionation which makes SCB lignin a great candidate for this purpose.

2.3 Delignification process

Delignification is a crucial process in the pulp and paper industry in consists in the deconstruction of lignocellulose structure by lignin breakdown and hemicellulose solubilization, aiming the release of cellulosic pulp. Industrial lignin is obtained as a subproduct of pulping process. Pulping process breaks the ester and ether linkages in the lignin structure, resulting in also called technical lignins, which they have substantial differences in structure compared to native lignin. There are two main types of delignification process (**Figure 5**): sulfur process (Kraft and sulfite) and sulfur-free process (soda and organosolv). **Figure 6** shows the main differences among the technical lignins.

Figure 5 – Common pulping process and the resulting technical lignin.



Source: (LAURICHESSE; AVÉROUS, 2014).

The most used methods in pulping are the sulfur processes. However, these methods use chemicals with a hazardous environmental impact. Alternatively, the organosolv process has gained more strength due to its use of recoverable and reusable organic solvents decreasing the process impact (AVELINO et al., 2019; CHOTIROTSUKON et al., 2021). In addition, organosolv can produce high-quality and high-purity lignin that can be used in the synthesis of high-added value products. Essentially, the technical lignins depends mostly from the lignocellulose source and the pulping process.

2.3.1 Sulfur process

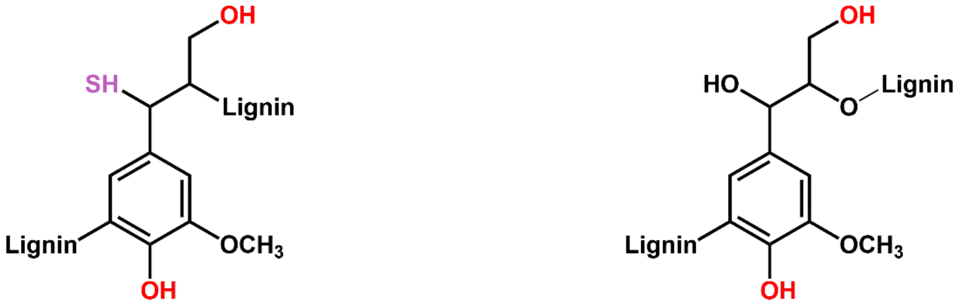
Kraft and sulfite process are the two main industrially available pulping process. These processes aim to the separation of pure cellulose pulp from the lignin which produces Kraft lignin and lignosulfonate, respectively. Kraft pulping is a full chemical pulping method using sodium hydroxide and sodium sulfide, with other sodium salts, such as sodium carbonate and sodium thiosulfate as minor components, at pH above 12 (known as kraft liquor), at 160–180 °C, corresponding to about 800 kPa (120 psi) steam pressure, for 0.5–3h to dissolve much of the lignin of wood fibers (BAJPAI, 2018; WOOL, 2005).

Kraft pulping disrupts the lignocellulose by the breakdown of relatively weak ether bonds, α- and β-aryl bonds, in the lignin structure during cooking. The main products of kraft pulping are cellulosic pulp and kraft lignin. This rupture increases the hydroxyl groups in lignin. Kraft lignin is formed by high amount of condensed structures, low sulfur content (1–2%), and a high level of phenolic hydroxyl groups with high molecular weight ranging 1000–3000 g mol^{-1} (LAURICHESSE; AVÉROUS, 2014).

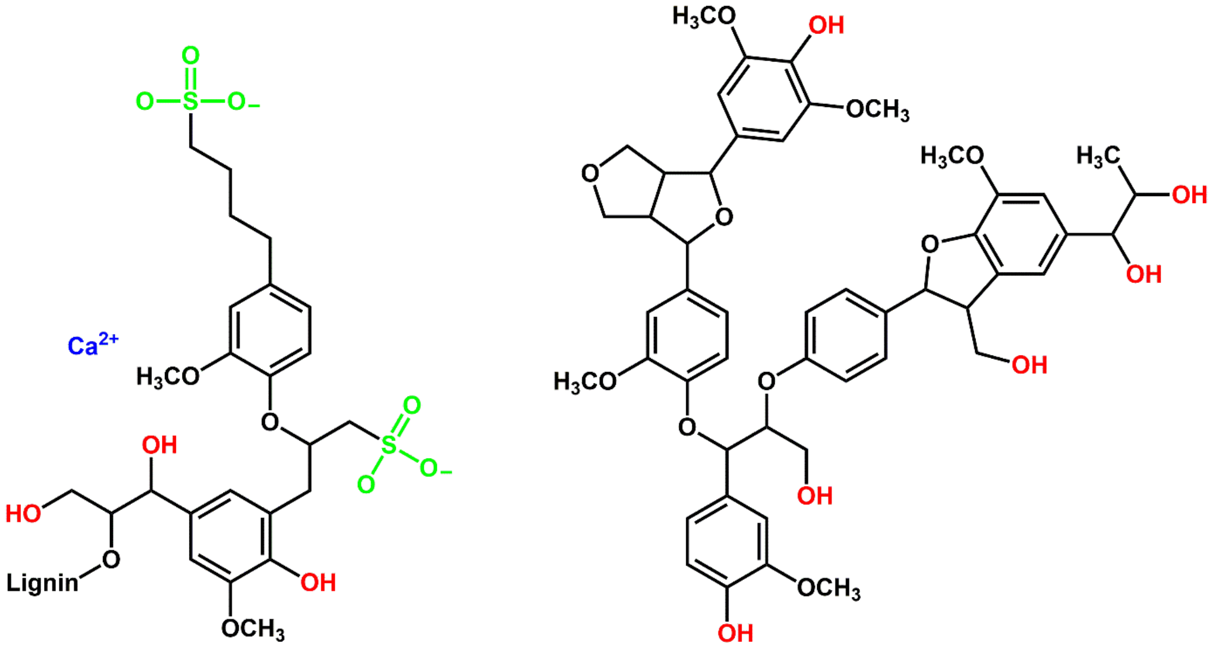
On the other hand, sulfite process is usually conducted under acid or neutral conditions, sulfur dioxide and/or bisulfite ions react with lignin to produce water-soluble sulfonated lignins that are degraded by acid hydrolysis reactions (HINTZ, 2001). In water, the pulping conditions transforms the sulfur dioxide in sulfurous acid (H_2SO_3), leading the degradation eventually sulfonation of the lignin by replacing a hydroxyl group with a sulfonate group in the aliphatic side chain. This reaction allows the lignin solubilization and then the separation from the cellulose in non-precipitated form (NIAOUNAKIS, 2015).

Interestingly, the most used pulping process is kraft process which is gradually replacing the sulfite process, however lignosulfonate from the sulfite process remains the largest commercial source of lignin, with a capacity 1.4 million tons and annual global production estimated at 1.1 million tons (MILLER et al., 2016).

Figure 6 – Main differences among the technical lignins.



Kraft lignin **Soda lignin**



Calcium lignosulfonate **Organosolv lignin**

Source: The author.

Sulfite pulping is the second most important chemical pulping process, but its market share has decreased drastically (5%) with the rise of the more versatile and efficient kraft process (SCHUTYSER et al., 2018). The lignosulfonates market is consolidated, and its primary applications are surfactants, bonding agents for pelletization, dispersants in ceramics and concrete admixtures (DESSBESELL et al., 2020). Borregaard is the main player in lignosulfonate market leading with 40% of the market (**Table 2**).

Lignosulfonates are typically highly degraded and condensed by the formation of new C–C linkages and decrease of β-O-4 content, with a higher sulfur content (4–8 wt%) compared to kraft lignin. Due to their unique properties, lignosulfonates have a wide range of uses, such as animal feed, pesticides, surfactants, additives in oil drilling, stabilizers in colloidal suspensions, and as plasticizers in concrete admixtures (ARO; FATEHI, 2017). Kraft lignin also has a wide application field as additives, biofuel, BTX, activated carbon, phenolic resins, carbon fibres, phenol (DESSBESELL et al., 2020).

Table 2 – Lignin Market and the main companies.

Company	**Capacity (10^3 tons)**	**Market share (%)**
Borregaard	600	40
Domsjö Fabriker	120	8
Nippon Paper	100	8
Weili Gourp	90	7
Wuhan East China Chem.	80	6
Tembec	60	5
Shenyang Zingzhenghe Chem.	50	4
Ingevity	40	3
Suzano	20	2
Kondopoga	160	11
Others	80	6
Total	1400	100

Source: (MILLER et al., 2016).

However, sulfur lignins are it is more difficult to be applied in higher value-added applications mostly due to the presence of sulfur, higher molecular weight, lower purity, greater presence of condensed structures, which hinder the reactivity of these lignins. Alternatively, sulfur-free lignins, such as soda and organosolv lignin, have less of those involved setbacks.

2.3.2 Sulfur-free process

Two methods are used as sulfur-free process for lignin extraction: soda process and organosolv. Soda process uses alkali, with or without anthraquinone, in order to solubilize the lignin. This pulping process involves heating the biomass to 140–170 °C under pressure in the presence of 13–16 wt% of alkali usually sodium hydroxide. Soda pulping process generates the soda lignin, which the method is mainly applied for non-wood material such as bagasse, hemp, straws and, to a certain extent, for hardwoods (DOHERTY; MOUSAVIOUN; FELLOWS, 2011).

Non-woody biomass typically has a lower lignin content, a more open structure, and a larger portion of alkali-labile ester linkages (SCHUTYSER et al., 2018). Unlikely kraft process, soda pulping does not implement sulfide salts, only alkali. However, soda process is less efficient than kraft due to no presence of a strong nucleophile compound. Soda lignin has found application in areas such as the production of phenolic resins, animal nutrition, and dispersants (VISHTAL; KRASLAWSKI, 2011).

Organosolv is an emerging which is attractive of the biorefinery point-of-view, due to the possibility of recover all three major biomass components (**Figure 7**). Organosolv is a process that aims to solubilize lignin using aqueous organic solvents under specific temperature and pressure conditions, with or without the use of a catalyst. Various solvents can be applied, including alcohols (methanol, ethanol, butanol), polyols (ethylene glycol, glycerol), cyclic ethers (THF, dioxane), organic acids (formic acid, acetic acid), and ketones (acetone, MIBK) are generally used in the process. An interesting choice is low boiling alcohols, such as ethanol, because their ease of recovery and low cost.

Typical organosolv conditions for woody biomass are temperatures about 160–190 °C, pretreatment time of 30–60 min, and ethanol concentration of 40–60% (ZHU; PAN, 2010). Depending on the biomass and catalyst used, the process can take place at temperatures above 200 °C (KUMAR; SHARMA, 2017). Commercial success of the organosolv for pulp and paper industries or fuel industry is limited. The increased interest in lignin as a resource for value added chemicals currently makes organosolv more focused on lignin than on pulp or fuel (MILLER et al., 2016).

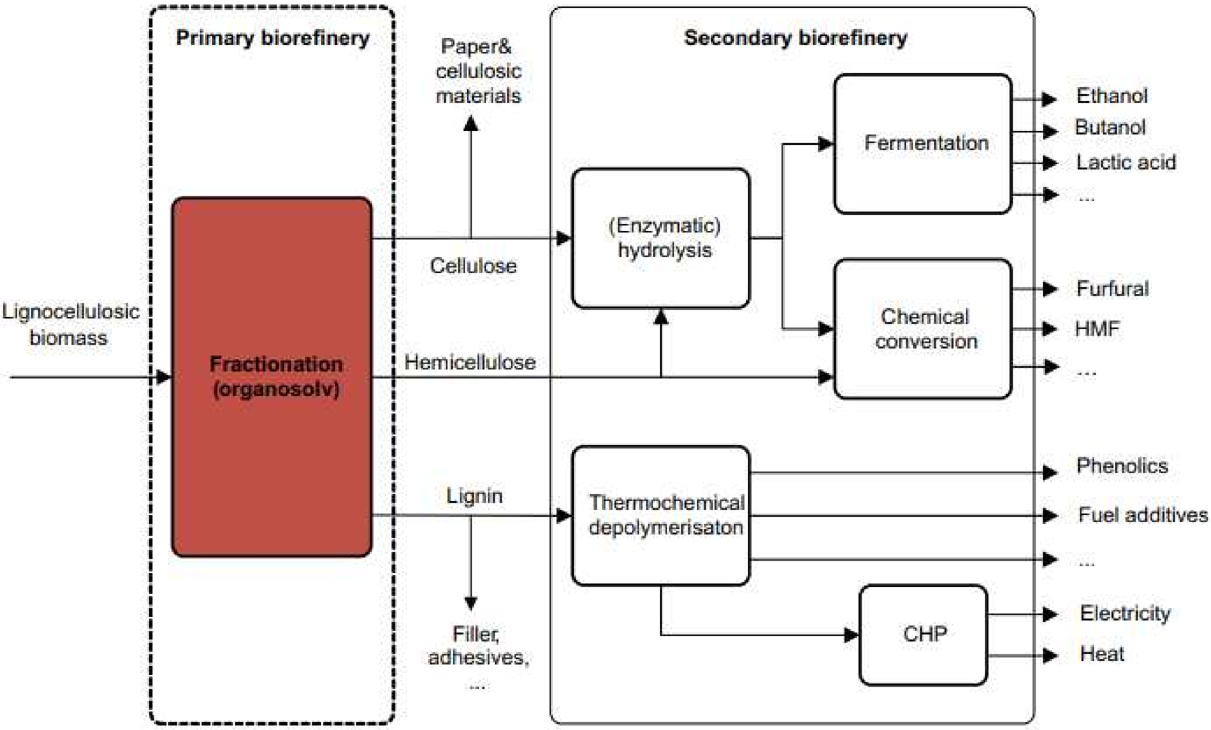
Organosolv method that has the advantages of a high organic solvent recovery (>99%), a higher energy efficiency than the current industrial processes and, very importantly, it offers the possibility to recover all constitutive wood components without destructive degradation of any of these components (WOOL, 2005). Organosolv pulping enables the efficient fractionation of lignocellulose in its three major constituents: a solid cellulose pulp, a lignin precipitate, and an aqueous hemicellulose-derived stream (SCHUTYSER et al., 2018).

The extraction of lignin by organosolv from the lignocellulosic material consists of three main steps: solvolysis, which is the slower step and involves breaking the ether bonds of lignin, especially α–O–4 (β–O–4 is more resistant to breakage hydrolytic than α–O–4); solvation, in which the lignin fragments are solubilized by the solvent; and dissolution where the lignin/solvent mixture forms a final liquid phase (**Figure 8**) (BORAND; KARAOSMANOĞLU, 2018).

It is noteworthy that in the first step, the acid-catalyzed attack of water on lignin promotes the cleavage of the ether bonds. Hemicelluloses are also hydrolyzed to C5 and C6 sugars, while a small part of the cellulose can undergo the same process. Subsequently, lignin is recovered as insoluble precipitated by adding water to the system and lowering the pH.

Acetosolv is the organosolv process that uses acetic acid as a solvent and is generally operated at low temperatures close to 110 °C and atmospheric pressure (AVELINO et al., 2018). Ethanosolv, an organosolv involving ethanol (EtOH) as a solvent, is operated at high temperature and pressure (PAN et al., 2006, 2007). These more aggressive conditions are necessary because lignin is lesser soluble in ethanol than acetic acid. In acid-catalyzed ethanosolv, the solvent/water ratio must be optimal for the organosolv to run efficiently. When alcohols are used, with EtOH in particular being very popular, this process typically yields clean lignins with excellent retention of the high β-aryl ether content, and contains very low carbohydrate, ash and other non-lignin derived impurities (ZIJLSTRA et al., 2020).

Figure 7 – Organosolv-based lignocellulosic biorefinery.



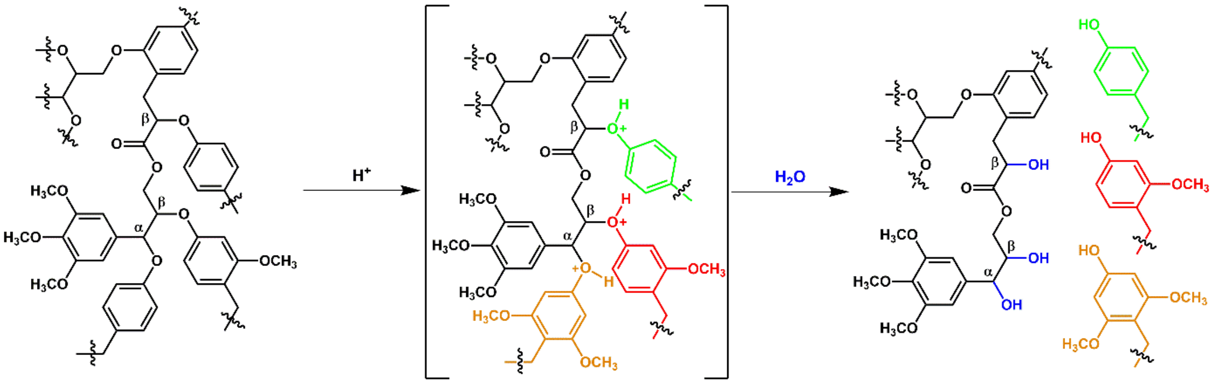
Source: (WILDSCHUT et al., 2013).

In the ethanosolv, low ethanol concentrations result in high concentrations of hydronium ions that help cleave α–O–4 and β–O–4 bonds in lignin, while higher concentrations increase lignin solubility (PAN et al., 2007). Additionally, the use of ethanol is lesser toxic than other solvents and almost complete recovered, which is the biggest advantage of the process that reduces operating costs (KOO et al., 2012). In addition, chemical recovery in organosolv can isolate lignin and carbohydrate in the liquid phase: the first as a solid material after precipitation and the last as hydrolyzed sugar, both with potential application as chemicals (ZHAO; CHENG; LIU, 2009).

Only 1 to 2% of the lignin obtained in conventional large-scale methods is used in commercial applications, with the major fraction used in combustion for energy generation. In contrast, organosolv generates almost pure lignin in an easily recoverable form. Organosolv lignin has characteristics that stand out, such as a narrow range of molecular mass, being sulfur free, having a hydrophobic characteristic, low ash, and residual carbohydrates. Solvent distillation recovery and recycling can minimize the involved higher costs in the process (AVELINO et al., 2019). In addition, organosolv requests more environmentally friendly chemicals compared to traditional sulfur processes. **Table 3** shows the main differences in the types of technical lignin structure. The differences in the structure can lead to changes in the reactivity in the lignin.

Organosolv lignins are quite different from other technical lignins. Organosolv lignin is an excellent feedstock for high-value lignin because of its unique physical and chemical properties, such as high purity, reactivity, and thermal fusibility, its low and uniform molecular weight, and abundant reactive side chains available for further chemical reactions (VISHTAL; KRASLAWSKI, 2011; ZHU; PAN, 2010).

Figure 8 – Representation of the hydrolysis mechanism of α–O–4 e β–O–4 bonds in the lignin structure.



Source: The author.

Table 3 – Some structure characteristics of technical lignins.

	Sulfur lignins		**Sulfur-free lignins**	
	Kraft	**Lignosulfonate**	**Soda**	**Organosolv**
Raw materials	Softwood Hardwood	Softwood Hardwood	Annual plants	Softwood Hardwood Annual plants
Purity	Medium-high	Medium	–	High
Solubility	Alkali Organic solvents	Water	Alkali	Wide range of organic solvents
M_n (g mol^{-1})	1000–5000	1000–50000 (up to 150000)	800–3000	500–5000
Polydispersity	2.5–3.5	4.2–8	2.5–3.5	1.5–2.5
T_g (°C)	140–150	130	140	90–110
Ash (%)	0.5–3.0	4.0–8.0	0.7–2.3	1.7
Carbohydrates (%)	1.0–2.3	–	1.5–3.0	1–3
Application	Additives, biofuel, BTX, activated carbon, phenolic resins, carbon fibers, phenol	Additives in bitumen, vanillin, feedstock for refinery	–	Activated carbon, phenolic resins, carbon fibers, vanillin, phenol derivatives

Note: M_n: Number-average molar mass.

Source: (DESSBESELL et al., 2020; LAURICHESSE; AVÉROUS, 2014; VISHTAL; KRASLAWSKI, 2011).

In recent years several researchers evaluated the extraction and characteristics of organosolv lignin from CF, SCB, and OPMF. PINHEIRO et al. (2017) investigated the characteristics of acetosolv lignin from SCB. They obtained lignin with yield around 64% and typical grass type lignin, with the presence of H, G, and S units. The relative proportion of H units was greater than the others units, which could indicate presence of a larger number of active sites, available for reactions in the aromatic ring.

SOUZA et al. (2016) obtained high-purity acetosolv lignin from OPMF, lignin yield around 63%, and they observed a FTIR peak at 1166 cm^{-1}, which could indicate the presence of HGS-type lignin according FAIX (1991). In our previous studies, the presence of that peak was also observed and corroborated by 2D-HSQC spectra (MARQUES et al., 2020, 2021). We observed that OPMF and SCB are HGS-type lignin with presence of oxidized structure such as ferulate and *p*-coumarate. The lignins were obtained by acetosolv extraction with quite high-yield and high-purity lignins.

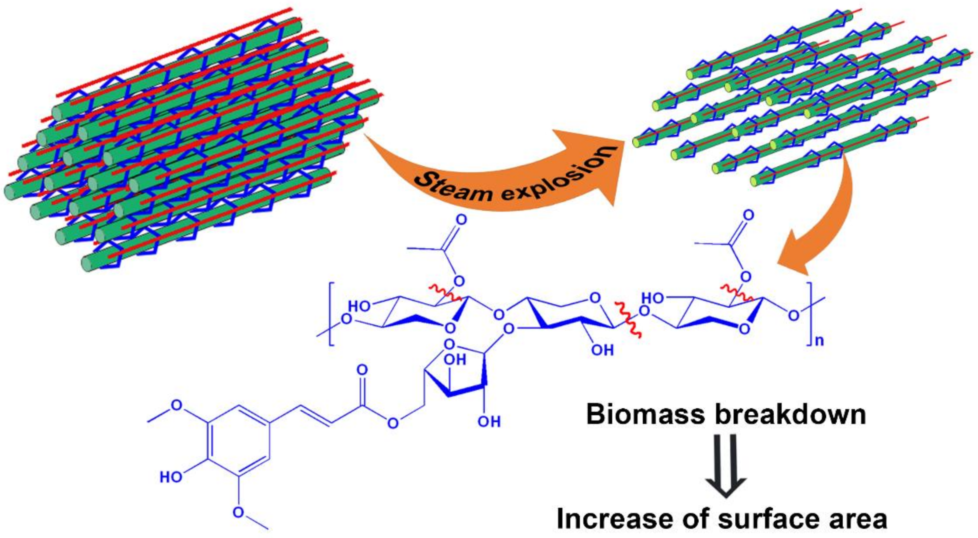
SCHMETZ et al. (2016) found HGS lignin with purity around 90% and moderate lignin yield (60%) extract from tall fescue ethanol organosolv. Similarly, OUYANG et al. (2015) obtained high-purity lignin (94%) composed by HGS monolignols with moderate to low lignin yield about 41%, using a combination of steam explosion and ethanosolv. These results show that organosolv is a method that high-purity lignin can be obtained, indicating the possible application without major purification.

2.3.3 Steam explosion pretreatment

In order to improve the delignification, the use of a pretreatment gained popularity over the years. Commonly, biomass in general has a quite rigid structure, due to lignin which acts like a glue maintaining the wall cell compact. This attribute granted by the lignin is called recalcitrance. Recalcitrance makes the lignin extraction a high-energy and chemical-consuming process. Physical and/or chemical pretreatments have been investigated for the improvement of energy efficiency, for decrease chemical use, and/or recalcitrance. Usually, pretreatments involve milling, ultrasonic pretreatment, acid hydrolysis, alkaline treatment, hydrothermal treatment, and steam explosion (HARMSEN et al., 2010). **Figure 9** shows the effect of pretreatment on the increase of surface area and the breakdown of recalcitrance.

Steam explosion, also known as autohydrolysis, is the most widely employed physico-chemical pretreatment method for any lignocellulosic biomass because of its potential for disrupting crystallinity of cellulose, delignification, and easy hydrolysis of the hemicelluloses (SINGH; SUHAG; DHAKA, 2015). Technically, the steam explosion equipment (**Figure 10**) is composed by a boiler responsible for the steam generation that supplies a reactor, which is subjected to a sudden depressurization. During depressurization, the material is ejected from the reactor and is recovered in the explosion tank (JACQUET et al., 2015).

Figure 9 – Pretreatment effect on lignocellulosic biomass.



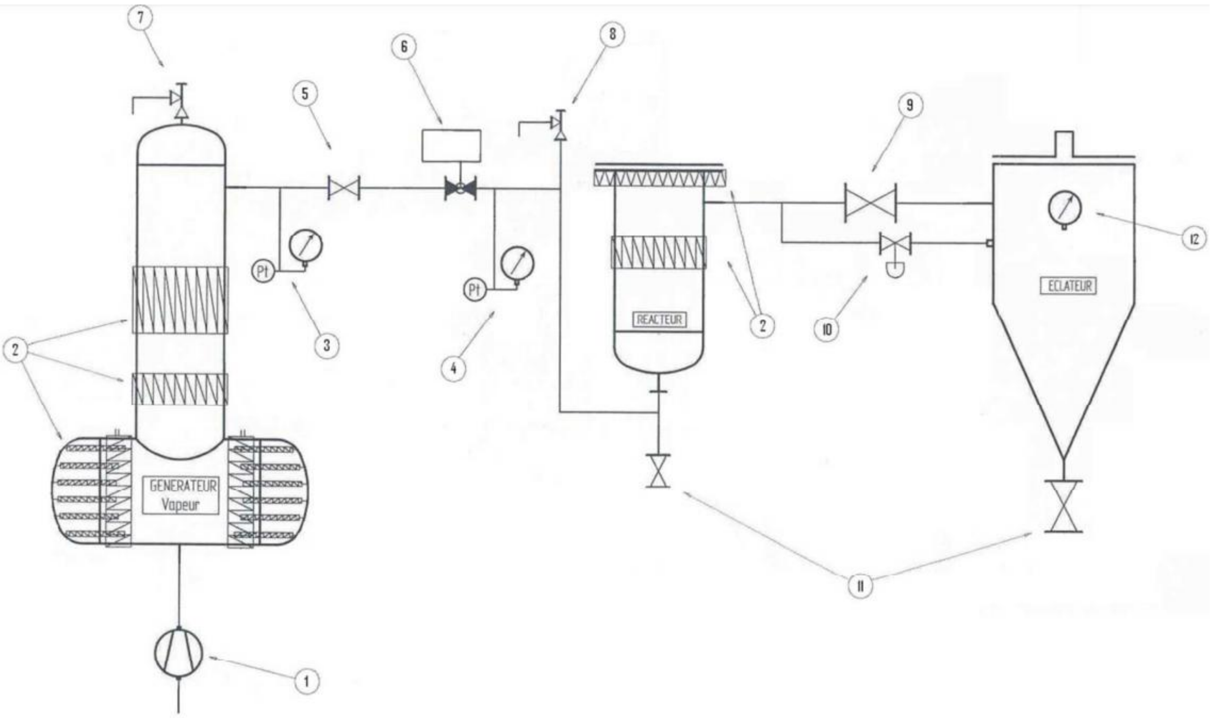
Note: Green: cellulose; Blue: hemicellulose; Red: lignin.
Source: Adapted from (MARQUES et al., 2021).

Steam explosion is a thermophysico-chemical process which provides mechanical destructuration of lignocellulosic material by a combination of two steps: vapocracking and explosive decompression. Chemical reactions are initiated by thermo-hydrolyzed of biomass (MANIET et al., 2017). This pretreatment causes the breakdown of biomass components by steam heating and shearing forces due to the expansion of moisture and hydrolysis of glycosidic bonds by the organic acid formed during the process (SINGH; SUHAG; DHAKA, 2015).

Steam explosion is affected by residence time, temperature, chip size, and moisture content (KUMAR et al., 2009). This process can be only applied with water, pressure, and heat, and does not use any environmentally harsh chemicals. Accordingly, during the pretreatment process, the biomass is subjected to a high pressure and temperature (0.7–4.8 MPa; 160–280 °C) for the desired reaction time (from several seconds to a few minutes) (MARQUES et al., 2020). **Table 4** summarizes recent studies about lignin extraction by organosolv.

During steam treatment such as steam explosion, an almost simultaneous depolymerization and repolymerization reactions takes place in the lignin due to the acidity created during the treatment (LI; HENRIKSSON; GELLERSTEDT, 2007). Carbonium ions are the common intermediate for both reactions routes which are originated from benzyl alcohol structures in the lignin aliphatic chain (**Figure 11**). The intermediate may break the ether bonds, leading to lignin depolymerization or may react with an electron-rich carbon in an adjacent aromatic ring, leading to a stable carbon–carbon linkages resulting in repolymerization. Only under extremely mild conditions of steam treatment can this reaction be suppressed (LI; HENRIKSSON; GELLERSTEDT, 2007).

Figure 10 – Steam explosion pilot plan.

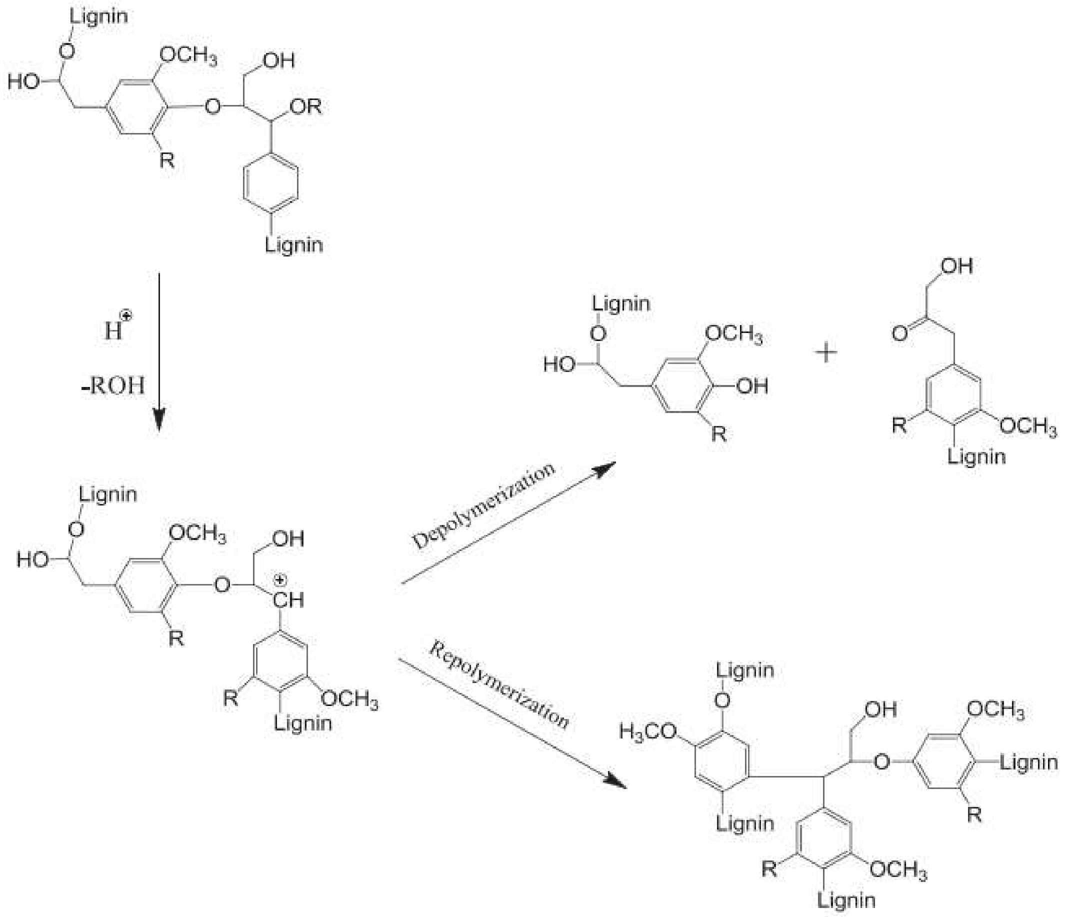


Note: 1. High pressure pump, 2. Heaters, 3. Gauges of steam boilers, 4. Gauges of reactor, 5. Isolation valve, 6. Charging valve, 7. Safety steam boiler valve, 8. Safety reactor valve, 9. Explosion valve, 10. Purge Valve, 11. Recovery valves, 12. Gauge of explosion tank.
Source: (JACQUET et al., 2015).

One of advantage of steam explosion is the increase of surface area that occurs due acid-catalyzed hydrolysis followed by explosive decompression which takes place in the reactor. The increase of surface area promotes better contact of chemicals, i.e., solvent, catalyst, and water, in the lignocellulose, leading to improvement of lignin extraction. MICHELIN et al. (2018) using uncatalyzed ethanosolv obtained low purity lignin, around 55%. In their study, it was applied the hot water pretreatment in order to evaluate its effect in the ethanosolv. The pretreatment improved the purity of obtained lignin (55% to 87–93%) as well as the lignin yield (42.3 to 56.9–61.8%).

WANG and CHEN (2016) obtained an increase of lignin extraction using steam explosion. The yields of corn stalk extracted from untreated and steam exploded corn stalk were 9.8% and 59.3%, respectively. It was found that steam explosion increases the surface area of the biomass making the subsequential process easier to takes place.

Figure 11 – Competition between depolymerization and repolymerization reactions during steam explosion.



Source: (LI; HENRIKSSON; GELLERSTEDT, 2007).

MANIET et al. (2017) successfully obtained a great increase of lignin extraction from fescue using steam explosion followed formic and acetic acid organosolv, from 30% to almost 100%. Values near 100% could be an indicative of presence of the "pseudolignin", which is formed by polymerization of polysaccharides degradation products. Similarly, (OUYANG et al., 2015) obtained improvement of lignin yield using steam explosion followed by ethanosolv. 1 The lignin yield was improved from 6.81% to 40.94%.

Recently, steam explosion was applied in order to improve the energy efficiency of the process by decreasing the reaction time in the acetosolv extraction (MARQUES et al., 2021). Steam explosion followed by acetosolv improved the lignin yield by approximately 15% and 17% in OPMF and SCB, respectively. For SCB, it was possible to decrease the reaction time in four-fold while maintaining the lignin yield. This result was not achieved for OPMF probably because higher recalcitrance of this biomass.

2.4 Optimization of delignification process

Each lignin has its own unique chemical properties, determined by (i) the fractionation method, (ii) the fractionation severity, and (iii) the biomass source (SCHUTYSER et al., 2018). Furthermore, knowing how each these parameters acts on the lignin structure and its behavior during extraction process could support further lignin application depend on its reactivity (**Figure 12**).

Regarding extraction process, organosolv seems to be an appropriated method that do not substantially modify the lignin structure, not only for produce a high-yield and high-quality lignin, but the absence of sulfur makes it more suitable for chemical modification. On the other hand, the source of lignin also plays a great role in the lignin structure. Optimization methods often is applied in biorefinery approach in order to maximize biomass delignification, lignin yield, enzymatic hydrolysis of the biomass, among others.

Table 4 – Recent studies about lignin extraction by organosolv.

Biomass	**Method**	**Reagent**	**Condition**	**Yield**	**Reference**
Hybrid poplar	Organosolv	Ethanol (25–75%) H_2SO_4 (0.83–1.67%)	155–205 °C	~74%	(PAN et al., 2006)
Lodgepole pine	Organosolv	Ethanol (48–82%) H_2SO_4 (0.76–1.44%)	153–187 °C 43–77 min	~79%	(PAN et al., 2007)
Miscanthus	Organosolv	Ethanol (65%) H_2SO_4 (1.2%)	190 °C 60 min	52%	(HAGE et al., 2009)
Switchgrass	Organosolv	Ethanol (75%) H_2SO_4 (0.9%)	180°C 60 min	60.5%	(HU et al., 2012)
Wheat straw	Organosolv	Ethanol (50–80%) H_2SO_4 (0–30 mM)	170–210 °C 60–120 min	84%	(WILDSCHUT et al., 2013)
Eucalyptus	Organosolv	Ethanol (30–70%)	190–200 °C 45–75 min	3.92–63.4%	(YÁÑEZ-S et al., 2014)
Oil palm mesocarp fiber	Organosolv	Acetic acid (93%) HCl (0.3%)	115°C 180 min	63.0%	(SOUZA et al., 2016)

Coconut fiber	Organosolv	Acetic acid (93%) HCl (0.3%)	115°C 180 min	30.1%	(NASCIMENTO et al., 2016)
Tall fescue	Organosolv	Ethanol (92%) H_2SO_4 0.32 M	148 °C	60%	(SCHMETZ et al., 2016)
Sugarcane bagasse	Organosolv	Acetic acid (95%) HCl (0.1%)	187°C 40 min	64.3%	(PINHEIRO et al., 2017)
Oil palm mesocarp fiber	Organosolv	Acetic acid (93%) HCl (0.3%)	115°C 180 min	48.5%	(NOGUEIRA et al., 2019)
Eucalyptus	Organosolv	Ethanol (50%) H_2SO_4 (1%)	160 °C 10 min	66.5%	(CHOI et al., 2019)
Banana peel	Organosolv	Acetic acid (70–90%) HCl (2%)	110 °C 60–180 min	20.7–35.2%	(NASCIMENTO et al., 2021)
Corncob	HW + organosolv	Ethanol (20–60%)	140–180 °C 40–120 min	33.4–61.8%	(MICHELIN et al., 2018)
Corncob	SE + organosolv	Ethanol (80%)	SE: pre-soaked 0.5% H_2SO_4, 10h. Then 1.5 MPa, 5 min Organosolv: 160 °C, 120 min	40.94%	(OUYANG et al., 2015)

Fescue	SE + organosolv	SE (Log R_o 1.4–4.2) Formic acid/acetic acid/water (50/30/20%)	107 °C 180 min	30–100%	(MANIET et al., 2017)
Corncob residue	SE + organosolv	Dioxane (85%)	SE: pre-soaked 0.01 M HCl, 90 °C, 120–720 min	21.2–57.3%	(ZHANG et al., 2019)
Oil palm mesocarp fibers	SE + organosolv	Acetic acid (93%) HCl (0.3%)	SE: 168 °C, 10 min Acetosolv: 115 °C, 180 min	46–56%	(MARQUES et al., 2020)
Oil palm mesocarp fibers **Sugarcane bagasse**	SE + organosolv	Acetic acid (93%) HCl (0.3%)	SE: 168 °C, 10 min Acetosolv: 115 °C, 180 min	OPMF: 70.21% SCB: 90.3%	(MARQUES et al., 2021)
Triticale straw	MW-assisted organosolv	Ethanol (27–95%) H_2SO_4 (0–1 N)	83–167 °C	91%	(MONTEIL-RIVERA et al., 2012)
Sugarcane bagasse	MW-assisted organosolv	Acetic acid (90%), HCl (2.0%)	MW: 0,5 kW 110 °C, 30 min	77–84%	(AVELINO et al., 2019)
Sugarcane bagasse	O_2-assisted organosolv	Ethanol (30–70%)	130–170 °C 40–120 min	[a]83.3%	(LI et al., 2018)

[a] Percentage of Lignin removal from the biomass.

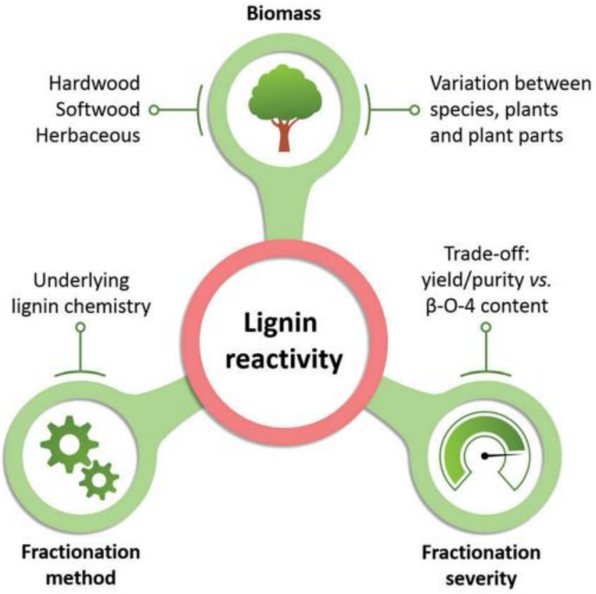
Note: HW: Hot water; MW: Microwave; O_2: Oxygen gas; SE: Steam explosion.

Source: The author.

One-factor-at-a-time method (OFAT) is quite popular in optimization studies. The OFAT method consists of selecting a starting point, or baseline set of levels, for each factor, and then successively varying each factor over its range with the other factors held constant at the baseline level (MONTGOMERY, 2017). After all experiment runs are performed, a series of graphs are usually plotted in order to evaluate how the response variable is affected by varying each factor while all other factors are held constant.

Some researchers preferred OFAT when the data acquisition is abundant and cheap which leads to an ease data treatment, requiring less effort. However, it is not the most indicated approach when several variables are applied because the required great number of experiments. One of disadvantage of the OFAT is lead to an unnecessarily large number of experimental runs. Moreover, the major disadvantage of the OFAT strategy is that it fails to consider any possible interaction between the factors (MONTGOMERY, 2017).

Figure 12 – Main factors that determines the lignin reactivity and further application.



Source: (SCHUTYSER et al., 2018).

OFAT experiments are always less efficient than other methods based on a statistical approach to design (MONTGOMERY, 2017). The best approach to evaluate several factors is the factorial method. In this approach, all factors vary at the same time, instead of one at a time. Factorial method has the main advantages: (i) it requires less experimental runs, being resource saving method (energy, time, chemicals), often scarce; (ii) the estimates of the effects of each factor are more precise; (iii) the interaction between factors can be estimated systematically; and (iv) there is experimental information in a larger region of the factor space (CZITROM, 1999).

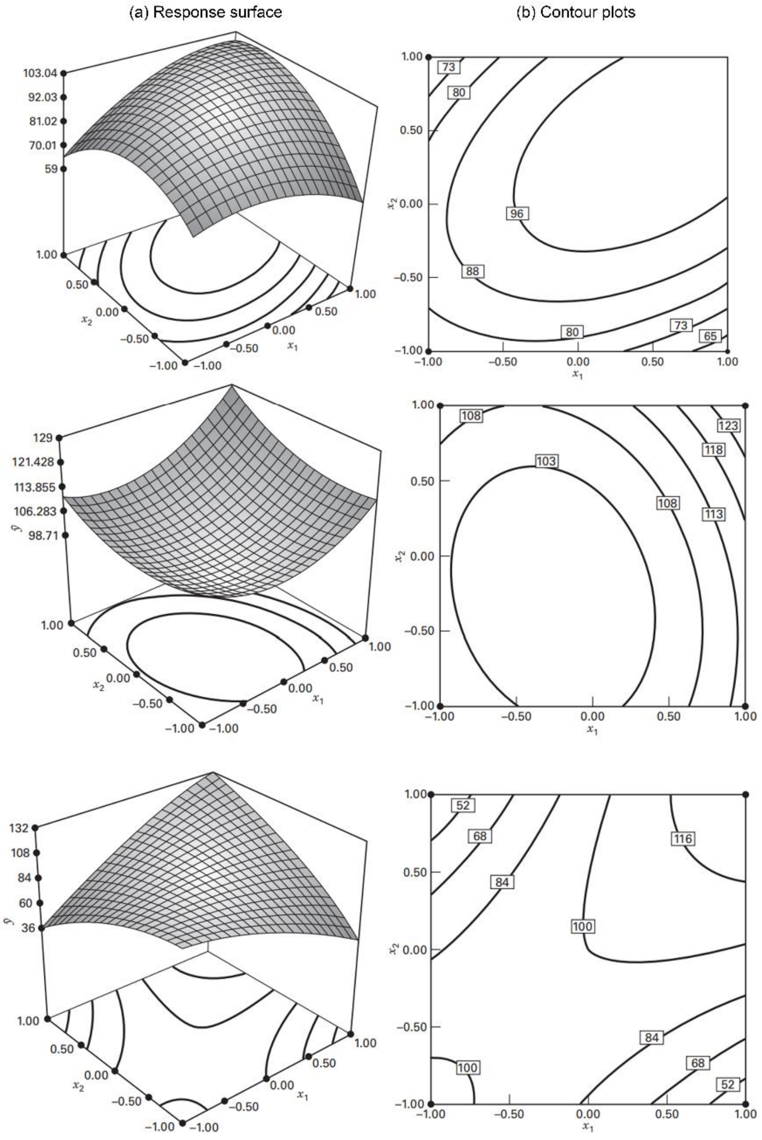
However, OFAT and common factorial method usually results in a first-order model. First-order models cannot indicate an optimum condition where the response variable is maximum or minimum within the experimental domain. When the data is relatively close to the optimum response, the model usually turn in a curvature, i.e the first derivative of the curve (model) equals 0. The curvature could represent a point of maximum response, a point of minimum response, or a saddle point (**Figure 13**). The second derivative is used to determine the existence of saddle points. In most cases, the second-order model is adequate to fit the obtained data.

Central composite design (CCD) is the most popular class of statistical designs, first described by BOX and WILSON (1951). CCD can fit a second-order model in order to provide a curvature and optimum values. Generally, the CCD consists of a 2^k factorial (or fractional factorial) where k is the numbers of factors (process variables), 2k axial or star runs and n_C center runs (MONTGOMERY, 2017). The center points must be replicated for the determination of the experimental error and to ensure the reproducibility of the obtained data. The total number of experimental runs is determined by sum of factorial points, axial points, and center points. CCD approach usually implements the response surface methodology (RSM). The objective of RSM is to develop an empirical model of the process and a 3-D graph that can be plotted in order to obtain information how the process variables affect the response. Nowadays, the common software to analyze CCD and RSM statistical packages such as SAS, MINITAB, STATISTICA, and Design Expert.

Regarding biomass fractionation method and process severity, the most important parameters in lignin extraction are temperature, reaction time, type of solvent, presence or absence of catalyst, and biomass/solution ratio. In addition, the selection of parameters ranges also affect the statistical results once the variable effect may be maximized, minimized, or significant inexistent. In the past years, several studies of optimization of the organosolv lignin extraction and evaluation the influence of process variables on the response were carried out.

PARAJÓ et al. (1993) studying acetosolv process on the pine wood observed that lignin yield improves with the increase of the catalyst and acetic acid concentrations. They showed that around 90% of acetic acid is sufficient to maximize lignin extraction. PINHEIRO et al. (2017) found that reaction time did not significatn influence acetosolv extraction and temperature had a great effect on lignin extraction. In their study, it was also demonstrated that 95% of acetic acid is the best concentration for lignin extraction.

Figure 13 – Response surface and contour plot illustrating a surface with a maximum, minimum, and saddle.



Source: (MONTGOMERY, 2017).

PAN et al. (2006) evaluated the effect of temperature, reaction time, H_2SO_4 and ethanol concentration on the lignin extraction from hybrid poplar. It was found that the maximum temperature of 195 °C was enough to maximize lignin extraction. Temperatures higher than 195 °C seemed to lead an excessive depolymerization caused by the high temperature reducing the recovery of lignin (PAN et al., 2006). Ethanol concentration of ~65% was applied to a maximize the lignin yield. According the study, delignification during ethanol organosolv is a combination of the depolymerization and solubilization of lignin. Lower ethanol concentrations promote high acid-catalyzed cleavage of α- and β- ether bonds in lignin structure due to higher hydrogen ion concentrations, whereas high ethanol concentrations increase lignin solubilization.

Therefore, a balance between the ethanol-water ratio may exist for lignin extraction, according to MONTEIL-RIVERA et al. (2012). NI and HU (1995) found the optimum ethanol concentration for lignin removal is in the range of 55-70%. PAN et al. (2007) found that increasing the reaction temperature and ethanol concentration (~75%) in lignin extraction from lodgepole pine caused higher lignin yields. The reaction time did not affect the delignification process. The same behavior was observed in a previous study of hybrid poplar (PAN et al., 2006).

LI et al. (2018) investigated the OFAT method to optimize the oxygen-assisted ethanol organosolv from SCB. They observed that temperature higher than 160°C did not significant influenced the lignin extraction, as well as the reaction time higher than 80 min. They obtained that lower ethanol concentration led to a higher lignin removal, ~83%. This result is quite inconsistent with the literature for ethanosolv, probably because of oxygen-assisted process which may lead to a less concentration of ethanol.

WILDSCHUT et al. (2013) in OFAT method found that most influential process parameters in ethanosolv are temperature, ethanol concentration, and catalyst concentration. They found that higher reaction temperature increases delignification and higher solvent concentration (80%) inhibits lignin extraction. Their study showed a drop in delignification upon an increase of the ethanol concentration from 60% to 80%. However, in these experiments, they did not apply catalyst which may hindered that increase of delignification since the optimum ethanol concentration for lignin dissolution is around 80%. Lower amounts of hydronium ion may inhibit the breakage of lignin-carbohydrate complex.

MICHELIN et al. (2018) optimized lignin extraction by a factorial design 2^3 from corncob using ethanosolv. They found that ethanol concentration significant affect lignin yield. However, temperature (140–180 °C) and reaction time (20–60 min) did not influence. This result supports that selection of parameters range is one more information that should be evaluated before the optimization. A larger range from temperature and reaction time could have been applied in order to obtain more information about the effects of the process variables.

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3 STEAM EXPLOSION PRETREATMENT IMPROVES ACETIC ACID ORGANOSOLV DELIGNIFICATION OF OIL PALM MESOCARP FIBERS AND SUGARCANE BAGASSE

Abstract

Steam explosion can be used to pretreat lignocellulosic materials to decrease energy and chemical consumption during pulping to obtain environmentally friendly lignin and to improve lignin yield without changing its structure. The objective of this study was to evaluate the extraction of lignin from oil palm mesocarp fibers and sugarcane bagasse using steam explosion pretreatment followed by acetosolv. The biomasses were pretreated at 168 °C for a reaction time of 10 min. Steam explosion combined with acetosolv at lower severities was also carried out. Steam explosion followed by acetosolv increased the lignin yield by approximately 15% and 17% in oil palm mesocarp fibers and sugarcane bagasse, respectively. In addition, steam explosion decreased the reaction time of acetosolv four-fold while maintaining the lignin yield from sugarcane bagasse. Similar results were not obtained for oil palm mesocarp. High-purity and high-quality lignins were obtained using steam explosion pretreatment with structural characteristics similar to raw ones. Sugarcane bagasse lignin seems to be a better option for application in material science due its higher lignin yield and higher thermal stability. Our findings demonstrate that steam explosion is efficient for improving lignin yield and/or decreasing pulping severity.

Keywords: Lignocellulosic fiber; Severity; Two-step treatment; Physical and chemical treatment; Lignin characterization.

3.1 Introduction

Many essential polymers and chemicals used in industries are aromatic compounds, leading to a strong worldwide dependence on products derived from non-renewable sources (Ragauskas et al., 2014). One renewable alternative source of aromatic compounds is lignin, the second most abundant natural polymer on the planet, which is environmentally friendly and biodegradable, exhibits antioxidant properties, and displays antimicrobial activity (Collins et al., 2019; Tuck et al., 2012).

Lignin is present in several lignocellulosic biomasses and waste products, with a worldwide production estimated as approximately 1 × 10^{13} tons per year, with lignin content ranging from 15 to 40%. This indicates a potential lignin production of at least 1.5 × 10^{12} tons per year (Carvajal et al., 2016; Zoghlami and Paës, 2019). In Brazil, two of the main lignocellulosic wastes are oil palm mesocarp fiber (OPMF) and sugarcane bagasse (SCB). OPMF and SCB are generated by pressing palm oil fruits and sugarcane stems, respectively, to obtain palm oil and sugarcane juice. It is estimated that during the Brazilian harvest period of 2019-2020, 2.04 × 10^5 tons of OPMF and 2.1 × 10^8 tons of SCB were produced (CONAB, 2020; Lee and Mariatti, 2008; Pereira et al., 2020; Zakaria et al., 2014), with approximately 35% and 25% lignin content (Pandey et al., 2000; Souza et al., 2016), respectively, resulting in a potential lignin production of 7.0 × 10^4 tons from OPMF and 5.1 × 10^7 tons from SCB. Thus, these residues have great potential for lignin extraction due to their abundance, low cost, renewable nature, and underuse (Sindhu et al., 2016). Currently, they are underused as energy sources in mill boilers or discarded as waste. Previous studies have reported that a significant variety of new polymeric materials and high value-added chemicals such as polyurethanes, polybenzoxazines, polyesters, carbon fibers, epoxide, and phenolic resins can be produced from lignin (Abarro et al., 2016; Laurichesse and Avérous, 2014; Upton and Kasko, 2016).

However, despite being present in large amounts in several lignocellulosic biomasses, lignin is not readily available and must be extracted. Different processes have been used for lignin extraction, such as the Kraft process, the sulfite process, soda pulping, and organosolv (Grossman and Wilfred, 2019; Laurichesse and Avérous, 2014; Zakzeski et al., 2010). The organosolv process is an interesting alternative because it extracts high-quality lignins, which are primarily unaltered, purer, and less condensed than lignins derived from other extraction processes (Brosse et al., 2009). In this pulping process, organic solvents are used for lignin dissolution by the cleavage of α-aryl ether and β-aryl ether linkages (McDonough, 1993). Furthermore, the organic solvents can be distilled and reused, making this process greener than traditional ones.

Lignin extraction is a high-energy and chemical-consuming process (Carvajal et al., 2016). Different lignocellulosic biomass pretreatments have been investigated for improving energy efficiency and decreasing chemical use and/or recalcitrance: milling, ultrasonic pretreatment, acid hydrolysis, alkaline treatment, hydrothermal treatment, and steam explosion (Harmsen et al., 2010). Steam explosion is a promising pretreatment due to its capability to break the recalcitrance of biomass with low energy consumption and with few or no chemicals (Jacquet et al., 2015; Maniet et al., 2017). In this pretreatment, the lignocellulosic material is maintained in a reactor at high temperature and pressure for a certain time. The reactor is then suddenly depressurised, causing explosive decompression. The steam explosion creates a mechanical effect due to the instantaneous expansion force and a chemical effect due to high-temperature cooking (Wang and Chen, 2016). The mechanical effect causes fiber shattering, which increases the specific surface area of the lignocellulosic material and the contact between the biomass and the chemicals in the subsequent processes (Marques et al., 2020). The chemical effects are due to the hemicellulose-derived organic acids produced at high temperatures, which allow hydrolysis and dissolution of most of the hemicellulose and part of the cellulose, as well as cleavage of lignin-carbohydrate linkages (Jacquet et al., 2015).

Steam explosion is usually applied to increase the efficiency of enzymatic hydrolysis and fermentation in the production of second-generation ethanol (Jacquet et al., 2015). This pretreatment is also used in extracting bioactive compounds from plant tissues, due to: (i) the formation of micropores that increase the specific surface area of the material (Chen and Chen, 2011; Sui and Chen, 2014); (ii) increase of the lignin yield in further alkaline extraction and organosolv (Maniet et al., 2017; Ouyang et al., 2015; Wang and Chen, 2016; Zhang et al., 2019); and (iii) increase in cellulose pulp yield from oil palm mesocarp fiber with a potential to decrease the severity of the delignification process (Marques et al., 2020). Severity is a process parameter described as a function of time and temperature to predict conditions for lignocellulosic decomposition (Overend et al., 1987).

Steam explosion may cause modification of lignin structure due to depolymerisation and repolymerisation reactions that occur nearly simultaneously among the monomeric units of lignin (Li et al., 2007; Lora and Wayman, 1980). In the high-severity steam explosion process, lignin β-O-4 aryl ether linkages are predominantly hydrolysed, releasing new free phenolic groups. Moreover, acid-catalysed recombination occurs between aromatic C_6 or C_5 and a formed carbon ion, usually located on the aliphatic C_α. Delignification efficiency increases as process severity increases, up to a certain limit. In high-severity autohydrolysis, the delignification rate may decrease due to formation of new condensed C–C bonds such as β-β, β-1, and β-5 substructures by repolymerisation reactions (Li et al., 2007).

In this study, steam explosion was evaluated as a pretreatment of oil palm mesocarp fiber and sugarcane bagasse, prior to lignin extraction using acetic acid organosolv to decrease the reaction time. The physical and chemical properties of the obtained lignins under optimum extraction conditions were evaluated for possible use as building blocks for high-value-added products.

3.2 Material and methods

3.2.1 Biomasses

Oil palm mesocarp fiber (OPMF) and sugarcane bagasse (SCB) were donated by Oldesa Óleo de Dendê Ltda (Nazaré-BA, Brazil) and Diageo Brasil Ltda (Paraipaba-CE, Brazil), respectively. The biomasses were maintained in a cold chamber at -18 °C for further analysis and experiments. Prior to use, the OPMF and SCB were air-dried at 50 °C until reaching a constant weight, ground in a knife mill and sieved. The fibers that passed through the 5-mesh (4-mm aperture) sieve were used for experiments.

The OPMF was mainly composed of cellulose (23.5%), hemicellulose (20.8%), lignin (35.9%), extractives (10.4%), and ash (9.2%). The SCB was composed of cellulose (36.4%), hemicellulose (20.1%), lignin (29.9%), extractives (6%), and ash (5.4%).

3.2.2 Steam explosion pretreatment

For each steam explosion assay, 200 g of material was added to the preheated reactor (Metalúrgica Metalquim Ltda, São Paulo, Brazil) at 168 °C (Marques et al., 2020). After a reaction time of 10 min, the material was ejected from the reactor and underwent explosive decompression. The exploded fibers (EF) were collected and filtered using a nonwoven fabric to separate them from the liquid fraction. The EFs were lyophilised, stored at room temperature (~27 °C), and used in processes described in subsections 2.3, 2.4, and 2.5. Severity of the steam explosion was calculated based on the modified equation described by Overend et al. (1987) (Equation 1).

$$\log R_o = \log\left(t \times \exp\left(\frac{T-100}{14.75}\right)\right) \tag{1}$$

where R_o is the severity factor of the pretreatment, t is the reaction time (min), and T is the reaction temperature (°C). R_o is usually expressed as a log function to simplify the data.

3.2.3 Acetosolv process

Acetosolv was carried out using either the raw or the exploded biomasses with 93% (w/w) acetic acid and 0.3% (w/w) HCl as catalyst in reflux at 115 °C for 180 min, following Benar et al. (1999). Further experiments with decreasing reaction time were carried out at 90, 45, and 22.5 min. The fiber:solution ratio for OPMF and SCB was 1:10 and 1:20, respectively. SCB required a higher ratio of fiber:solution due to fiber swelling, which hinders the process. After reaction time was complete, the mixture was filtered using 28-µm pore filter paper and washed with a 2-fold volume of warm acetic acid (99.7%) at 80 °C until the wash liquid was colourless. All the filtered liquid, rich in soluble lignin and referred to as black liquor (BL), was stored for subsequent lignin recovery. All solid fractions, rich in cellulose, that remained in the filter paper was discarded. However, in further investigations, the solid fraction could be applied in the obtention of high value-added products such as cellulose nanoparticles (microfibrils or nanocrystals).

3.2.4 Lignin recovery

The BL was concentrated under reduced pressure until 10% of the initial volume remained for subsequent recovery of the solvent. The solution was added to warm distilled water (60 °C) at a ratio of 1:10 (v:v) and allowed to precipitate lignin for 24 h. The precipitated lignin was filtered using an 8-µm pore filter paper, washed with distilled water until the pH reached approximately 7, and dried in an air-circulation oven at 45 °C until constant mass was reached. The lignin yield (Y_L) was calculated using Equation 2.

$$Y_L = \left(\frac{m_L}{m_{IL}}\right) \times 100 \qquad (2)$$

where Y_L is the yield of lignin extraction on a dry basis (%), m_L is the obtained lignin on a dry basis (g), and m_{IL} is the initial mass of lignin in the fibers before the process (g).

3.2.5 Physical and chemical characterisation

The raw and exploded lignins were characterised according to a previous study (Marques et al., 2020) by Klason’s lignin (purity), Fourier-transform infra-red spectroscopy (FTIR), nuclear magnetic resonance (NMR), thermogravimetry (TGA), derivative thermogravimetry (dTG), and gel permeation chromatography (GPC) analysis.

Lignin purity (Klason's lignin) measurement was performed based on the standard method (TAPPI T 222 om-02) for acid-insoluble lignin in wood and pulp (TAPPI, 2002).

Fourier transform infrared spectroscopy (FTIR) spectra were obtained using a PerkinElmer Spectrum Two FT-IR spectrometer with KBr pellets and 5% (w/w) sample concentration (Marques et al., 2020). Spectra were recorded between 4000 cm^{-1} and 400 cm^{-1} with a resolution of 4 cm^{-1} using the arithmetic average of 32 scans. FTIR data were processed and analysed using the PerkinElmer Spectrum IR software.

Nuclear magnetic resonance (NMR) spectra were collected using a 600 MHz DD2 NMR spectrometer (Agilent) equipped with a 5-mm One Probe (^{2}H-^{19}F/^{15}N-^{31}P) with a z-axis field gradient (Pinheiro et al., 2017). The sample powder (50 mg) was dissolved in 500 μL of DMSO-d6, with the aid of an ultrasonic bath for 24 h to promote better solubilisation. Data analysis was performed using MestReNova v. 12.0. The DMSO solvent peak at δ_C/δ_H 39.5/2.49 was utilised as an internal reference. The relative abundances of the lignin units were calculated based on the volume integration of the cross-peaks of each structure and expressed as overall percentage, with summation of *p*-hydroxyphenyl (H), guaiacyl (G), and syringyl (S) units equal to 100%, as previously reported (Wen et al., 2013). Lignin monomers in their oxidised forms as oxidised syringyl (S'), ferulate (FA), and *p*-coumarate (PCA) were included as part of each related monomer. Data analysis was performed using MestReNova v. 12.0.

Gel permeation chromatography (GPC) was performed using an LC-20CE chromatograph (Shimadzu) equipped with an SPD-20A UV-Vis refractive index detector at a wavelength of 254 nm (Avelino et al., 2019a). The solvent used as the mobile phase was tetrahydrofuran (THF, HPLC grade). An injection volume of 20 μL and mobile phase flow of 1 mL min^{-1} was used in a Shimadzu GPC 803 column at 40 °C. Lignin samples were solubilised in THF at a concentration of 1 mg mL^{-1}.

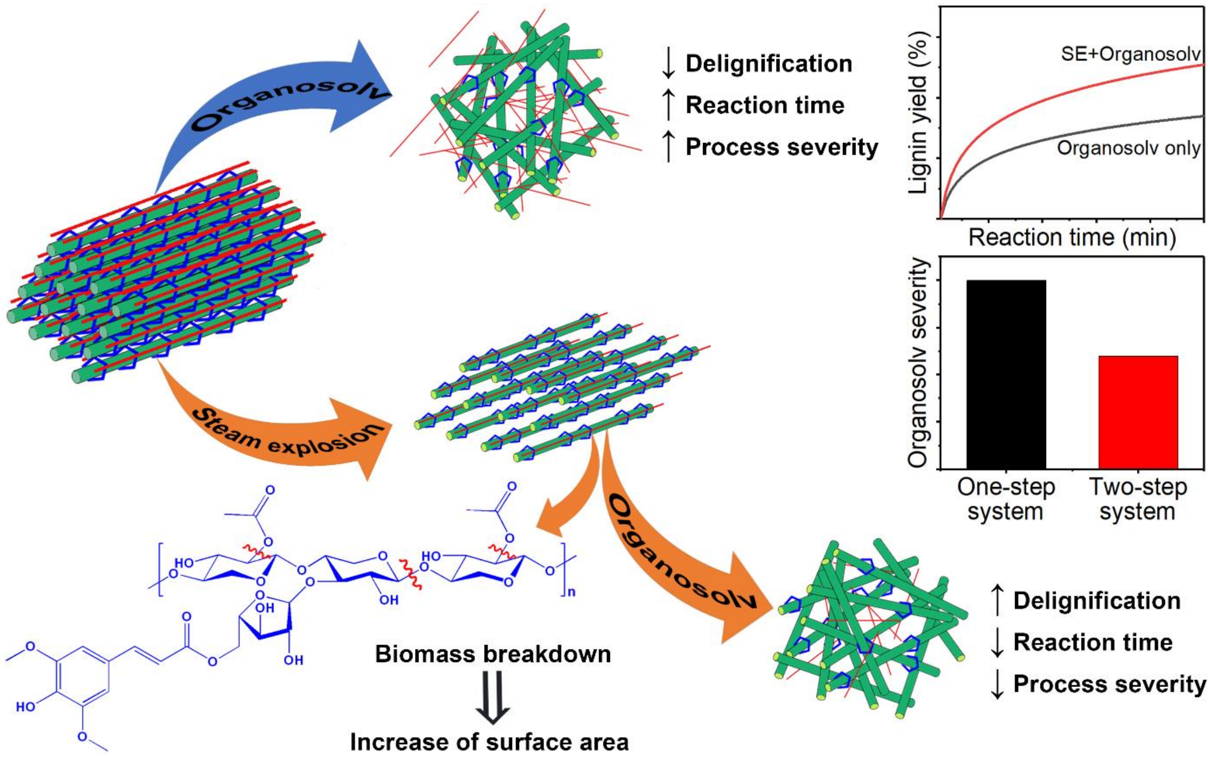
Thermogravimetry (TGA) and derivative thermogravimetry (dTG) analyses were performed using an STA 6000 thermal analyser (PerkinElmer) (Marques et al., 2020). All measurements were performed under N_2 atmosphere with a gas flow of 30 mL min^{-1}, heating rate of 10 °C min^{-1}, and heated from 30 °C to 700 °C. The sample masses used in the analyses were approximately 10 mg each.

3.3 Results and discussion

3.3.1 The effect of steam explosion on lignin yield

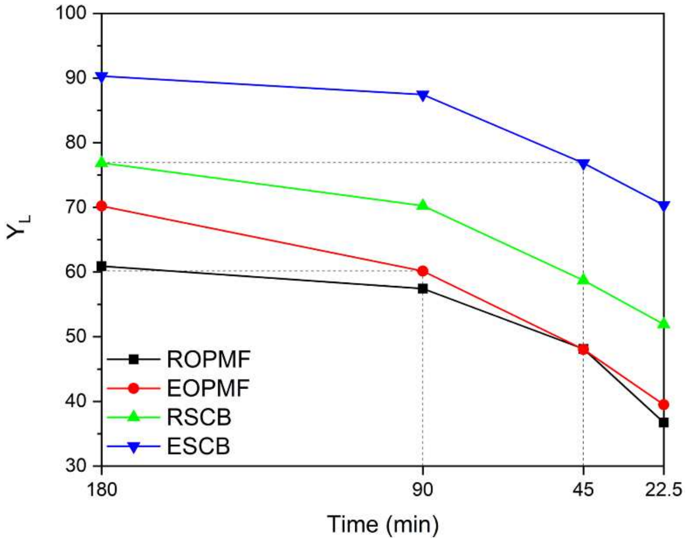
During steam explosion, the biomass lignin-carbohydrate complex undergoes hydrolysis of hemicellulose, catalysed by organic acids formed at high temperatures and pressures. Moreover, the mechanical effect of fiber disruption caused by explosive vapour expansion facilitates lignin extraction (Jacquet et al., 2015). Breakdown the biomass linkages and increased specific surface area are the main effects of steam explosion, resulting in a biomass that is more susceptible to subsequent pulping processes such as acetosolv (**Figure 14**) (Marques et al., 2020). At the reference acetosolv reaction time (180 min), the use of steam explosion as pretreatment resulted in significantly higher lignin yield than the acetosolv extraction from raw fibers (**Figure 15**). As mentioned above, this is the result of the greater specific surface area, exposing the lignins for further chemical extraction via acetosolv (Ouyang et al., 2015; Wang and Chen, 2016). The enhancement of lignin extraction yield after steam explosion is attributed not only to the increase in specific surface area, but also to the chemical attack of organic acids formed during the high-severity process, when amorphous cellulose and hemicellulose are degraded to hexoses and pentoses, and further degraded to acetic acids and other organic acids (Ouyang et al., 2015; Ramos, 2003).

Figure 14 – Main effect of steam explosion pretreatment on the biomass to improve delignification.



Source: The author.

Figure 15 – Lignin yields (Y_L) by steam explosion followed by acetosolv at reaction times 180, 90, 45, and 22.5 min from raw oil palm mesocarp fibers (ROPMF), and exploded oil palm mesocarp fibers (EOPMF), raw sugarcane bagasse (RSCB), and exploded sugarcane bagasse (ESCB)



Source: The author.

Depolymerisation and repolymerisation reactions compete via formation of a carbanium-ion in common during steam explosion. At high severities (R_o>3.2), repolymerisation reactions seem to dominate. Under such conditions, the formation of new condensed substructures occurs in lignin structure (C-C new bonds type β-β, β-1, and β-5) (Li et al., 2007). These new linkages are more difficult to hydrolyse, which hinders biomass delignification.

However, the steam explosion in this study was carried out at a severity of 3.0. This led to a majority of depolymerisation reactions, which facilitate lignin extraction, without the formation of condensed structures in the lignin. Maniet and co-workers studied the effect of increased steam explosion severity on lignin extraction yield (Maniet et al., 2017). The lignin yield did not significantly increase at severity above 3.2, supporting our findings. Furthermore, the lignin amount in the exploded fiber remained similar to the untreated fiber (37.7 ± 2.6% for OPMF, 28.2 ± 1.6% for SCB), due mostly to the lower severity of the steam explosion which was not able to degrade significantly the lignin in the fiber. Additionally, the exploded fibers were not washed after steam explosion which allowed the hydrolyzed hemicellulose remained in the fiber impacting the relative lignin content. Previous study showed no significant changes in the relative lignin content of in the biomass exploded at higher severity (3.7) (Marques et al., 2020).

The results show that SCB is less recalcitrant than OPMF, and therefore more easily hydrolysed. This is probably due to the higher amount of OPMF lignin that maintains more rigid and compact fibers, hindering lignin extraction. Furthermore, it is well known that the chemical properties of lignin depend directly on the plant species that originate the biomass, the extraction process, and the additional chemicals added for lignin extraction (Grossman and Wilfred, 2019). The proportion of lignin monomers and oxidised monomers, such as ferulates and coumarates, contribute to recalcitrance by hindering extraction (Ragauskas et al., 2014). In addition, the structure and composition of plant cell walls are distinct between the two biomasses, resulting in the observed differences in lignin production and characteristics. **Figure 15** shows the results of lignin extraction via steam explosion and acetosolv at reference and lower reaction times.

Steam explosion pretreatment promoted an increase in the lignin yield when the acetosolv standard condition was used for both biomasses. The increase in lignin yield was in agreement with the reported literature (Maniet et al., 2017; Ouyang et al., 2015). Decreasing the acetosolv reaction time reduces process efficiency, and the Y_L of both types of biomass (raw and exploded) decreased. The best Y_L values of the raw biomasses were achieved by the exploded ones at shorter reaction times, i.e., ~90 min for the exploded OPMF, and ~45 min for the exploded SCB (the reference reaction time for both raw biomasses was 180 min). These shorter reaction times leads to a reduced process severity and energy consumption which indicates a greener approach. Therefore, it was possible to reduce in 75% the energy consumption in acetosolv maintaining the lignin yield the for SCB. The difference between SCB lignin yields at 45 min was ~30% when using steam explosion pretreatment (**Figure 15**). However, the difference between OPMF lignin yields at 90 min was not significant, with an increase of merely 5%. In this case, it would be better to use the steam explosion pretreatment followed by acetosolv with the reference reaction time (180 min) to achieve a higher Y_L of ~70% (an increase of ~15%). The steam-explosion effect is more pronounced in biomass with lower lignin content, which is probably due to the higher recalcitrance promoted by lignin, hindering the mechanical and chemical attack of steam explosion on lignocellulosic biomass. It is possible to overcome this difference by increasing steam explosion reaction time for biomasses with higher lignin content.

Steam explosion followed by organosolv was found to be more efficient in the lignin extraction than the low transition temperature mixtures (LTTM) (Balaraman and Rathnasamy, 2020; Yiin et al., 2018). Saha et al. successfully achieved similar yield using ionic liquid at higher temperature from SCB (Saha et al., 2017). For OPMF, Rashid et al. obtained higher lignin yield than the present study (Rashid et al., 2018). Despites being two-step process, steam explosion followed by organosolv seems to be more advantageous than these processes, due lesser and cheaper chemicals involved, shorter reaction time, high-quality end-products such as lignin and cellulose, and possible solvent recovery. However, organosolv is still facing challenges that hinders its competitive commercialization due high process cost (i.e., the solvent type and solvent recovery system) (Zhang et al., 2016). The combination with steam explosion can reduce process severity process, which leads to a more feasible technology. **Table 5** summarizes recent studies about lignin extraction using several treatments.

Therefore, in this study, we defined an acetosolv reaction time of 180 min for the raw SCB and 45 min for pretreated SCB (severity process reduction with maintenance of lignin yield), and 180 min for raw and pretreated OPMF lignin extraction process (lignin yield improvement). Accordingly, lignins extracted from the several processes were designated as RSCL, ESCL, ROPL, and EOPL (R and E represent raw and exploded fibers, respectively).

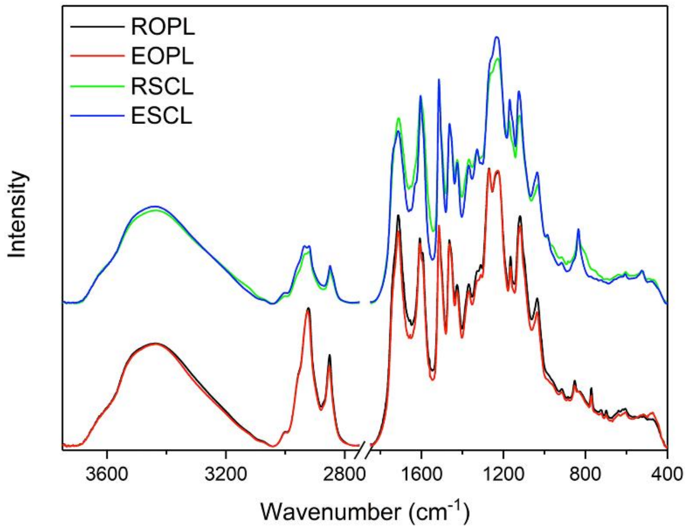
Table 5 – Lignin yield obtained from several lignocellulosic biomass and delignification processes.

Sample	**Method**	**Reagent**	**Condition**	**Yield**	
Oil palm mesocarp fiber	Organosolv	Acetic acid (93%), HCl (0.3%)	115°C, 180 min	63.0%	Souza et al., 2016
Corncob	Steam explosion plus organosolv	Ethanol (80%)	SE: pre-soaked 0.5% H_2SO_4, 10h. Then 1.5 MPa, 5 min Organosolv: 160°C, 120 min	40.94%	Ouyang et al., 2015
Corncob residue	Steam explosion plus organosolv	Dioxane (85%)	SE: pre-soaked 0.01 M HCl, 90°C, 120-720 min	21.2–57.3%	Zhang et al., 2019
Sugarcane bagasse	Organosolv	Acetic acid (95%), HCl (0.1%)	187°C, 40 min	64.3%	Pinheiro et al., 2017
Sugarcane bagasse	Microwave-assisted Organosolv	Acetic acid (90%), HCl (2.0%)	MW: 0,5 kW, 110°C, 30 min	77–84%	Avelino et al., 2019
Sesame straw	Microwave-assisted lignin solubilization by LTTM	CLG	MW: 0.7 kW, 12 min	63.2%	Balaraman and Rathnasamy, 2020
Sugarcane bagasse	Ionic liquid	1-ethyl-3-methylimidazolium acetate	140°C, 120 min	90.1%	Saha et al., 2017
Oil palm mesocarp fiber	Ionic liquid	Pyridinium formate	88.8°C, 240 min,	91.2%	Rashid et al., 2018
Sugarcane bagasse	Hot water plus alkaline treatment	NaOH (15%)	HW: 70°C, 120 min Alkaline: 98°C, 90 min	86%	Moubarik et al., 2013
Corn stalk	Steam explosion plus alkaline treatment	NaOH	SE: 1.1-1.8 MPa, 5-10 min Alkaline: 10 g/L NaOH, 120°C, 120 min	5.98–9.43%	Wang and Chen, 2014
Oil palm mesocarp fiber	Organosolv	Acetic acid (93%), HCl (0.3%)	115°C, 180 min	48.5%	Nogueira et al., 2019

3.3.2 The effect of steam explosion on lignin structure

The main characteristics of functional groups in lignin and the structural changes caused by extraction processes were assessed using Fourier-transform infra-red spectroscopy. **Figure 16** shows the FTIR spectra for ROPL, EOPL, RSCL, and ESCL, which were standardised according to the reference band at 1513 cm^{-1}, attributed to the aromatic skeleton of lignin. Baselines were corrected at the same points in all spectra.

Figure 16 – FTIR spectra of raw oil palm mesocarp lignin (ROPL), exploded oil palm mesocarp lignin (EOPL), raw sugarcane bagasse lignin (RSCL), and exploded sugarcane bagasse lignin (ESCL).



Source: The author.

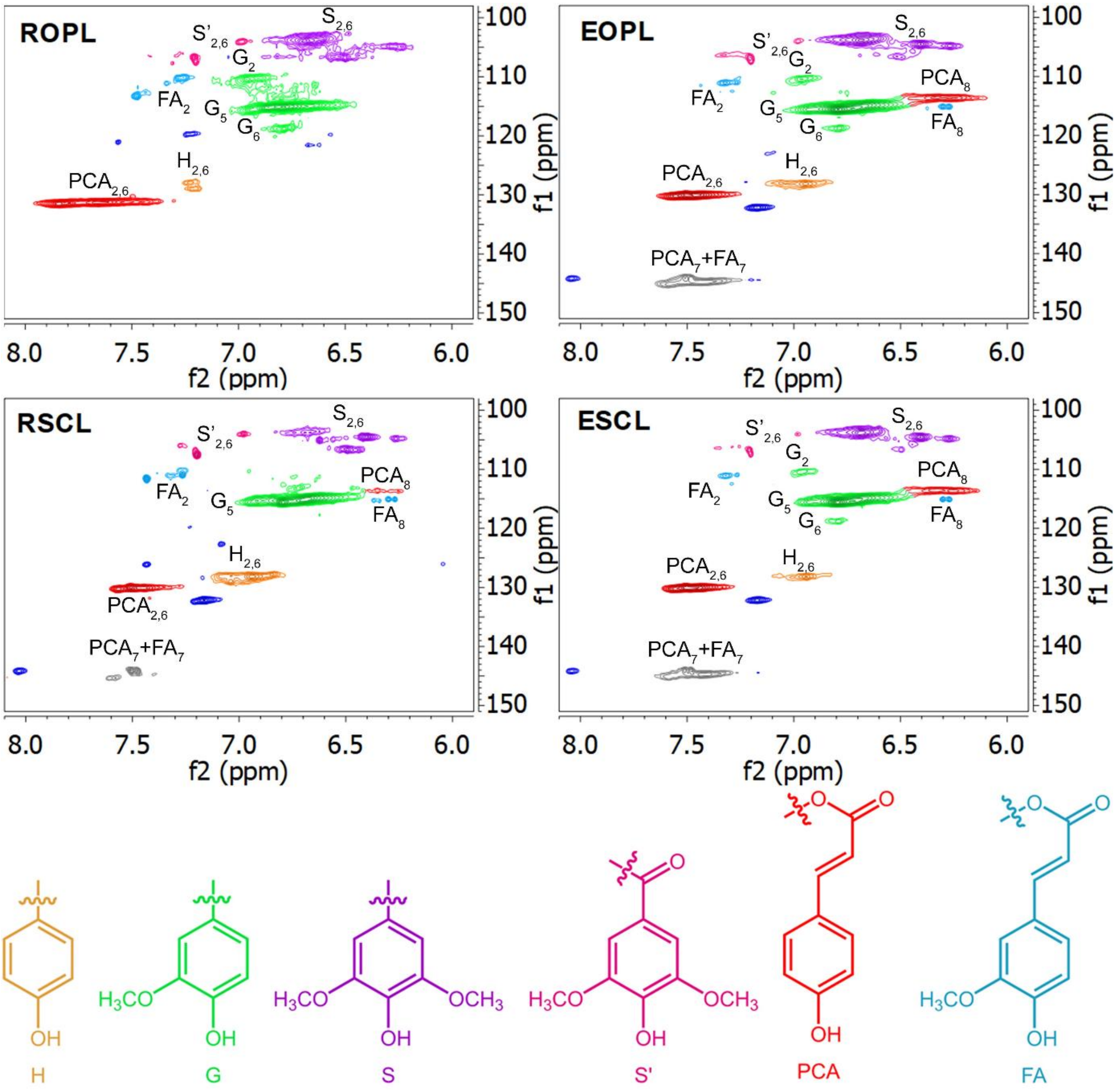
Broad bands were observed in the spectral range of 3700-3000 cm^{-1}, which were attributed to the stretching vibration of the aliphatic and phenolic -OH groups in hydrogen bonding (Moubarik et al., 2013). Absorption bands relative to aliphatic -CH groups from methyl and methylene stretches appeared at 2924 cm^{-1} and 2852 cm^{-1}, respectively. These bands were more prominent in OPMF lignins, probably due to the presence of residual oil remaining during the industrial oil-extraction process. OPMF presents 5–6% of fatty acids, mostly lauric, hexadecenoic, and oleic acid (Dal Prá et al., 2016).

The almost imperceptible shoulder-type peak observed around 1740 cm^{-1} may indicate partial acetylation promoted by the acetic acid used in the acetosolv extraction process. The band at 1710 cm^{-1} (combined to 1268, 1166, and 1117 cm^{-1}) is attributed to the C=O stretch in the unconjugated ketone, carbonyl, and ester groups, which is related to the residual lignin-carbohydrate complexes (LCC) that remained in lignin linked by ester bonds (Avelino et al., 2019a). This band is slightly shorter in the exploded lignins than in the raw ones, indicating a decrease in hemicellulose content, a typical effect of the steam-explosion process at high severity (Wang and Chen, 2014). However, despite the removal of hemicellulose, all values of lignin purity were approximately the same: that is, 85.8% for ROPL, 87.9% for RSCL, 86.8% for EOPL, and 84.4% for ESCL. These values are similar to those reported by Pinheiro et al. (2017) and Souza et al. (2016) using acetosolv. The low severity of the steam explosion used in this study likely did not significantly enhance hemicellulose hydrolysis. On the other hand, higher severity would improve lignin purity while decreasing lignin yield due to the formation of new condensed structures by repolymerisation reactions, as seen in a previous study (Marques et al., 2020).

FTIR spectra showed that the lignin structure was composed of all 3 types of monomers: *p*-hydroxyphenyl (H), guaiacyl (G), and syringyl (S) units. Strong absorptions were observed around 1600 cm^{-1} and 1513 cm^{-1} (C=C stretching of aromatic ring), 1462 cm^{-1} (CH deformations), and 1425 cm^{-1} (aromatic skeletal vibrations coupled with CH in plane deformation), which are related to aromatic skeletal vibrations from lignin. Other vibrations typically from lignin were observed as well, such as in 1268 cm^{-1} and 1222 cm^{-1} attributed to guaiacyl units, as well as C-C and C=O stretches. Moreover, the band at 1121 cm^{-1} (typical GS lignin) combined with 1166 cm^{-1} (typical HGS lignin) suggests that all lignins belong to the HGS type, according to the classification system proposed by Faix (1991). The spectra profiles of all extracted lignins were quite similar, which is another indication that the "core" of lignin structure was not significantly affected by the low-severity steam explosion pretreatment and acetosolv process, as demonstrated in previous work (Marques et al., 2020).

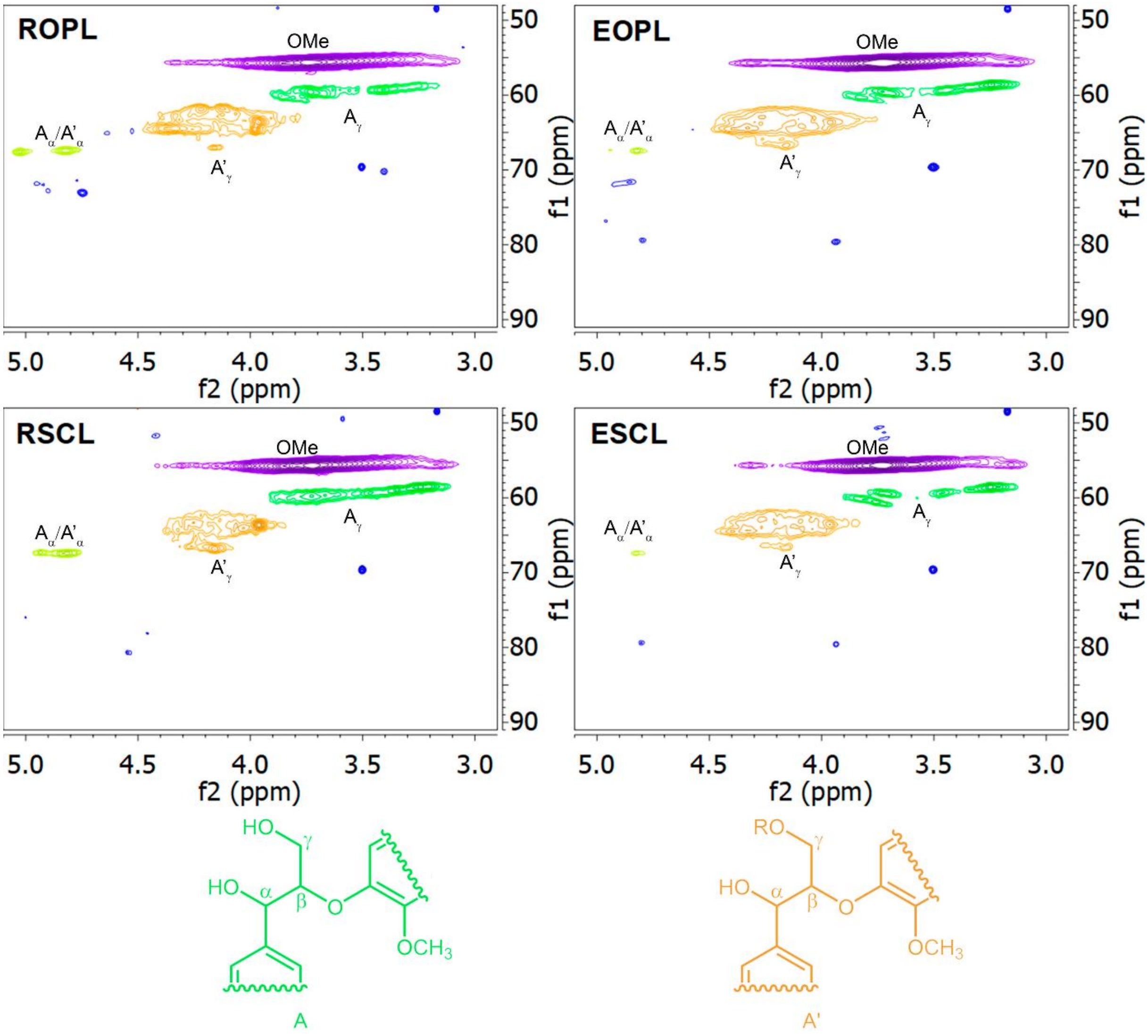
The lignin structural characterisation was also assessed using two-dimensional heteronuclear single quantum coherence spectroscopy (2D-HSQC). The spectra of lignin indicate three characteristic regions of ^{13}C-^{1}H correlations corresponding to the non-oxygenated aliphatic region, oxygenised aliphatic side chain region, and aromatic region. Structural information for the aromatic region (δ_C/δ_H 150-100/8.0-6.0) and side chain region (δ_C/δ_H 90-50/5.0-3.0) is provided in **Figure 17** and **Figure 18**, respectively. The ^{13}C-^{1}H signal correlations of the 2D-HSQC spectra were assigned according to previous studies (Avelino et al., 2019a; Pang et al., 2017; Wen et al., 2013; Zhang et al., 2019).

Figure 17 – Aromatic region of the 2D-HSQC spectra of raw oil palm mesocarp lignin (ROPL), exploded oil palm mesocarp lignin (EOPL), raw sugarcane bagasse lignin (RSCL), and exploded sugarcane bagasse lignin (ESCL).



Source: The author.

Figure 18 – Side-chain region of the 2D-HSQC spectra of raw oil palm mesocarp lignin (ROPL), exploded oil palm mesocarp lignin (EOPL), raw sugarcane bagasse lignin (RSCL), and exploded sugarcane bagasse lignin (ESCL).



Source: The author.

All lignins extracted from both biomasses with or without steam explosion pretreatment showed similar signatures, indicating few structural modifications, in agreement with FTIR results. The aromatic region in the lignins suggests the presence of syringyl, guaiacyl, and *p*-hydroxyphenyl units, in accordance with FTIR results.

Syringyl units showed different cross-signals at δ_C/δ_H 103.9/6.67 ($S_{2,6}$), while guaiacyl units showed different specific cross-signals at δ_C/δ_H 118.8/6.79, δ_C/δ_H 115.6/6.80, and δ_C/δ_H 110.4/6.96 (G_6, G_5, and G_2, respectively). However, it was not possible to detect correlations related to G_2 and G_6 in RSCL. The *p*-hydroxyphenyl units showed signals at δ_C/δ_H 128.1/6.95 and δ_C/δ_H 115.1/6.70 ($H_{2,6}$ and $H_{3,5}$, respectively). Cross-signals of oxidised syringyl units at δ_C/δ_H 115.1/6.70 (S'$_{2,6}$) and signals for the ester of *p*-coumaric acid at δ_C/δ_H 130.1/7.48 and δ_C/δ_H 115.1/6.29 (PCA$_{2,6}$ and PCA$_8$, respectively) were observed. The signal at δ_C/δ_H 144.0/7.50 was attributed to the overlapping of C_7-H_7 correlations for the ester of *p*-coumaric acid and etherified ferulic acid structures (PCA$_7$ and FA$_7$).

In the oxygenised aliphatic region (δ_C/δ_H 90-50/6.0-2.5), a typical strong signal for lignin was observed in δ_C/δ_H 55.8/3.72, attributed to methoxyl groups. The predominant presence of the β-O-4 substructures in δ_C/δ_H 59.6/3.20-3.80 (C_γ-H_γ), δ_C/δ_H 67.4/4.82 (C_α-H_α), and δ_C/δ_H 63.3/4.25 (acylated C_γ-H_γ) confirms that the lignins are mainly composed of A-type structures, which means that the monomers are linked by β-O-4 alkyl-aryl ether bonds. The acetosolv process results in partial acetylation of aliphatic hydroxyls in the α- or γ-positions of the lignin structure, which was confirmed by a slight shoulder-type peak at 1740 cm^{-1} in their FTIR spectra. It was not possible to detect signs of other lignin substructures in the oxygenised aliphatic region formed by the repolymerisation of lignin (β-β, β-1, β-5).

It is worth pointing out that the relative proportions of monomers, S/G, and H/G ratios were very similar to each other (**Table 6**). This shows that the steam explosion did not significantly change the lignin structure. Furthermore, the relative proportions in the SCB were similar to previous studies using organosolv process (Avelino et al., 2019a). However, Nogueira et al. and Pinheiro et al. found respectively OPMF and SCB with high content of H and G units which probably related to differences in the conditions in the biomasses plantations such as weather, soil type, etc (Nogueira et al., 2019; Pinheiro et al., 2017).

Table 6 – Relative content of lignin monomers based on the integration of 2D-HSQC cross-peaks of raw oil palm mesocarp lignin (ROPL), exploded oil palm mesocarp lignin (EOPL), raw sugarcane bagasse lignin (RSCL), and exploded sugarcane bagasse lignin (ESCL).

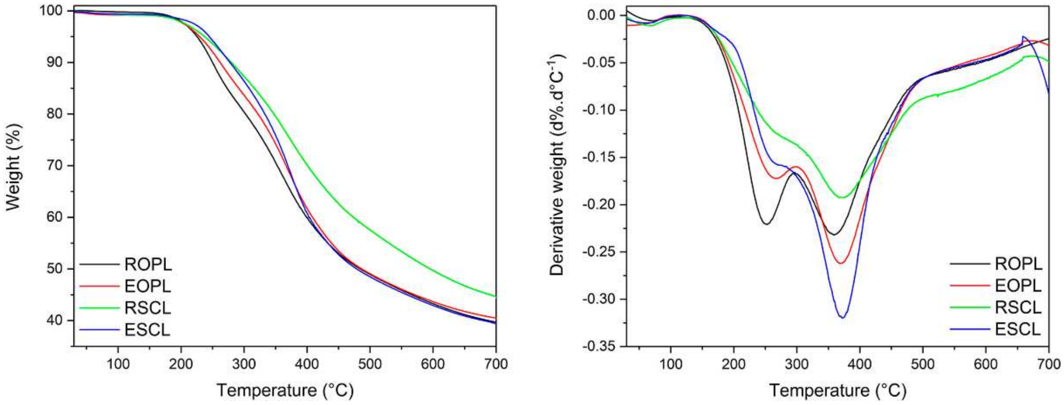
Sample	H (%)	G (%)	S (%)	FA (%)	PCA (%)	S/G ratio	H/G ratio
ROPL	25	46	28	2	23	0.6	0.5
EOPL	28	48	24	5	22	0.5	0.6
RSCL	26	51	23	6	15	0.5	0.5
ESCL	28	49	23	7	22	0.5	0.6

As a consequence of autohydrolysis, steam explosion pretreatment causes competition between two types of acid-catalysed reactions: depolymerisation and repolymerisation. Repolymerisation reactions seem to dominate only in severity (log R_o) above 3.2 (Li et al., 2007). The absence of other types of lignin substructures supports the hypothesis that under the imposed conditions (log $R_o = 3.0$), depolymerisation reactions predominantly occurred during the process. In addition, the lignin structures are composed mainly of H and G units, indicative of very reactive lignins suitable for high-value-added applications, such as in the resins and materials fields.

3.3.3 The effect of steam explosion on lignin thermal characteristics

Thermal characteristics of lignin were assessed using thermogravimetric analysis. The TGA/dTG curves of lignins are shown in **Figure 19**. All lignins show similar thermal stability, with a small weight loss (less than 1%) up to 100 °C, which is probably water. The exploded lignins showed a slight improvement in the initial temperature of degradation (T_{onset}), probably due to the removal of impurities such as hemicellulose, as observed in **Table 7**.

Figure 19 – Thermogravimetric curves (TGA and dTG) for raw oil palm mesocarp lignin (ROPL), exploded oil palm mesocarp lignin (EOPL), raw sugarcane bagasse lignin (RSCL), and exploded sugarcane bagasse lignin (ESCL).



Source: The author.

Table 7 – Thermal events for raw oil palm mesocarp lignin (ROPL), exploded oil palm mesocarp lignin (EOPL), raw sugarcane bagasse lignin (RSCL), and exploded sugarcane bagasse lignin (ESCL).

Sample	**T_{onset} (°C)**	**T_{max} (°C)**	**CY (%)**	**LOI (%)**
ROPL	198.5	360.0	39.7	33.4
EOPL	208.0	370.8	40.5	33.7
RSCL	212.1	373.3	44.7	35.4
ESCL	218.4	372.5	39.4	33.3

Source: The author.

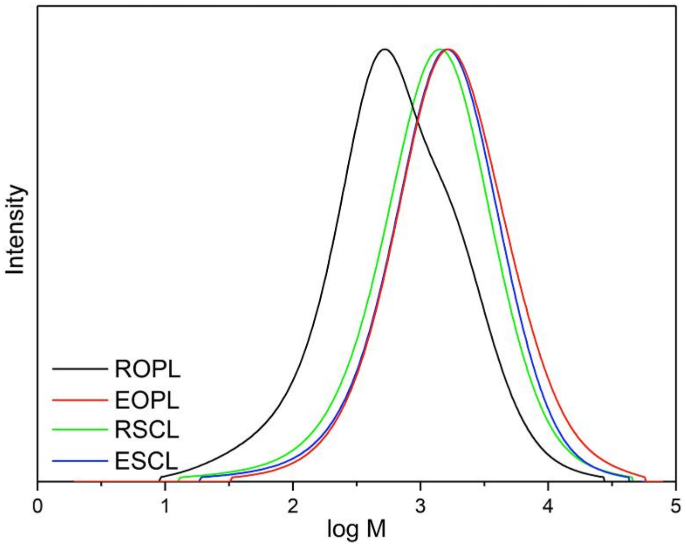
Lignins showed the first thermal degradation event occurring in a range from 200 to 300 °C, related to the presence of impurities such as hemicellulose and/or low molecular weight lignin. In the second thermal event, the maximum temperature of weight loss occurred in the range from 360 °C to 375 °C and is attributed to the cleavage of internal lignin bonds. Lignins presented similar char residue at 700 °C, around 40%, which is likely a mixture of carbonaceous residue and ash from degradation and/or condensation of aromatic rings in the inert atmosphere (Sun et al., 2001). The exploded lignins presented similar T_{onset} and T_{max} to previous studies but with higher char residue (Avelino et al., 2019a; Souza et al., 2016).

Char residue, also known as char yield (CY), is related to the ability of a material to be flame-retardant. The limit oxygen index (LOI) is the minimum O_2 concentration required to maintain combustion (after ignition) in a polymer and can be used to relate flame retardancy and CY. This relation is expressed as a percentage by the equation (van Krevelen, 1975): $LOI = 17.5 + 0.4CY$. Samples with LOI greater than 28 ($CY > 26.3$) can be considered self-extinguishing, a material that would stop burning after the removal of the fire or ignition source (Mallakpour and Zadehnazari, 2017). According to **Table 7**, the CY of lignins is higher than 26.3, which means that the lignins may be a fire-retardant material. OPMF and SCB organosolv lignins in this study present higher LOIs than coconut shell lignins obtained by similar processes (Avelino et al., 2019b). This indicates that the biomass source plays a major role in the structure and properties of lignin. Application of these lignins as a phenol substitute in resins or adhesives may grant the self-extinguishing property to the new material.

3.3.4 The effect of steam explosion on lignin molecular weight

Gel permeation chromatography (GPC) was used to determine the number average molecular weight ($\overline{M}_n$), weight average molecular weight ($\overline{M}_w$), and polydispersity index (PDI, $\overline{M}_w/\overline{M}_n$) of all extracted lignins. The chromatograms of the molar weight distributions are shown in **Figure 20**, and **Table 8** summarises the data obtained from the chromatograms.

Figure 20 – GPC images for raw oil palm mesocarp lignin (ROPL), exploded oil palm mesocarp lignin (EOPL), raw sugarcane bagasse lignin (RSCL), and exploded sugarcane bagasse lignin (ESCL).



Source: The author.

Table 8 – Number average molecular weight ($\bar{M}_n$), weight average molecular weight ($\bar{M}_w$) and polydispersity index (PDI) for raw oil palm mesocarp lignin (ROPL), exploded oil palm mesocarp lignin (EOPL), raw sugarcane bagasse lignin (RSCL), and exploded sugarcane bagasse lignin (ESCL).

Sample	**$\bar{M}_n$ (g.mol^{-1})**	**$\bar{M}_w$ (g.mol^{-1})**	**PDI**
ROPL	317	1614	5.1
EOPL	945	3926	4.2
RSCL	603	2913	4.8
ESCL	723	3161	4.4

Source: The author.

Steam explosion pretreatment resulted in an extracted lignin with higher molar weight and lower polydispersity than those extracted without this pretreatment, which is in line with previous work (Marques et al., 2020). Steam explosion may have promoted the increase in specific surface area due to fiber shattering, enabling the extraction of lignins with higher molecular weights. This led to narrowing of the polydispersity, with a more pronounced effect in the OPMF lignins. The higher molecular weight lignin may also be related to the breakdown of the aryl-ether bonds (more likely β-O-4 bonds) in the lignin structure, followed by repolymerisation reactions during the steam explosion (Li et al., 2007). Repolymerisation reactions increase the number of carbon-carbon bonds that are more difficult to break, leading to high molecular weights. The increase in the molecular weight after steam explosion pretreatment may indicate that condensation reactions have occurred (Zhang et al., 2019). High molecular weight lignins seem to be less reactive and less suitable for condensation reactions in adhesives and resin reactions (Mansouri and Salvadó, 2006). However, steam explosion promoted a significant increase in molecular weight only in exploded OPMF lignin, which could make EOPL less reactive than ESCL. This fact makes both raw and exploded SCB lignin more suitable to synthesis in materials science than OPMF lignins.

3.4 Conclusions

Steam explosion pretreatment can be used to improve lignin extraction from sugarcane bagasse and oil palm mesocarp fiber, either by decreasing acetosolv severity via reaction time reduction, or by increasing lignin yield. Biomasses with lower lignin content, such as sugarcane bagasse, are more affected by the pretreatment, with which the acetosolv reaction time can be reduced to 25% of the reference value, maintaining the same lignin yield. Biomasses with higher lignin content are more resistant to this type of pretreatment. However, maintaining the same acetosolv reaction time (and severity), the pretreatment improved lignin yield by 16%. In addition, high-purity and high-quality lignins were obtained using steam explosion pretreatment; these lignins had structural characteristics similar to those of lignin extracted from raw fibers. Sugarcane bagasse lignin seems to be a better option than oil palm mesocarp fiber lignin for application in material science because of its higher lignin yield and higher thermal stability.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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4 OPTIMIZATION BY RESPONSE SURFACE METHODOLOGY OF ETHANOSOLV LIGNIN EXTRACTION FROM COCONUT FIBER, OIL PALM MESOCARP FIBER, AND SUGARCANE BAGASSE

Abstract

The optimization of lignin recovery from coconut fiber (CF), oil palm mesocarp fibers (OPMF), and sugarcane bagasse (SCB) using ethanol organosolv was investigated as well as the resulting lignin characteristics. Ethanol organosolv lignin recovery was successfully optimized, and the lignin yield (Y_L) was maximized. Ethanol concentration and temperature higher than 74% and 187°C maximized the Y_L, playing a significant role in lignin yield. Y_L was higher for SCB than for others biomasses. High-purity and high-quality lignins were obtained with slightly different structural characteristics among the raw materials. The obtained lignins were HGS type with purity higher than 86%. SCB lignin seemed to be a better choice than CF and OPMF lignin for application in aromatic polymerization, because of its higher lignin yield, higher purity, higher thermal stability, and more reactive sites.

Keywords: Biomass; Lignocellulosic fiber; Central composite design; Lignin characterization; Ethanol organosolv.

4.1 Introduction

The substitution of non-renewable resources, especially products derived from the petrochemical industry, has increased interest in the utilization of lignocellulosic biomass. Lignocellulosic biomass is currently used as an energy source in industrial ovens and boilers. This represents underutilization or a low rate of return on biomass use. This is because these types of biomasses are rich in macromolecules with potential industrial interest, particularly lignin. Lignin is a phenol-rich biomacromolecule that can be used in the development of several technologies and high-value-added products such as phenolic-based resins and adhesives, polyurethane foams, hydrogels, anti-UV and antimicrobial additives, among others (JĘDRZEJCZAK et al., 2021; MENG et al., 2019; NASCIMENTO et al., 2021).

Lignins are complex amorphous aromatic polymers with three-dimensional cross-linked structures, mainly composed of three phenylpropane units: *p*-coumaryl alcohol (H), coniferyl alcohol (G), and sinapyl alcohol (S) (LI et al., 2020). Lignins can be classified based on their abundance of these basic units as type-G (softwood lignin), type-GS (hardwood lignin), type-H-G-S (grass lignin), and type-H-G (compression wood lignin) (LI et al., 2015). It is estimated that the annual production of lignin varies in the range of 5–36 × 10^8 tons (BAJWA et al., 2019).

Lignin is usually obtained as a byproduct of the pulp and paper industry: kraft lignin, soda lignin, and lignosulfonate. The process for obtaining these lignins often involves several chemicals with potential environmental hazards. A possible solution is the use of organosolv lignin extraction, which is a greener process for obtaining high-yield and high-quality lignin, showing interest characteristics such as lower carbohydrate content, lower molecular weight, higher reactive sites, among others (BROSSE; SANNIGRAHI; RAGAUSKAS, 2009; EL HAGE et al., 2010; MARQUES et al., 2021; WEI KIT CHIN et al., 2020). The organosolv process is based on the solubilization of hemicellulose and lignin from biomass using recoverable organic solvents, such as methanol, ethanol, acetic acid, acetone, or mixtures of organic solvent and water in the temperature range of 100−250 °C for several minutes or hours (KAZZAZ; FATEHI, 2020). The literature reports that the organosolv extraction efficiency is a function of solvent type and concentration, reaction temperature and time, catalyst, and biomass recalcitrance (MARQUES et al., 2021; THORESEN et al., 2020). The resulting lignin characteristics depend on its chemical structure and properties, which in turn depend on the biomass source (FAIX, 1991). Therefore, process optimization is required to achieve the highest lignin recovery after precipitation.

Process optimization aims to determine the best reaction conditions for maximum lignin yield. In addition, it can give a lignin extraction pattern behavior in relation to those variables, which makes it possible to manipulate the structure of the lignin depending on the conditions employed. Process optimization can be conducted using the central composite design (CCD), allied to the response surface methodology (RSM), which allows modeling several variables in the same experiment, saving experiment time and consumables with high statistical power.

In the past few years, our group has been working on the improvement of biopolymer extraction and characterization from important worldwide biomasses such as coconut fiber (CF), oil palm mesocarp fiber (OPMF), and sugarcane bagasse (SCB), aiming at sustainable approaches and biomass valorization (MARQUES et al., 2020, 2021; NASCIMENTO et al., 2016; PINHEIRO et al., 2017; ROSA et al., 2010). These biomasses play a major role worldwide, mostly in Brazil, Malaysia, India, China, Indonesia, and the Philippines due to their abundance, underutilization, and being a renewable source of biopolymers of industrial interest, such as cellulose nanocrystals and lignin. There are no reports in the literature that aimed to evaluate the best conditions for ethanosolv lignin extraction and the characteristics of lignin obtained from CF, OPMF, and SCB, which presents an opportunity to promote biomass valorization.

In this study, the organosolv process using ethanol as a solvent (hereafter referred to as ethanosolv) was optimized as an extraction method for lignin from CF, OPMF, and SCB, three important Brazilian lignocellulosic biomasses. The lignin characteristics under each optimum condition were evaluated by thermal behavior, chemical structure, and composition using Klason lignin (purity), two-dimensional heteronuclear single quantum coherence spectroscopy (2D-HSQC), Fourier transform infrared spectroscopy (FTIR), gel permeation chromatography (GPC), thermogravimetry analysis (TGA), and differential scanning calorimetry (DSC), in order to assess their use as building blocks or additives for high-value-added products, such as resins, adhesives, low molecular weight phenolic compounds, and multifunctional hydrocarbons.

4.2 Material and methods

4.2.1 Biomasses

In this study, CF, OPMF, and SCB were used as lignocellulosic biomass. The CF, OPMF, and SCB used were supplied by Embrapa Agroindústria Tropical (Fortaleza, Brazil), Embrapa Amazônia Oriental (Pará, Brazil), and DIAGEO (Paraipaba, Brazil), respectively. The biomass was dried in an air-circulating oven at 50 °C until constant weight, and milled in a pilot mill (Fritsch Pulverisette 19 mill) with a 0.5 mm sieve. All solvents and reagents were of analytical grade and were used as received without any modification. The cellulose and lignin contents of the biomasses were analyzed according to TAPPI standard procedures (T203 cm-99 and T222 om-2). The holocellulose and hemicellulose contents were determined by the procedure described by Yokohama et al. (YOKOYAMA; KADLA; CHANG, 2002). The lignin concentration in CF, OPMF, and SCB are 32.2 %, 28.4%, and 24.1%, respectively. The main compositions of the studied biomasses are presented in **Table 9**.

Table 9 – Main composition of the studied biomasses.

Biomass	Cellulose	Hemicellulose	Lignin

CF	27.9%	23.0%	32.2%
OPMF	24.5%	28.4%	34.8%
SCB	37.6%	31.4%	24.1%

4.2.2 Ethanosolv process

Lignin extraction was performed in a mini high-pressure reactor (Berghof Highpreactor BR-300), with a total volume of 500 mL, without external agitation. First, 20 g (dry weight) of fiber were added to 200 mL of ethanol solution (in the studied range concentrations, **Table 10**) with sulfuric acid (0.5%, v/v) as the catalyst. After the designed reaction time, the reactor was cooled to ~25 °C and opened. The obtained hydrolyzed material was filtered using a Büchner funnel with 28 µm filter paper to separate the hydrolyzed material from black liquor (BL). The hydrolyzed solid material was washed with a two-fold warm (60 °C) ethanol solution at the same concentration used in the extraction process to extract the remaining lignin. To precipitate the lignin, the BL was diluted to three volumes of distilled water and left to rest for 24 h. The precipitated lignin was filtered using a paper filter with an 8 µm pore, washed with distilled water until constant pH, and dried in an air-circulating oven at 50 °C until a constant weight was achieved. The lignin yield was calculated using Equation 3.

$$Y = \left(\frac{m_L}{m_{IL}}\right) \times 100 \qquad (3)$$

where Y_L is the yield of lignin extracted on a dry basis (%), m_L is the obtained recovered lignin after precipitation on a dry basis (g), and m_{IL} is the initial mass (dry basis) of lignin in the fibers before the process (g). The mass of lignin was obtained using the Klason lignin method (Section 2.4.1).

4.2.3 Experimental design and statistical analysis

Temperature (T), reaction time (t), and ethanol concentration (C) were optimized by central composite design 2^3 (CCD). The CCD comprised eight factorial points, six axial points, and five center points, resulting in a total of 19 treatment points. Response surface methodology (RSM) was applied to determine the effects of T, t, and C on Y for CF, OPMF, and SCB.

Analysis of variance (ANOVA) was used to determine the effect of independent variables (T, t, and C) on the dependent variable Y (**Table 12**, **Table 13**, and **Table 14**). The p-values and lack of fit (LoF) as well as the coefficients of determination (R^2) were used to evaluate the suitability of the models. The models were validated by comparing the experimental results obtained under optimal conditions and the predicted values obtained by the models. Statistical analysis of the data and response surface plots was performed using Design Expert v. 11.

The conditions were as follows: temperature 156–224 °C; reaction time 26–94 min; and ethanol concentration, 35%–85% (v/v). The catalyst concentration (H_2SO_4 0.5%, v/v) was constant, as was the ratio of fiber to ethanol solution (1:10, w/v) in all experiments. The complete experimental matrix is presented in **Table 10**.

4.2.4 Lignin characterization

4.2.4.1 Lignin structure and composition

The purity of lignin samples was calculated as the sum of the acid-insoluble lignin (Klason lignin) and acid-soluble lignin (TAPPI, 2002). A lignin sample (1.0 g) was mixed with 17 mL of H_2SO_4 (72 wt%), ground in a mortar for 15 min at room temperature, and kept at rest for 24 h. The solution was diluted with deionized water until 4 wt% H_2SO_4 was added and refluxed for 4 h. Then, the system was cooled for 30 min at room temperature. The acid-insoluble lignin was obtained by vacuum filtration using a #4 sintered glass funnel and washed with deionized water until neutrality was achieved. The acid-insoluble lignin was dried in an air-circulation oven at 50 °C for 24 h. The acid-soluble lignin was calculated based on the UV absorbance at 215 nm and 280 nm of the diluted filtrate (4 wt% H_2SO_4, 1:10 by volume). All experiments were performed in triplicate.

2D-HSQC spectra were obtained using a 600 MHz DD2 NMR spectrometer (Agilent) equipped with a 5-mm One Probe (^2H-^{19}F/^{15}N-^{31}P) with a z-axis field gradient (MARQUES et al., 2020). The sample powder (50 mg) was dissolved in 500 µL of DMSO-d6 with the aid of an ultrasonic bath for 24 h to promote better solubilization. The DMSO solvent peak at δ_C/δ_H 39.5/2.49, was utilized as an internal reference. The relative abundances of the lignin units were calculated based on the volume integration of the cross-peaks of each structure and expressed as a percentage of the total summation with *p*-hydroxyphenyl (H), guaiacyl (G), and syringyl (S) units equal to 100 %, as previously reported (WEN et al., 2013). Lignin monomers in the oxidized forms, such as ferulate (FA) and *p*-coumarate (*p*CA), were included as part of each related monomer. Similarly, the relative contents of the lignin linkages were performed. Data analysis was performed using MestReNova v. 12.0.

FTIR spectra were obtained using a PerkinElmer Spectrum Two™ FT-IR spectrometer using KBr pellets with a sample concentration of 5 wt% (MARQUES et al., 2020). The spectra were recorded between 4000 cm^{-1} and 400 cm^{-1} with a resolution of 4 cm^{-1} using an arithmetic average of 32 scans. FTIR data were processed and analyzed using the PerkinElmer Spectrum™ IR software.

GPC analyses were performed using a Shimadzu LC-20AD (Kyoto, Japan) at 40 °C using a setup comprising two analytical GPC columns in series (Phenogel 5 μ 50 Å and Phenogel 5 μ 103 Å, 4.6 mm × 300 mm, Phenomenex) (AVELINO et al., 2019). HPLC-grade THF was used as mobile phase at flow rate of 0.35 mL min^{-1}. Lignin samples (2 mg) were dissolved in 2 mL HPLC-grade THF and then filtered using a 0.22 μm PTFE filter. The filtered solution (20 μL) was injected into the GPC system at a flow rate of 0.35 mL min^{-1} and monitored by UV–Vis detector (Shimadzu SPD-M20A) at 280 nm. Standard calibration was performed using polystyrene standards PSS (Mw range 162–1.3×10^5 g mol^{-1}).

4.2.4.2 Thermal behavior of lignins

TGA and derivative thermogravimetry (dTG) analyses were performed using an STA 6000 thermal analyzer (PerkinElmer) (AVELINO et al., 2019). All measurements were performed under N_2 atmosphere with a gas flow of 50 mL.min^{-1} and a heating rate of 10 °C.min^{-1} and heated from 30 °C to 900 °C. The mass of the sample was approximately 10 mg.

DSC analyses were performed using a TA Instruments calorimetry model Q20 (AVELINO et al., 2019). Lignin (5–7 mg) was first submitted to an annealing program (from 25 to 90 °C for 10 min and cooled from 90 °C to 0 °C for 3 min). Then, the sample was heated from 0 to 200 °C under a N_2 atmosphere at a flow rate of 50 mL min^{-1} and a heating rate of 10 °C min^{-1}. Hermetic closed aluminum pans were used in the experiment.

4.3 Results and discussion

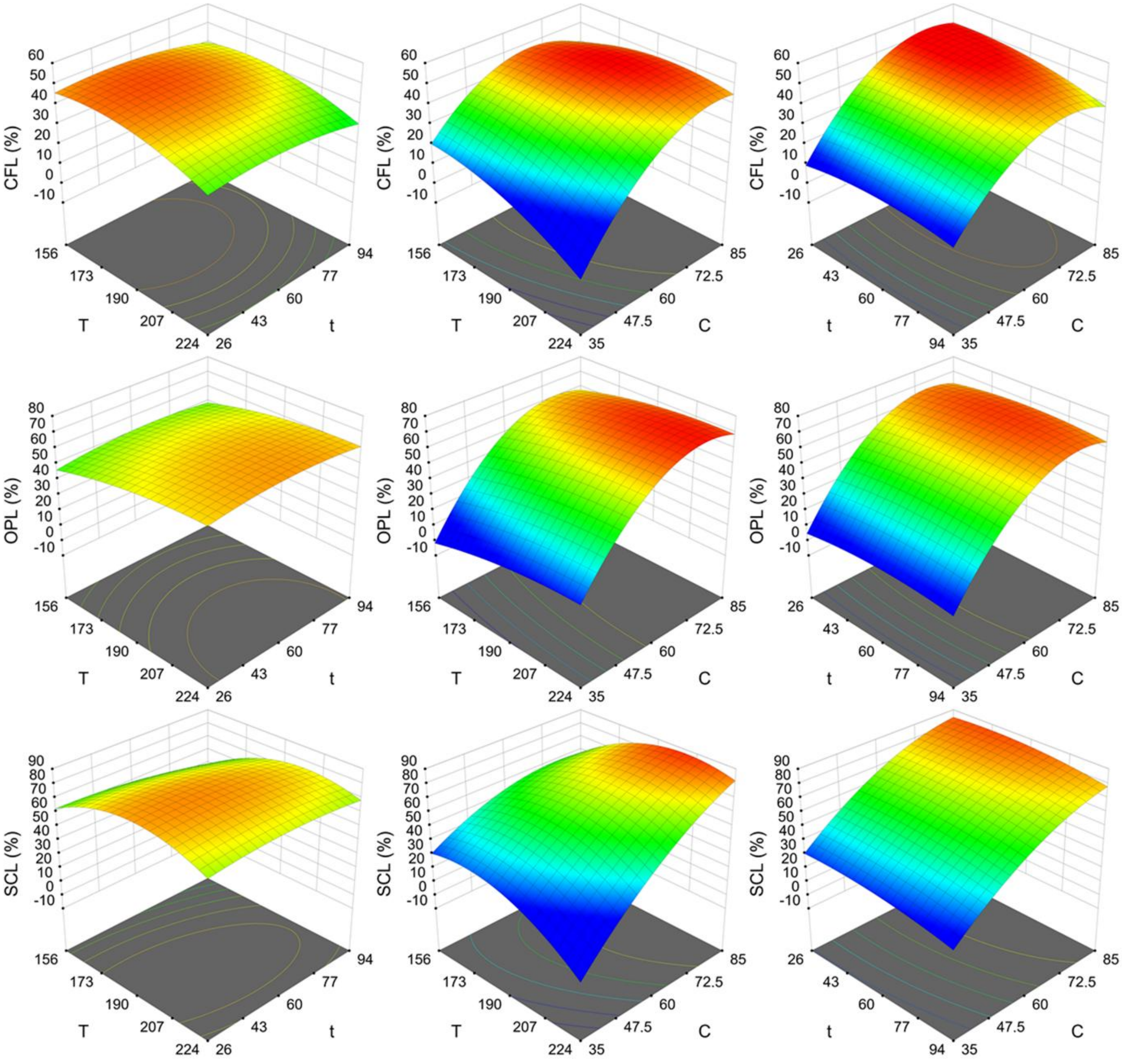
4.3.1 Ethanosolv process optimization

The results of the lignin extraction yield (Y_L) from CF, OPMF, and SCB according to the experimental matrix are summarized in **Table 10**. ANOVA was used to examine the significance of the mathematical models that were obtained from all biomasses (**Table 12**, **Table 13**, and **Table 14**). **Table 11** summarizes the effects of the variables on lignin yield.

The coefficient of determination (R^2) for CF, OPMF, and SCB was higher than 0.95, with a confidence interval of 95% ($\alpha = 0.05$), which is an indication of highly significant relationships between experimental values and values predicted by the models. Model p-values were less than 0.0001, showing that the lignin yield models are significant at a confidence interval of 95% and satisfied by Equations (4), (5), and (6).

The lack of fit (LoF) had no significant effect on the model. Therefore, there was no evidence of a lack of adjustment in the obtained models for all the fibers. Because the models were significant, it was possible to build response surfaces. **Figure 21** shows the response surface plots of the lignin yields for the biomasses as a function of two process variables. The other variable was kept constant at the central level.

Figure 21 – Effects of process variables on extraction yield of coconut fiber lignin (CFL), oil palm mesocarp fiber lignin (OPL), and sugarcane bagasse lignin (SCL). T (temperature), t (reaction time), and C (ethanol concentration)



Source: The author.

Table 10 – Independent and dependent variables of the experimental design and yield of ethanol organosolv lignin for CF, OPMF, and SCB.

Experiment	**Variables**			Y_{CF}	Y_{OPMF}	Y_{SCB}
	T	**t**	**C**			
1	170	40	45	35.87	26.59	54.00
2	170	40	75	51.55	61.57	68.51
3	170	80	45	30.74	25.08	41.94
4	170	80	75	44.74	63.78	67.04

5	210	40	45	21.84	36.83	34.09
6	210	40	75	51.00	74.04	77.88
7	210	80	45	19.80	38.42	36.58
8	210	80	75	42.06	71.76	71.76
9	156	60	60	46.58	56.98	56.30
10	224	60	60	39.11	61.89	53.81
11	190	26	60	44.23	57.22	70.44
12	190	94	60	45.87	61.31	61.60
13	190	60	35	13.88	12.01	27.28
14	190	60	85	50.09	66.15	90.60
15	190	60	60	44.22	64.69	71.46
16	190	60	60	51.84	56.96	67.78
17	190	60	60	44.96	61.33	67.85
18	190	60	60	49.02	61.98	64.24
19	190	60	60	45.93	62.46	67.29
avg 15 – 19	–	–	–	47.19	61.48	67.72
SD 15 – 19	–	–	–	3.18	2.83	2.56

Note: (1) avg 15 – 19: average of the central point experiments from 15 to 19.

(2) SD 15 – 19: standard deviation of the central point experiments from 15 to 19.

Source: The author.

$$Y_{CF} = -156.41162 + 1.22087\,T + 0.45469\,t + 2.31851\,C - 0.00508\,T^2 - 0.00313\,t^2 - 0.02610\,C^2 + 0.00030\,Tt + 0.00906\,TC - 0.00357\,tC \tag{4}$$

$$Y_{OPMF} = -321.02773 + 1.45026\,T + 0.49432\,t + 5.88651\,C - 0.00304\,T^2 - 0.00318\,t^2 - 0.03738\,C^2 - 0.00044\,Tt - 0.00131\,TC - 0.00007\,tC \tag{5}$$

$$Y_{SCB} = -289.77629 + 3.64991\,T - 0.37885\,t - 0.06210\,C - 0.01283\,T^2 - 0.00314\,t^2 - 0.01670\,C^2 + 0.00310\,Tt + 0.01640\,TC + 0.00083\,tC \tag{6}$$

Table 11 – Effect of variables on the increase of lignin yield from biomasses.

Biomass	**R^2**	**p-value**	**LoF**	**Variable**						**Y**
				Linear			**Quadratic**			
				T	**t**	**C**	**T^2**	**t^2**	**C^2**	
CF	0.9541	< 0.0001	0.4159	↓	–	↑↑	–	–	↓↓	↑

OPMF	0.9762	< 0.0001	0.2097	↑	−	↑↑	−	−	↓↓	↑
SCB	0.9661	< 0.0001	0.1021	−	−	↑↑	↓	−	↓	↑

↑ - Good and direct effect; ↓ - Good and inverse effect; ↑↑ - Great and direct effect; ↓↓ - Great and inverse effect
− - No significant effect.
Source: The author.

Variable T had a significant positive linear effect on Y for the OPMF. This means that the lignin yield increased when the temperature increased within the studied range. In contrast, T had a significant negative linear effect on Y for CF and a negative quadratic effect for SCB. For CF and SCB, lignin yield increases at temperatures below 200 °C, which is in accordance with previous optimization studies for ethanol organosolv (PAN et al., 2006, 2007). This result may be related to the lower recalcitrance of CF and SCB owing to the lower lignin content. Low recalcitrance biomass may require less energy in the form of heat to break the compact biomass structure and achieve maximum lignin recovery.

Variable C showed significant positive linear and negative quadratic effects for all biomass types. The variable C had the highest effect compared to the other variables, which indicates that lignin yield is highly dependent on the ethanol concentration in the studied range. Moreover, the negative quadratic effect indicates that there is an optimum maximum ethanol concentration within the studied range. Increasing the ethanol concentration to a range of 60%–80% led to an increase in lignin yield, as expected (WEI KIT CHIN et al., 2020). High ethanol content solutions favor the delignification due to the polar interactions that ethanol provides, leading to a better lignin solubilization (NOVO; CURVELO, 2019). Variable t had no significant effect on the response of all biomasses. The studied range of reaction times may have hindered the detection of the reaction time effect, i.e., the applied reaction time range resulted in small changes in lignin yield.

The models showed similarities between themselves. First, ethanol concentration played a greater positive role than temperature and reaction time on lignin yield, because it had a higher significance (lowest p-value) among the independent variables (data available in the Supplementary Material). This was also found in a previous study using corncob as a source of lignin (MICHELIN et al., 2018). The second similarity is that the reaction time did not affect the lignin yield within the studied range. Hence, the shortest reaction time may be used within this experimental domain. These behaviors were also observed by PAN et al. (2007), who found that increasing the reaction temperature and ethanol concentration in lignin extraction from lodgepole pine caused higher lignin yields. However, the reaction time did not affect the delignification process. The same behavior was observed in a previous study of hybrid poplar (PAN et al., 2006).

Table 12 – Analysis of Variance (ANOVA) for CF model.

CF	Sum of squares	df	Mean square	F-value	p-value	significance
Model	2187.205	9	243.023	20.810	0.00005	significant
T	121.746	1	121.746	10.425	0.01034	
t	29.829	1	29.829	2.554	0.14446	
C	1476.601	1	1476.601	126.439	0.00000	
Tt	0.117	1	0.117	0.010	0.92262	
TC	59.063	1	59.063	5.057	0.05110	
tC	9.178	1	9.178	0.786	0.39842	
T^2	56.437	1	56.437	4.833	0.05549	
t^2	21.407	1	21.407	1.833	0.20878	
C^2	470.727	1	470.727	40.308	0.00013	
Residual	105.105	9	11.678			
LoF	64.770	5	12.954	1.285	0.41588	not significant
Pure Error	40.335	4	10.084			
Cor Total	2292.310	18				

Table 13 – Analysis of Variance (ANOVA) for OPMF model.

OPMF	Sum of squares	df	Mean square	F-value	p-value	significance
Model	5224.481	9	580.498	41.017	0.00000	significant
T	200.185	1	200.185	14.145	0.00448	significant
t	3.485	1	3.485	0.246	0.63163	
C	4053.915	1	4053.915	286.442	0.00000	significant
Tt	0.244	1	0.244	0.017	0.89846	
TC	1.233	1	1.233	0.087	0.77454	
tC	0.003	1	0.003	0.000	0.98812	
T^2	20.146	1	20.146	1.423	0.26333	
t^2	22.140	1	22.140	1.564	0.24256	
C^2	965.386	1	965.386	68.212	0.00002	significant
Residual	127.374	9	14.153			
LoF	95.411	5	19.082	2.388	0.20973	not significant

Pure Error	31.963	4	7.991			
Cor Total	5351.855	18				

Table 14 – Analysis of Variance (ANOVA) for SCB model.

SCB	Sum of squares	df	Mean square	F-value	p-value	significance
Model	4493.489	9	499.277	28.515	0.00001	significant
T	17.256	1	17.256	0.986	0.34678	
t	75.057	1	75.057	4.287	0.06832	
C	3709.137	1	3709.137	211.836	0.00000	significant
Tt	12.280	1	12.280	0.701	0.42401	
TC	193.592	1	193.592	11.056	0.00887	significant
tC	0.490	1	0.490	0.028	0.87082	
T^2	359.572	1	359.572	20.536	0.00142	significant
t^2	21.486	1	21.486	1.227	0.29670	
C^2	192.774	1	192.774	11.010	0.00897	significant
Residual	157.585	9	17.509			
LoF	131.296	5	26.259	3.995	0.10210	not significant
Pure Error	26.289	4	6.572			
Cor Total	4651.075	18				

Delignification during ethanol organosolv is a combination of the depolymerization and solubilization of lignin. Lower ethanol concentrations promote high acid-catalyzed cleavage of ether bonds in lignin structure due to higher hydrogen ion concentrations, whereas high ethanol concentrations increase lignin solubilization. Therefore, a balance between the ethanol-water ratio may exist for lignin extraction, according to MONTEIL-RIVERA et al. (2012). Later, the authors reported that lignin yield increases with ethanol concentration, catalyst concentration, and temperature. These findings are similar to this study.

PINHEIRO et al. (2017) investigated lignin extraction from sugarcane bagasse using acetic acid organosolv and found similar reaction time and temperature effects to this work. However, because lignin is more soluble in acetic acid than ethanol, a lower temperature is necessary to maximize the lignin extraction. XU et al. (2006) studied several types of organic solvents and their proportions in organosolv pulping at 85 °C for 4h. Aqueous organic acid was more effective for delignification of wheat straw than aqueous organic alcohol under the conditions used. In contrast, organic acids are more toxic and corrosive than ethanol, making ethanol more suitable for this type of extraction. As demonstrated above, the three biomasses led to three different extraction conditions, indicating that the delignification process occurs differently according to the biomass. Nevertheless, it was demonstrated here that the delignification process is strongly dependent on the ethanol concentration and temperature.

The models indicate a set of conditions that maximize the response, also known as critical values (**Table 15**). In summary, the observed values under the optimal conditions were very close to the predicted values, which shows the great capability of RSM to predict lignin yield in the studied range for all biomasses. The higher lignin yield obtained here indicates that ethanol organosolv leads to greater cleavage of ether bonds compared to other processes. The higher the cleavage of ether bonds in the lignin substructures, the higher the dissolution of lignin fragments (NASCIMENTO et al., 2016). Accordingly, recovered optimized lignins from CF, OPMF, and SCB were designated as coconut fiber lignin (CFL), oil palm mesocarp fiber lignin (OPL), and sugarcane bagasse lignin (SCL).

Table 15 – Optimal condition, predicted yield (Y_P), observed yields (Y_O), and purity for the obtained lignin from the biomasses.

Biomass	**Condition**			**Y_P (%)**	**Y_O (%) ***	**P (%) ***
	T (°C)	**T (min)**	**C (%)**			
CF	187	26	74	52.5	51.6 ± 3.2	86.3 ± 3.1
OPMF	218	26	75	68.7	73.9 ± 2.2	88.7 ± 1.5
SCB	200	26	85	85.7	83.4 ± 1.7	97.3 ± 4.9

Note: *Values are the mean of triplicate measurements ± standard deviation.

Source: The author.

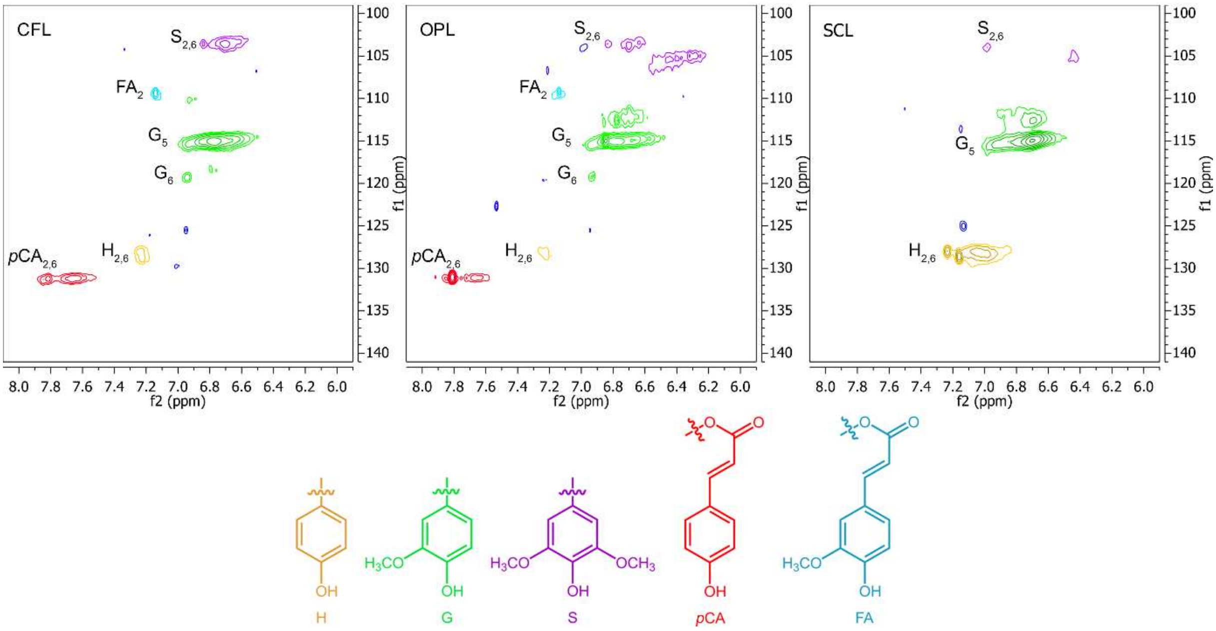
4.3.2 Lignin characteristics

4.3.2.1 Lignin structure and composition

The structural elucidation of lignins was evaluated by 2D-HSQC spectroscopy. Structural information for the aromatic region (δ_C/δ_H 150–100/8.0–6.0) is provided in **Figure 22**. **Table 16** shows the relative contents of lignin monomers (H, G, and S). The ^{13}C-^{1}H signal correlations of the 2D-HSQC spectra were assigned according to previous studies (MARQUES et al., 2021; WEN et al., 2013).

All extracted lignins were composed of similar monomer units, composed of syringyl (S), ferulate (FA), guaiacyl (G), *p*-hydroxyphenyl (H), and *p*-coumarate (*p*CA) units in different proportions, according to the biomass source (**Table 16**). The detection of oxidized monolignols, such as FA and *p*CA, could indicate the presence of carbohydrates linked to the lignin structure. It was not possible to detect oxidized structures to sugarcane bagasse lignin, indicating that SCL has high purity among the samples according **Table 16**.

Figure 22 – Aromatic region of the 2D-HSQC spectra of coconut fiber lignin (CFL), oil palm mesocarp fiber lignin (OPL), and sugarcane bagasse lignin (SCL).



Source: The author.

Table 16 – Relative content of lignin monomers and linkages based on the integration of 2D-HSQC cross-peaks of coconut fiber lignin (CFL), oil palm mesocarp fiber lignin (OPL), and sugarcane bagasse lignin (SCL).

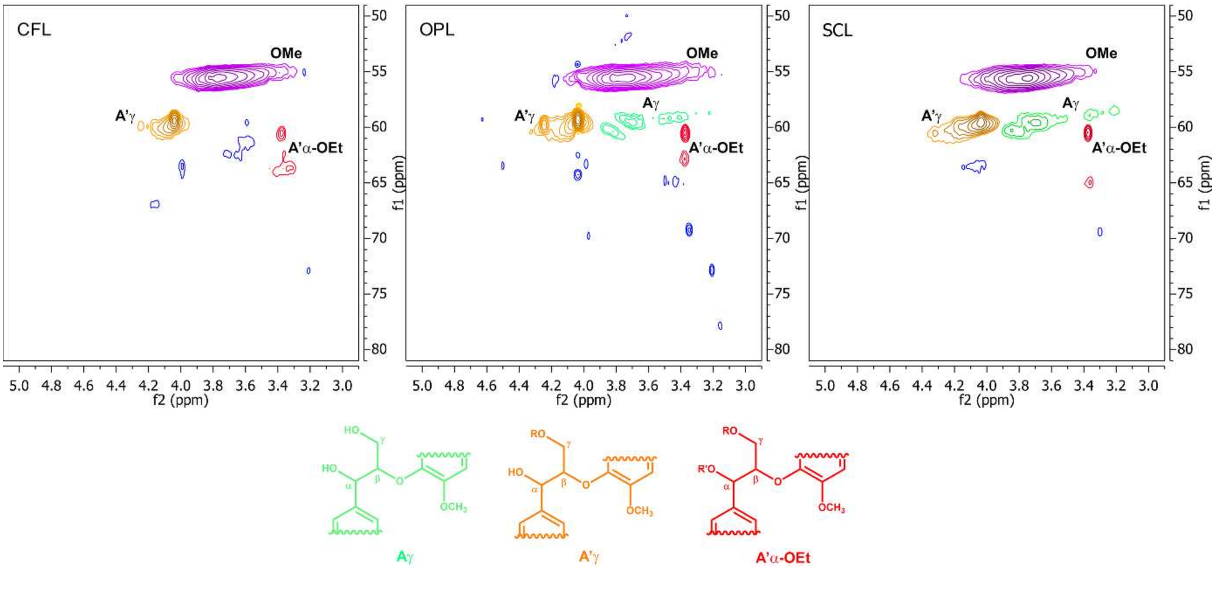
Sample	**H (%)**	**G (%)**	**S (%)**	**FA (%)**	**pCA (%)**	**Aγ (%)**	**A’γ (%)**	**A’α (%)**
CFL	22.0	59.5	18.5	3.1	11.9	11.7	64.8	23.4
OPL	20.1	55.9	24.0	3.0	12.3	18.1	70.1	11.8
SCL	25.9	61.1	12.9	–	–	31.5	57.1	11.4

Source: The author.

Lignins extracted from CF, OPMF, and SCB were classified as type HGS owing to the presence of the three basic units. The lignin monomers in this type of lignin usually vary in the range of 25%–50% S units, 25%–50% G units, and 10%–25% H units (LI et al., 2015). A high content of H units and low content of S units are the best structural characteristics for lignin application as building blocks in resins and adhesives. According to El Mansouri and Salvadó, H and G units have unsubstituted C-3 and C-5 positions in the aromatic rings of phenolic aryl propane units, which are important reactive sites for the preparation of lignin-based phenol–formaldehyde (e.g., adhesives, chelating resins, and ion exchange resin) under alkaline conditions (MANSOURI; SALVADÓ, 2006).

Regarding the oxygenated aliphatic region of the 2D-HSQC (**Figure 23**), it was observed that all lignin were composed of similar linkages, such as Aγ (non-acetylated β-aryl ether), A'γ (acetylated β-aryl ether), and Aα (ethoxylated β-aryl ether). **Table 16** shows the relative content of the linkages. The presence of Aα suggested that the ethanol organosolv may insert ethoxyl groups in the aliphatic portion of the lignins. This behavior was observed in other studies (BAUER et al., 2012; ZIJLSTRA et al., 2020). Under acid conditions and high temperature, benzylic cation intermediate forms that could lead to oxidation (Hibbert ketones) or condensation reaction in the presence of elevated water content. When ethanol content is higher, ethoxylation could occurs at the carbon-α of the lignin aliphatic portion, suppressing degradation reactions (ZIJLSTRA et al., 2020).

Figure 23 – Aromatic region of the 2D-HSQC spectra of coconut fiber lignin (CFL), oil palm mesocarp fiber lignin (OPL), and sugarcane bagasse lignin (SCL).

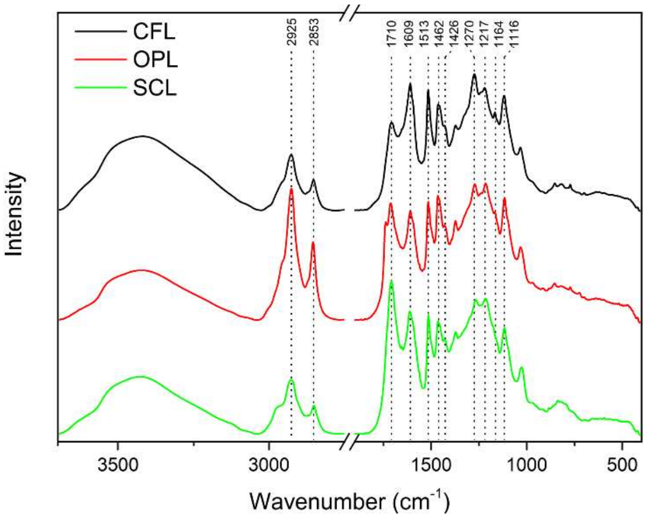


Source: The author.

The functional group characteristics of the lignins and the structural differences among the biomasses were assessed using FTIR spectroscopy. **Figure 24** shows the FTIR spectra of CFL, OPL, and SCL. The spectra were standardized according to the reference band at 1513 cm^{-1}, which was attributed to the aromatic skeleton of lignin. Baselines were corrected at the same points in all spectra.

Stretching vibrations of the aliphatic and phenolic -OH groups in hydrogen bonding were observed in the spectral range of 3700–3000 cm^{-1}. The aliphatic CH groups from the methyl and methylene stretches appeared at 2925 cm^{-1} and 2853 cm^{-1}, respectively. In the OPL, these bands were more prominent than CFL and SCL, which is related to the presence of residual oil remaining during the industrial oil extraction process (MARQUES et al., 2021).

Figure 24 – FTIR spectra of coconut fiber lignin (CFL), oil palm mesocarp fiber lignin (OPL), and sugarcane bagasse lignin (SCL).



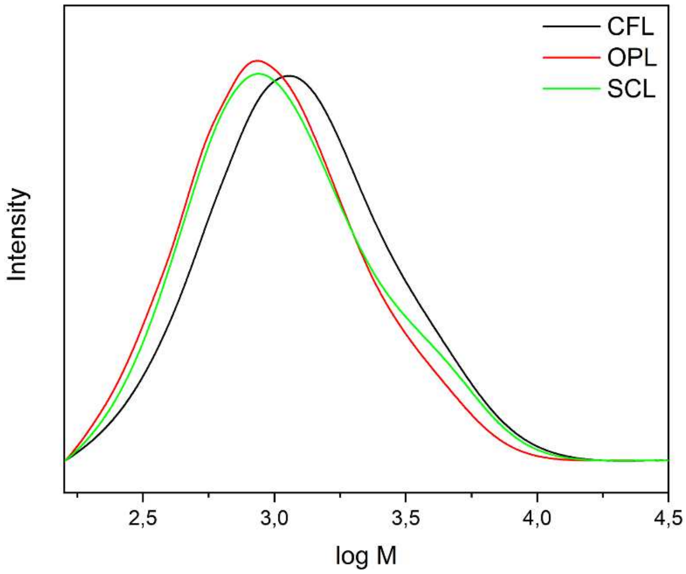
Source: The author.

The band around 1710 cm^{-1} is attributed to the C=O stretch related to residual carbohydrates, which is indicative of lignin-carbohydrate complexes (LCCs) that remain in lignin linked by ester bonds (AVELINO et al., 2019). This band is higher in SCL, associated with the high amount of carbohydrate in sugarcane bagasse, which was not hydrolyzed despite the high temperature of the extraction. However, SCL showed higher purity (**Table 15**) among the lignins, which could be associated with the presence of some pseudo-lignin. Pseudo-lignin is a lignin-like material that is formed under high severity low-pH biomass pretreatments, being a combination of carbohydrate and lignin degradation products (SHINDE et al., 2018). Pseudo-lignin differs mainly from real lignin due to presence of condensed structures derived from furfural (FF) and 5-hydroxymethylfurfural (5-HMF). In addition, a characteristic carbohydrate band was found at 1041 cm^{-1}, assigned to C–O and C–C stretching vibrations in polysaccharides (RATANASUMARN; CHITPRASERT, 2020).

Strong absorptions related to aromatic skeletal vibrations from lignin were observed at 1609 cm^{-1}, 1513 cm^{-1}, 1462 cm^{-1}, and 1426 cm^{-1}. Additionally, all three types of monomers were present in the lignin spectra: *p*-hydroxyphenyl (H), guaiacyl (G), and syringyl (S) units at 1116 cm^{-1} (typical GS lignin) combined with 1164 cm^{-1} (typical HGS lignin), and vibrations at 1270 cm^{-1} and 1217 cm^{-1} attributed to guaiacyl units, as well as C-C and C=O stretches. This suggests that all lignins belong to the HGS type (FAIX, 1991) which was confirmed by RMN analysis.

GPC curves were used to evaluate the molecular weight distributions of the lignins. **Table 17** summarizes the molecular weight data obtained from **Figure 25**. All lignins presented a similar molecular weight and low polydispersity index, as expected for organosolv lignins (KAZZAZ; FATEHI, 2020). Organosolv lignins usually have lower molecular weights than other lignin types (i.e., kraft or lignosulfonate), which could be related to lower steric hinder and a higher reactivity.

Figure 25 – GPC curves of coconut fiber lignin (CFL), oil palm mesocarp fiber lignin (OPL), and sugarcane bagasse lignin (SCL).



Source: The author.

Table 17 – Apparent $\bar{M}_w$ (weight average), $\bar{M}_n$ (number average), and polydispersity ($\bar{M}_w/\bar{M}_n$) coconut fiber lignin (CFL), oil palm mesocarp fiber lignin (OPL), and sugarcane bagasse lignin (SCL).

Sample	**$\bar{M}_n$ (g.mol^{-1})**	**$\bar{M}_w$ (g.mol^{-1})**	**PDI**
CFL	879	1535	1.75
OPL	734	1233	1.68
SCL	771	1357	1.76

Source: The author.

Previous studies using the acetosolv method reported higher $\overline{M}_w$ for lignins from CF, OPMF, and SCB (MARQUES et al., 2020; PINHEIRO et al., 2017). This may indicate that ethanosolv is a better method for breaking the β-O-4 linkages in the lignin structure. CFL showed the highest molecular weight among the lignins, which could be related to the lower severity of optimized ethanosolv extraction since organosolv extensively cleaved some inter-unit bonds in lignin, which is a function of the treatment time, temperature, and acidity of the medium (EL HAGE et al., 2010).

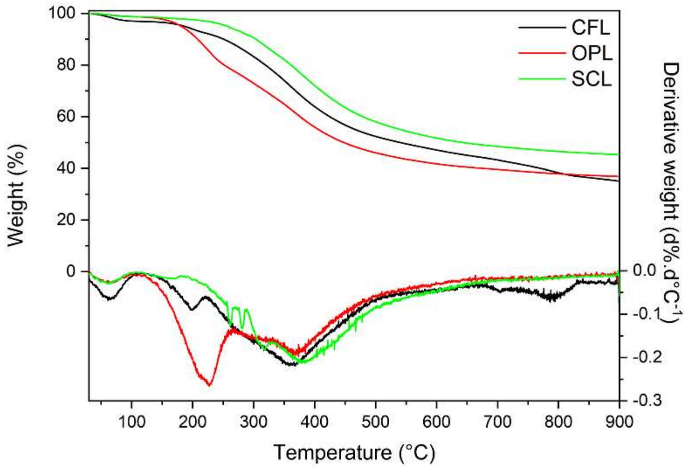
4.3.2.2 Lignins thermal behavior

The thermal properties of the lignins CFL, OPL, and SCL were evaluated through the analysis of thermal stability by TGA/dTG analyses and state transition analysis by DSC. **Table 18** summarizes the obtained thermal data, such as the onset degradation temperature (T_{onset}), maximum degradation temperature (T_{max}), char yield (CY), and glass transition temperature (T_g).

Figure 26 and **Figure** 27 show the TGA, dTG, and DSC curves, respectively. As shown in **Figure 26**, all lignins presented similar thermal profiles with some differences. OPL showed the lowest T_{onset} and T_{max}, probably related to the high content of impurities present in the OPMF lignins, such as residual oil. A previous study showed higher T_{onset} values obtained from dewaxed organosolv lignin from OPMF (OLIVEIRA et al., 2017). The absence of residual oil can improve the thermal properties of the OPL. However, SCL showed the best thermal properties with the highest T_{onset}, T_{max}, and CY related to high purity, as mentioned in **Table 15**.

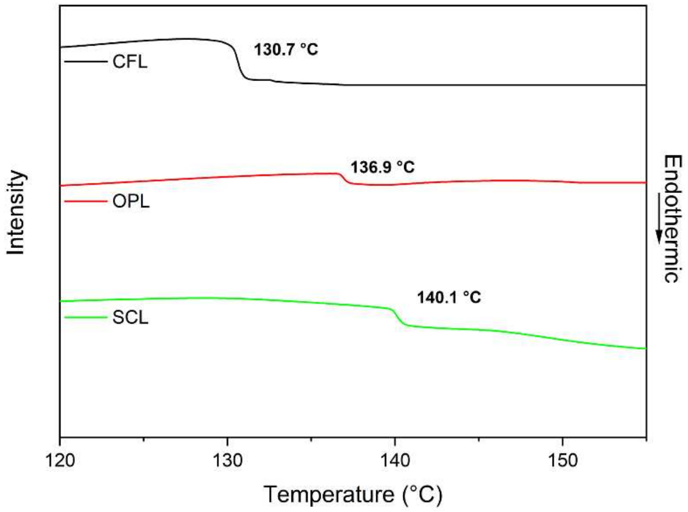
The CY is related to the potential of a material for flame retardancy. The relation is expressed as a percentage of the limiting oxygen index (LOI) using the following equation (VAN KREVELEN, 1975): $LOI = 17.5 + 0.4CY$. A CY higher than 26.3% (LOI > 28%) indicates that the polymer is self-extinguishing. All lignins showed CY values higher than 26.3%, indicating their potential to be applied in a material with a self-extinguishing characteristic. In addition, the use of lignin as an additive in polymeric materials can improve the thermal behavior, such as self-extinguishing and fire-retardant properties (CAYLA et al., 2016; DAI et al., 2020; SHUKLA et al., 2019).

Figure 26 – Thermogravimetric curves (TGA and dTG) of coconut fiber lignin (CFL), oil palm mesocarp fiber lignin (OPL), and sugarcane bagasse lignin (SCL).



Source: The author.

Figure 27 – DSC curves of coconut fiber lignin (CFL), oil palm mesocarp fiber lignin (OPL), and sugarcane bagasse lignin (SCL).



Source: The author.

Table 18 – Onset degradation temperature (T_{onset}), maximum degradation temperature (T_{max}), char yield (CY), limiting oxygen index (LOI), and glass transition temperatures (T_g) of the studied lignins.

Sample	**T_{onset} (°C)**	**T_{max} (°C)**	**CY (%)**	**LOI (%)**	**T_g (°C)**
CFL	174.8	359.2	35.0	31.5	130.7
OPL	172.9	227.3	36.9	32.3	136.9
SCL	234.4	383.0	45.3	35.6	140.1

Source: The author.

Amorphous polymers such as lignin undergo a state transition called glass transition (T_g), which is a transition from a glass-like rigid solid to a more flexible, rubbery compound. T_g is associated with material processability and indicates the start of molecular chain mobility when sufficient energy is supplied in the form of heat (PINHEIRO et al., 2017).

Several factors affect the T_g of lignin factors, such as the presence of low molecular weight contaminants (including water and solvents), extraction method, chemical modification, molecular weight, thermal history, and crosslinking (ALZAGAMEEM et al., 2018; MICHELIN et al., 2018). T_g is also related to the polymer molecular weight, which means that a high molecular weight is usually associated with a high T_g.

In addition, a high glass transition temperature is associated with strong bonding, probably due to hydrogen interactions, which hinder the mobility of the lignin chains. In **Table 18**, the lignins showed similar T_g values in a narrow temperature range of 130–140 °C. This indicates that the obtained lignins have strong inter- and intramolecular bonds. The obtained T_g values are in accordance with the literature, which shows a range from 100 to 150 °C for organosolv lignins (ALRIOLS et al., 2009; AVELINO et al., 2019; OLIVEIRA et al., 2017; RAMEZANI; SAIN, 2018).

4.4 Final discussion

The process of lignin extraction and characteristics, from the extraction process to compositional features and thermal behavior, have been elucidate in previous sections. Regarding the extraction process, SCB was highlighted because of its higher lignin recovery (83%) and the production of high-purity lignin (97%). Considering the potential use of lignin for phenolic polymerization reactions, the presence of abundant reactive sites in the aromatic ring is one of the most important features. Among the studied lignins, SCL showed the highest content of reactive sites, H and G units, and the lowest content of unreactive sites, S unit. This makes lignin more suitable for application in resins and adhesives. However, CFL and OPL also showed interesting monomeric composition, with over 75% of H or G units.

Another important characteristic of aromatic polymerization is its molecular weight. All studied lignins showed lower molecular weights, which may indicate lower steric hindrance around the phenolic reactive sites compared to other technical lignins (KAZZAZ; FATEHI, 2020). The lower steric hindrance of the lignin chains improves the contact between the reactants and the reactive sites, which leads to a better reactivity, making them more suitable for polymerization reactions (MANSOURI; SALVADÓ, 2006). These characteristics are important attributes for polymerization in lignin-based phenol–formaldehyde, such as adhesives, chelating resins, and ion exchange resins. This was clearly better in the sugarcane bagasse lignin than in the other lignin types. Moreover, all lignins showed high values of T_{onset} and LOI, indicating their potential for application in polymeric blends with high thermal degradation, which could also provide self-extinguishing and fire-retardant characteristics for these materials.

4.5 Conclusions

The ethanol organosolv method was successfully optimized using a central composite design based on response surface methodology. The ethanol concentration and temperature played a significant role in the lignin yield. However, reaction times within the range of 26–94 min did not influence the lignin yield. A reaction time of 26 min was sufficient to maximize the lignin yield. In addition, temperature, and ethanol concentrations higher than 187 °C and 74%, respectively, were required to maximize the lignin yield among the biomasses. The lignin yield varied according the type of biomass: 51.6% for CF, 73.9% for OPMF, and 83.4% for SCB. The obtained models were significant with p-values less than 0.0001, and there was no evidence of a lack of adjustment in the models. High-purity and high-quality lignins were obtained from optimized ethanol organosolv. These lignins had slightly different structural characteristics, mainly because of the raw materials from which they were extracted. SCB lignin seems to be a better choice than CF lignin and OPMF lignin for application in material science because of its higher lignin recovery, higher purity, higher thermal stability, and the presence of more reactive sites for polymerization in the aromatic ring. However, CF and OPMF cannot be set aside as a source of this macromolecule, because the lignins may require some purification.

4.6 Acknowledgements

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5 FINAL CONSIDERATIONS

This work demonstrated that organosolv delignification and steam explosion (SE) followed by organosolv delignification are interesting technologies for obtainment of high-yield and high-quality lignin from agroindustrial biomasses. The chemical and physical effects of steam explosion may increase the specific surface area of the lignocellulose leading to improvement in the subsequent process.

Furthermore, steam explosion at 168 °C and reaction time of 10 min provided a great improvement in organosolv. Acetosolv process was clearly improved by the increase of lignin yield over 15% in the SCB and OPMF and decrease of reaction time in four-fold while maintaining the lignin yield from SCB. Lower severity of SE (3.0) seemed to direct depolymerization reaction over repolymerization reaction of lignin structure. SE lignins showed properties that allows the application in phenolic resins such as phenol-formaldehyde adhesives and polybenzoxazine. It was possible to obtain lignin with high yield, high purity, high H and G units and low content of S unit, and low molecular weight.

Ethanol organosolv also was optimized using a central composite design based on response surface methodology. The most significant process variables were ethanol concentration and temperature which played a significant role in the lignin yield. It should have a balance in ethanol/water ratio due to ethanosolv be a combination of the depolymerization and solubilization of lignin. The lower ethanol concentrations, the higher hydrogen ion concentrations which cleavages ether bonds in lignin; high ethanol concentrations increase lignin solubilization. Temperature increase conduct to a more breakages of carbohydrate and hydrolisys and further better lignin solubilization. Reaction time did not influence in the variable range.

Moreover, high-purity and high-quality lignins were obtained from CF, OPMF, and SCB using optimized ethanosolv. Slightly different structural characteristics were detected, mainly because of the raw materials from which they were extracted. SCB lignin presented higher lignin yield, higher purity, higher thermal stability, and more reactive sites for polymerization which indicate phenolic resins application. Comparing the applied methods, ethanosolv led to better properties in lignin structure compared to acetosolv and SE followed by acetosolv. However, those later have milder conditions compared to optimized ethanosolv.

The obtained lignins have important characteristics that make them suitable to be applied as building block in lignin-based phenol-formaldehyde and polybenzoxazine resins as a substitute of petroleum-based products such as phenol. Compared to phenol, lignin is more available, less toxic, and, less expensive which make it an interesting candidate for this application. However, lignin is less reactive than phenol. For this purpose, the lignin should be reactive in the *ortho* position in the aromatic ring. Higher content of H and G units increase the lignin reactivity due the more presence of free *ortho* position.

The obtained lignins in this study, independent of the method, showed higher amount of H and G units (higher than 70% when combined) which may improve their reactivity. In addition, the lignin with low molecular weight is indicated to this application. In addition, lignins obtained in this thesis present characteristics of high reactivity with formaldehyde without needing further treatment. SCB lignins showed higher yield and purity, lower molecular weight, higher content of H and G units, higher thermal stability, and higher LOI which seems to be a better option over CF and OPMF lignins. These characteristics of organosolv lignin have made it an (almost) ready-made material that depends mainly on the extraction method and source of biomass that is extracted.

Finally, it can be concluded that OD and SEOD can be considered an interesting technology for obtention of high-yield and high-quality lignins from biomass with properties that allowed to be applied as building blocks in several technological applications mainly phenolic resins without any purification or method to increase reactivity.

6 PERSPECTIVES

In order to provide tailor-made lignins by varying the process parameters of steam explosion and ethanosolv, evaluation of process variables effects on lignin structure are required. Antioxidants, microbiological activity and cytotoxicity should be applied aiming widening of the range of lignin use as alternative petroleum-based compounds in other areas such as food, cosmetics and medical for example.

Lastly, the application of obtained lignins in synthesis of high-add valued products may be interesting of the point of view of increase of biomass valorization. Since organosolv lignin are better for this type of application as they do not require major modifications, the applied methods would help to establish as an alternative to traditional sulfur methods to obtain high-quality lignins.

7 PUBLICATIONS

7.1 Papers related to the thesis

International Journal of Biological Macromolecules 175 (2021) 304–312

Contents lists available at ScienceDirect

International Journal of Biological Macromolecules

journal homepage: http://www.elsevier.com/locate/ijbiomac

Steam explosion pretreatment improves acetic acid organosolv delignification of oil palm mesocarp fibers and sugarcane bagasse

Francisco Pereira Marques, MSc [a], Amanda Kelly Lima Soares, MSc [b], Diego Lomonaco, PhD [c], Lorena Mara Alexandre e Silva, PhD [d], Sandra Tédde Santaella, PhD [e], Morsyleide de Freitas Rosa, PhD [d], Renato Carrhá Leitão, PhD [d],*

[a] *Departament of Organic and Inorganic Chemistry, Federal University of Ceará, CEP: 60440-900 Fortaleza, CE, Brazil*
[b] *Escola de Química, Federal University of Rio de Janeiro, Rio de Janeiro, RJ, Brazil*
[c] *Departament of Organic and Inorganic Chemistry, Federal University of Ceará, 60440-900 Fortaleza, CE, Brazil*
[d] *Embrapa Agroindústria Tropical, Rua Dra. Sara Mesquita, 2270, CEP: 60511-110 Fortaleza, CE, Brazil*
[e] *Institute of Marine Science, Federal University of Ceará, Avenida da Abolição, 3207, CEP: 60165-081 Fortaleza, CE, Brazil*

I&EC research
Industrial & Engineering Chemistry Research

pubs.acs.org/IECR Article

Optimization by Response Surface Methodology of Ethanosolv Lignin Recovery from Coconut Fiber, Oil Palm Mesocarp Fiber, and Sugarcane Bagasse

Francisco P. Marques, Aldo S. Colares, Maria N. Cavalcante, Jessica S. Almeida, Diego Lomonaco, Lorena M. A. Silva, Morsyleide de Freitas Rosa, and Renato C. Leitão*

Cite This: *Ind. Eng. Chem. Res.* 2022, 61, 4058–4067 **Read Online**

7.2 Papers related to extra projects

Food Hydrocolloids 95 (2019) 487–495

Contents lists available at ScienceDirect

Food Hydrocolloids

journal homepage: www.elsevier.com/locate/foodhyd

Antioxidant films from mango kernel components

Pedro E.F. Melo[a], Ana Priscila M. Silva[a], Francisco P. Marques[b], Paulo R.V. Ribeiro[c], Men de sá M. Souza Filho[c], Edy S. Brito[c], Janice R. Lima[d], Henriette M.C. Azeredo[c,e,*]

[a] Federal University of Ceara, Department of Chemical Engineering, Campus Pici, Bl. 709, 60455-760, Fortaleza, CE, Brazil
[b] Federal University of Ceara, Department of Organic and Inorganic Chemistry, Campus Pici, Bl. 940, 60440-900, Fortaleza, CE, Brazil
[c] Embrapa Agroindústria Tropical, R. Dra. Sara Mesquita, 2270, Fortaleza, CE, 60511-110, Brazil
[d] Embrapa Agroindústria de Alimentos, Av. das Américas, 29501, Guaratiba, Rio de Janeiro, RJ, 23020-470, Brazil
[e] Embrapa Instrumentação, R. 15 de Novembro, 1452, Caixa Postal 741, São Carlos, SP, CEP 13560-970, Brazil

I&EC research
Industrial & Engineering Chemistry Research

Article

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Microwave-Assisted Organosolv Delignification: A Potential Eco-Designed Process for Scalable Valorization of Agroindustrial Wastes

Francisco Avelino,[†] Francisco Marques,[‡] Amanda K. L. Soares,[§] Kássia T. Silva,[||] Renato C. Leitão,[‡] Selma E. Mazzetto,[||] and Diego Lomonaco[*,||]

[†] Federal Institute of Education, Science and Technology of Ceará, Iguatu, Ceara 63503-790, Brazil
[‡] Embrapa Agroindustria Tropical, Rua Dra. Sara Mesquita, 2270, Planalto do Pici, Fortaleza, Ceara 60511-110, Brazil
[§] Department of Organic Chemistry, Institute of Chemistry, Federal University of Rio de Janeiro, 21941-909 Rio de Janeiro, Rio de Janeiro, Brazil
[||] Department of Organic and Inorganic Chemistry, Federal University of Ceara, Fortaleza, Ceara 60440-900, Brazil

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Industrial Crops & Products

journal homepage: www.elsevier.com/locate/indcrop

Steam explosion pretreatment to obtain eco-friendly building blocks from oil palm mesocarp fiber

Francisco Pereira Marques[a], Lorena Mara Alexandre Silva[b], Diego Lomonaco[a], Morsyleide de Freitas Rosa[b], Renato Carrhá Leitão[b,*]

[a] Departament of Organic and Inorganic Chemistry, Federal University of Ceará, 60440-900, Fortaleza, CE, Brazil
[b] Embrapa Agroindustria Tropical, Rua Dra. Sara Mesquita, 2270, Planalto do Pici, 60511-110, Fortaleza, CE, Brazil

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journal homepage: http://www.elsevier.com/locate/ijbiomac

Tailored organosolv banana peels lignins: Improved thermal, antioxidant and antimicrobial performances by controlling process parameters

Lucas de Sousa Nascimento [a], Francisco Igor Dalles da Mata Vieira [a], Victória Horácio [a], Francisco Pereira Marques [b], Morsyleide Freitas Rosa [c], Severino Araújo Souza [a], Rafaella Martins de Freitas [a], Daniel Esdras Andrade Uchoa [b], Selma Elaine Mazzeto [b], Diego Lomonaco [b], Francisco Avelino [a,*]

[a] Federal Institute of Education, Science and Technology of Ceará, 63503-790 Iguatu, CE, Brazil
[b] Department of Organic and Inorganic Chemistry, Federal University of Ceará, 60440-900 Fortaleza, CE, Brazil
[c] Embrapa Agroindústria Tropical, Rua Dra Sara Mesquita 2270, Planalto do Pici, 60511-110 Fortaleza, CE, Brazil

7.3 Embrapa Technical reports

Comunicado 226
Técnico

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Dezembro, 2016
Fortaleza, CE

Pré-tratamento do Bagaço da Cana-de-açúcar por Explosão a Vapor Visando à Extração de Lignina pelo Processo Acetosolv

Renato Carrhá Leitão[1]
Francisca Gleyciara Cavalcante Pinheiro[2]
Amanda Kellly Lima Soares[3]
Maria Évilyn Paiva Albuquerque[4]
Francisco Pereira Marques Neto[5]
Maria do Socorro Vale[6]
Men de Sá Moreira de Souza Filho[7]
Morsyleide de Freitas Rosa[8]
Sandra Tédde Santaella[9]

COMUNICADO
TÉCNICO

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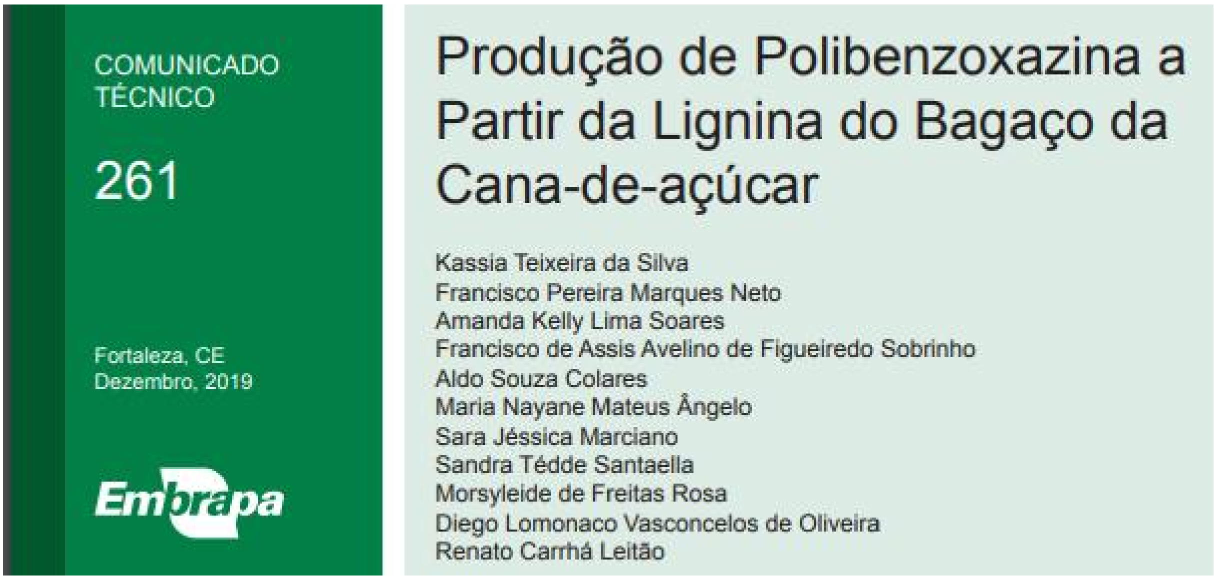
Fortaleza, CE
Agosto, 2019

Embrapa

Produção de Resinas Ligno-Fenol-Formaldeído a Partir do Bagaço da Cana-de-açúcar

Maria Évilyn Paiva Albuquerque
Amanda Kelly Lima Soares
Francisco Pereira Marques Neto
Francisca Gleyciara Cavalcante Pinheiro
Sandra Tédde Santaella
Morsyleide de Freitas Rosa
Diego Lomonaco Vasconcelos de Oliveira
Nágila Maria Pontes Silva Ricardo
Renato Carrhá Leitão



COMUNICADO
TÉCNICO

261

Fortaleza, CE
Dezembro, 2019

Embrapa

Produção de Polibenzoxazina a Partir da Lignina do Bagaço da Cana-de-açúcar

Kassia Teixeira da Silva
Francisco Pereira Marques Neto
Amanda Kelly Lima Soares
Francisco de Assis Avelino de Figueiredo Sobrinho
Aldo Souza Colares
Maria Nayane Mateus Ângelo
Sara Jéssica Marciano
Sandra Tédde Santaella
Morsyleide de Freitas Rosa
Diego Lomonaco Vasconcelos de Oliveira
Renato Carrhá Leitão

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