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

DISSERTAÇÃO

Strategies for improving eucalypt bleached Kraft pulp application

Sabrina Mayer de Almeida

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UNIVERSIDADE FEDERAL RURAL DO RIO DE JANEIRO
INSTITUTO DE FLORESTAS
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STRATEGIES FOR IMPROVING EUCALYPT BLEACHED KRAFT PULP APPLICATION

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

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RESUMO

ALMEIDA, Sabrina Mayer de. **Strategies for improving eucalypt bleached Kraft pulp application.** 2022. 70p. Dissertação (Mestrado em Ciências Ambientais e Florestais). Instituto de Florestas, Departamento de Produtos Florestais, Universidade Federal Rural do Rio de Janeiro, Seropédica, RJ, 2022.

Biorrefinarias são instalações que integram tecnologias e processos de conversão de biomassa para produção de bioenergia, bioquímicos, biocombustíveis e outros produtos de valor agregado. A madeira tem sido considerada a principal matéria-prima em uma biorrefinaria uma vez que muitas aplicações, como energia, químicos e materiais são possíveis considerando seu uso. Mas existem também oportunidades considerando produtos florestais já comerciais, como a polpa branqueada comercial, para produção de diversos produtos de celulose, como polpa solúvel, nanocelulose, xilitol, têxteis, etc. Processos alternativos como aplicação de líquidos iônicos, extração alcalina, hidrólise enzimática vem sendo reportados para produção de bioprodutos, devido sua capacidade de remover hemiceluloses seletivamente, garantindo a integridade das fibras de celulose e oferecendo mais oportunidades às fábricas. Por outro lado, a fração removida da polpa inicial não tem muitas aplicações descritas na literatura nem mesmo em escala industrial. Portanto, o principal objetivo desta pesquisa foi avaliar uma estratégia de aprimoramento dos usos de polpa Kraft comercial minimizando as perdas de material para geração de biomateriais potenciais, através do uso da tecnologia de extração alcalina a frio e aplicação do líquido iônico [2-HTEAF]mesy. Assim, esta disserção foi dividida em dois capítulos, onde o primeiro aborda o estado da arte da produção de polpa solúvel e o segundo avalia o uso de líquido iônico e extração alcalina a frio para produção de produtos de celulose de alto valor agregado. Os resultados mostraram que existem grandes oportunidades para produção de polpa solúvel e biomateriais na indústria de celulose. As plataformas de biorrefinaria possuem sinergia com as atuais instalações das fábricas de celulose, uma vez que sua integração seria facilitada pelo conhecimento prévio de processos e equipamentos necessários para fracionar os componentes da biomassa.

Palavras-chave: biorrefinaria; bioprodutos; extração alcalina; líquido iônico; polpa solúvel.

ABSTRACT

ALMEIDA, Sabrina Mayer de. **Strategies for improving eucalypt bleached Kraft pulp application.** 2022. 70p. Dissertation (Master Science in Environmental and Forestry). Institute of Forests, Department of Forest Products, Federal Rural University of Rio de Janeiro, Seropédica, RJ, 2022.

Biorefinery are facilities which integrate biomass conversion processes and technologies to produce bioenergy, biochemical, biofuels and others value-added products. The wood has been considered as the main raw material in a biorefinery industry since many applications, since many applications such as energy, chemicals and materials, are possible considering its use. But, there are also opportunities considering the already forest commercial products, such as the commercial bleached pulp, for producing several high added-value cellulose products, such as dissolving pulp, nanocellulose, xylitol, textiles, etc. Alternative processes such as ionic liquid application, caustic extraction, enzymatic hydrolysis have been reported to produce bio-products, due to the ability to selectively remove hemicelluloses, guaranteeing the integrity of cellulose fibers, delivering more opportunities to the pulp mills. On the other hand, the fraction removed from the initial pulp does not have many applications described in the literature, not even in industrial scale. Therefore, the main objective of this research was to evaluate a strategy for improving the uses of the commercial Kraft pulp minimizing material loss by the generation of the potential biomaterials, through the use of cold caustic extraction technology and application of the [2-HTEAF]mesy ionic liquid. Thus, this dissertation was divided in two chapters, being the first addresses to describe the state of the art of the dissolving pulp production and the second evaluates the use of ionic liquid and cold caustic extraction to produce high value-added cellulose products. The results showed that there are great opportunities for the production of dissolving pulp and biomaterials in the pulp mill. Biorefinery platforms have a synergy with the current pulp mill facilities, since their integration would be greatly facilitated by it already knowledge of processes and equipment necessary to fractionate biomass components.

Key words: biorefinery; bio-products; caustic extraction; ionic liquid; dissolving pulp.

SUMMARY

GENERAL INTRODUCTION

The growth of fossil materials consumption associated with economic and environmental issues have been questioned in the global policies worldwide in recent years. Therefore new production technologies, which aim at the full use of raw material for the production of several products, have been considered important alternatives to replace conventional means of production. The integrated biorefinery strategy is the growing concept that has potential to respond to these concerns.

Biorefinery, are facilities, somewhat analogous to the fossil refinery, which integrates biomass conversion processes and technologies to produce bioenergy, biochemical, biofuels and value-added products from biomass aiming at maximizing the added value along the sustainability pillars (FERREIRA, 2017; RESHMY et al., 2022; SINGH et al., 2022). This platform is a capital-intensive industry with large capital expenditure (CAPEX) that uses the feedstock resource base that is sustainably available at low cost to support a facility (HASSAN et al., 2019).

Biorefinering aims to exploit the maximum potential of lignocellulosic materials, which are basically composed of cellulose, hemicelluloses and lignin. The feedstock may be from agricultural and forestry crops (e.g. alfalfa, switch, poplar, eucalyptus), and agricultural residues (e.g. forest thinning, sawdust, sugarcane bagasse, rice husk, rice bran, corn stover, wheat straw and bran), and agroindustrial wastes, aquatic plants and algae, animal wastes, among others (FERREIRA 2017; HASSAN et al., 2019). The biomass components can be functionalized by different methods such as physical (e.g. steam explosion and liquid hot water), chemical (e.g. acid hydrolysis), biological (e.g. enzymatic hydrolysis, microbial fermentation), physiochemical (e.g. steam explosion and ammonia fiber expansion), thermochemical (e.g. pyrolysis, gasification, combustion) or other combinations of methods (e.g. fungal and physicochemical) (FERREIRA, 2017; HASSAN et al., 2019).

On the other hand, biorefinery platforms have emerged as an attractive strategy for being applied to the traditional pulp mill (LUNDBERG et al., 2014). The Integrated Forest Biorefinery implementation of a biorefinery plant into a receptor Kraft pulp mill is the most investigated type (AJAO et al., 2018). Ionic liquids based biorefinery is also innovation concept that may be considered an economically viable and environmental friendly future alternative to produces biofuels, valuable chemicals and other bio-products (NAZ; UROOS, 2020).

Chemical, physical, physiochemical and biological methods or their combination have been exploited for the production of bioproducts, however these processes are associated with harsh conditions (high temperature, pressure, toxic chemicals) and consequently high energy expenditure making them unfeasible (NAZ; UROOS, 2020). The association between ionic liquid and cold caustic extraction may be an alternative method to promotes chemical pulp upgrade and to produces high value-added cellulose products.

Cold caustic extraction is an alkaline purification stage usually takes place at low temperatures (20-50 °C) with high NaOH concentration, which aims to remove short chain hemicellulose and amorphous cellulose in the pulp (SYED et al., 2013; SIXTA et al. 2013; GONG et al., 2021), to produce cellulose products without much energy expenditure and with easy recovery of the reagent used in the process.

Ionic liquids, also referred to as “green” solvents, are versatile materials, non-volatile, non-flammable, thermic and chemical stable and recyclable (LI et al., 2012; ADELEYE et al., 2019) which can be used for various applications, such as engineering fluids, pre-treatment agents for wood grinding/biomass extraction, chemical separation, chemical fixation of carbon dioxide, nanoparticle formation, metal extraction, electro-chemistry applications, biological aid, etc. (CLOUGH et al. 2013; VEKARIYA, 2017; SINGH; SAVOY, 2020). They

can be used as solvents due to their better selectivity when compared with that of other conventional organic solvents (COTA et al., 2007) and their ability to modify cellulose structures, lose the rigid plant fiber structure, and remove lignin compounds (PENG et al., 2019). Tris(2-hydroxyethyl)ammonium methanesulfonate ([2-HTEAF]mesy) ionic liquid is an emerging solvent used for biomass fractionation which has great selectivity lignin and hemicelulloses and great development potential in the industrial application because it is novel eco-friendly and it has a low cost of synthesis (YANG et al. 2018).

High value bio-products such as biopharmaceuticals, biocosmetics, bionutrients, biochemical, biofertilizers, biomaterials, and biofuels may be produced into biorefinery (RESHMY et al., 2022). Dissolving pulp process, for example, may be considered a prototype of forest biorefinery due to quantitative separation and cost-effective utilization of the main components of wood (cellulose, hemicelluloses and lignin) (YANG et al., 2019). It is characterized for high cellulose content, trace amount of lignin, extractives and minerals, low hemicellulose and degraded cellulose contents (SIXTA, 2006; SIXTA et al., 2013; DUAN et al., 2015; GONG et al., 2017; YANG et al., 2019), uniformity in the degree of cellulose polymerization, (COLODETTE; GOMES, 2015; RESENDE et al, 2019), high reactivity, high brightness (YANG et al., 2019). It may be used to produces cellulose esters (sulfonate, nitrate and acetate), cellulose ethers (carboxymethyl, ethyl-, methyl-celluloses), fibers or films (e.g., Viscose, Lyocell) and other new cellulose-based products (SIXTA, 2006; SIXTA et al., 2013; DUAN et al., 2015; YANG et al., 2019).

Therefore, the main objective of this research was to evaluate a strategy for improving the uses of the commercial Kraft pulp minimizing material loss by the generation of the potential biomaterials, through the use of cold caustic extraction technology and application of the [2-HTEAF]mesy ionic liquid. Thus, this dissertation was divided in two chapters, being the first addresses to describe the state of the art of the dissolving pulp production and the second evaluates the use of ionic liquid and cold caustic extraction to produce high value-added cellulose products.

CHAPTER I: DISSOLVING PULP PRODUCTION: STATE OF THE ART

RESUMO

ALMEIDA, Sabrina Mayer de. **Dissolving pulp production: state of the art.** 2022. 17p. Capítulo I Dissertação (Mestrado em Ciências Ambientais e Florestais). Instituto de Florestas, Departamento de Produtos Florestais, Universidade Federal Rural do Rio de Janeiro, Seropédica, RJ, 2022.

A polpa solúvel é um produto de alto valor agregado caracterizado por alto teor de celulose, baixos teores de hemiceluloses, celulose degradada, lignina e extrativos, com alta reatividade, viscosidade e alvura adequadas de acordo com a aplicação comercial. É matéria-prima para a produção de uma série de derivados de celulose. Geralmente é feita de linters de algodão ou madeira, porém, o primeiro possui grandes exigências de água, fertilidade do solo e nutrientes em relação ao segundo, além disso, possui um preço mais elevado. Espécies de eucalipto apresentam baixo preço de produção, alta produtividade florestal, alto rendimento de polpação e qualidade da fibra. Os principais processos de produção são pré-hidrólise Kraft e polpação sulfito ácido, contudo métodos alternativos também vêm sendo reportados, tais como aplicação de líquidos iônicos, solventes eutéticos profundos, extração alcalina, hidrólise enzimática, entre outros. Por outro lado, se uma fábrica convencional de celulose for capaz de produzir polpa solúvel, esta seria uma estratégia para aumentar sua rentabilidade. Sendo assim, o objetivo deste capítulo foi abordar o estado da arte da produção de polpa solúvel, englobando os processos de produção, principais matérias-primas, produtores e fornecedores. A pesquisa mostrou um aumento significativo na demanda mundial por este produto e um grande interesse pela busca de métodos alternativos, economicamente viáveis e ambientalmente corretos. Além disso, mostrou que o Brasil também tem potencial para se tornar referência mundial na produção de polpa solúvel.

Palavras chave: novas tecnologias; hardwood; derivados de celulose.

ABSTRACT

ALMEIDA, Sabrina Mayer de. **Dissolving pulp production: state of the art.** 2022. 17p. Chapter I Dissertation (Master Science in Environmental and Forestry). Institute of Forests, Department of Forest Products, Federal Rural University of Rio de Janeiro, Seropédica, RJ, 2022.

Dissolving pulp is high value-added product characterized by high cellulose content, low contents of hemicellulose, degraded cellulose, lignin and extractives, with high reactivity, adequate viscosity and brightness according to the commercial application. It is the raw material for production of a range of cellulose derivatives. Usually, it is made of cotton linters or wood however, the first has great requirements for water, soil fertility and nutrients compared to the second moreover it has a higher price. Eucalyptus species have a low price of production, high forestry productivity, high pulping yield and fiber quality. The main production process are pre-hydrolysis Kraft and acid sulfite pulping, however alternative methods have also been reported, such as application of the ionic liquid and deep eutectic solvents, caustic extraction, enzymatic hydrolysis, among others. On the other hand, if a conventional pulp mill becomes able to produce dissolving pulp, this would be a strategy for increasing its profitably. Therefore, the objective of this chapter was to approach the state of the art of dissolving pulp production, encompassing the production processes, main raw materials, producers and suppliers. The research showed a significant increasing in world demand for this product and a great interest in the search for alternative, economically viable and environmentally friendly methods. Moreover, it showed that the Brazil has also a potential to become a global reference in the dissolving pulp production.

Key words: new technologies; hardwood; cellulose derivatives.

1 INTRODUCTION

Dissolving pulp is purified bleached pulp, produced by softwood and hardwood (LI et al., 2012) with high cellulose content, low content of hemicelluloses (3-6%) and low content of hemicelluloses, degraded cellulose, lignin, extractives and minerals (SIXTA, 2006; DUAN et al., 2015; GONG et al., 2017; YANG et al., 2019; RESENDE et al., 2019). It is the raw material for production of a range of cellulose derivatives such as viscose staple fibers (textiles, nonwovens, tire cord, industrial yarn, cellophane, sausage skin), cellulose esters (cigarette tows, films, high-quality plastics, acetate yarn), and ethers (explosives, paints, pharmaceuticals, cosmetics, binders) (SIXTA, 2006; SIXTA et al., 2013; COLODETTE, GOMES, 2015; DUAN et al., 2015; KUMAR; CHRISTOPHER, 2017; YANG et al., 2019).

Approximately 90% of dissolving pulp is produced by a low yield pulping process such as acid sulfite and pre-hydrolysis Kraft, with yield 30–35% and alfa-cellulose content of 90-92 and 94-96% respectively (DUAN et al., 2015; COLODETTE; GOMES, 2015; KUMAR; CHRISTOPHER, 2017; RESENDE et al., 2019). Usually it is made of cotton linters or wood, however the first has great requirements for water, soil fertility and nutrients compared to wood. Moreover, despite the high cellulose content, the higher price of cotton linters limiting their use for dissolving pulp production (KUMAR; CHRISTOPHER, 2017). Eucalyptus species are seen to increasingly dominate the world hardwood market (KUMAR; CHRISTOPHER, 2017), due to low price of production, high forestry productivity, adaptation to different environmental conditions, drought conditions and disease and high pulping yield (MAGATON et al., 2009; NEIVA et al., 2015).

In the last decade the dissolving pulp market has increased (GONG et al., 2021). Global production of dissolving pulp in 2019 reached 7.5 million tons, with a year-on-year increase of 6.1% compared to 2018. Analyzing the interval between 2015 and 2019, the dissolving pulp production capacity increased from 1.22 million tons to 1.58 million tons, while the import volume also increased from 2.25 million tons to 3.06 million tons (GONG et al., 2021). The prospective growth of the dissolving pulp mills in developing countries resulted in the increase of production capacity. The production capacity of dissolving pulp in these countries was 33% of the total global capacity in 2017, which represents an increase of 555 kilotons from 2016 (CHEN et al., 2019).

The increase on demand for dissolving pulp can be related with greater consumption of derivatives, mainly the viscose, associated with high prices and low availability of cotton (COLODETTE; GOMES, 2015) and it may be contributed to the increase of the number of Kraft pulp mills that uses the pulping process to convert traditional paper pulp to dissolving-grade pulp (DOU; TANG, 2017). Due to the growing demand for dissolving pulp is necessary the development of novel process concepts that combine manufacture of high purity cellulose pulps and advanced biorefinery concepts (SIXTA et al., 2013), in order to produce high-quality and low-cost dissolving pulp to alleviate the difference between supply and demand (GONG et al., 2021).

Several Kraft mills are being converted into dissolving pulp mills in order to meet the growing demand for this product (LUNDBERG et al. 2014), as Jari Celulose in Brazil. Two new mills were installed in Brazil to produce dissolving pulp from wood, Bracell (SP), and LD Celulose (MG) (IBA, 2021), destined for production of viscose, Lyocell and non-textiles (face masks, wet wipes, diapers, cellophane, cigarette filters, pharmaceuticals, etc). The country was the biggest supplier of dissolving pulp from wood to the USA, providing 177 thousand tons in 2021, which corresponds to 72% of total imports (INDEXBOX, 2022).

The main challenge in dissolving pulp production is the selective removal of hemicelluloses and ensures high pulp reactivity (DUAN et al., 2015). These impurities when presents in dissolving pulp can affect the pulp processability and the properties of the final products (DUAN et al., 2015). Many alternatives processes have been reported for extraction of low molecular weight carbohydrates, ensuring the quality of the pulp, such as ionic liquids, caustic extraction, enzymatic hydrolysis, organic electrolyte solutions and formic acid application (ZHU et al., 2006; ZAVREL et al., 2009; FROSCHAUER et al. 2013; SYED et al., 2013; SIXTA et al. 2013; SIXTA et al., 2015; WANG et al., 2016; JAHAN et al., 2016; CHENG et al., 2017; NAYEEM et al., 2017; BAJPAI, 2018; YANG et al. 2018; YANG et al., 2019; YANG et al., 2021; FRIEBEL et al., 2019; GONG et al., 2021).

These processes have a great potential to replace the conventional processes for dissolving pulp production and to reduce costs in the mill, since they can be implemented as an additional step in the production process without the needed to change the mill structure, reducing the use of chemicals and energy in the following steps. Therefore, the objective of this chapter was addresses the state of the art of the dissolving pulp processes, encompassing the main raw materials, conventional processes and new technologies.

2 STATE OF THE ART

2.1 Dissolving pulp

Dissolving pulp is purified bleached pulp, produced by softwood and hardwood (LI et al., 2012) with high cellulose content of 90-99% (SIXTA, 2006; GONG et al., 2017), low content of hemicelluloses (3-6%) and trace amount of lignin, extractives and minerals (SIXTA, 2006; DUAN et al., 2015; YANG et al., 2019), uniformity of the degree of cellulose polymerization, low content degraded cellulose (RESENDE et al., 2019), high reactivity, appropriate viscosity, high brightness and uniform molecular weight distribution (YANG et al., 2019).

The cellulose molecules and their properties, such as length and molecular weight distribution are the most important properties for this product (SYED et al., 2013). The high reactivity of cellulose can produce cellulose-end products with quality and demands lower reagents content, consequently decreasing production costs and environmental impact (DUAN et al., 2015). Non-cellulosic materials (lignin, extractives, hemicelluloses) are undesirable impurities in dissolving pulps and have negative effect on the final product quality (SYED et al., 2013). Hemicelluloses negatively affecting the cellulose filterability, xanthanation reaction in the viscose process, and viscose strength of the cellulose end products (KUMAR; CHRISTOPHER, 2017).

Dissolving pulp can be used as a raw material to produce cellulose derivatives, such as cellulose esters (sulfonate, nitrate and acetate), cellulose ethers (carboxymethyl, ethyl-, methyl-celluloses), fibers or films (e.g., Viscose, Lyocell) and other new cellulose-based products, which fit the sustainable strategy well (SIXTA, 2006; SIXTA et al., 2013; DUAN et al., 2015; YANG et al., 2019).

Dissolving pulp is so called due to its ability to dissolve in a solvent or be derivatized into a homogeneous solution which makes it completely chemically accessible and removes any remaining fibrous structure. Once dissolved, it can used as a starting material for manufacturing of cellulose derivatives (AMBJÖRNSSON et al. 2014; KUMAR; CHRISTOPHER, 2017; DYUNYASHEVA, 2017). The purpose of cellulose derivatization is

to make the cellulosic polymer soluble in several solvents, such as alkali, acetone, chloroform, etc. (RESENDE et al., 2019) (Figure 1).

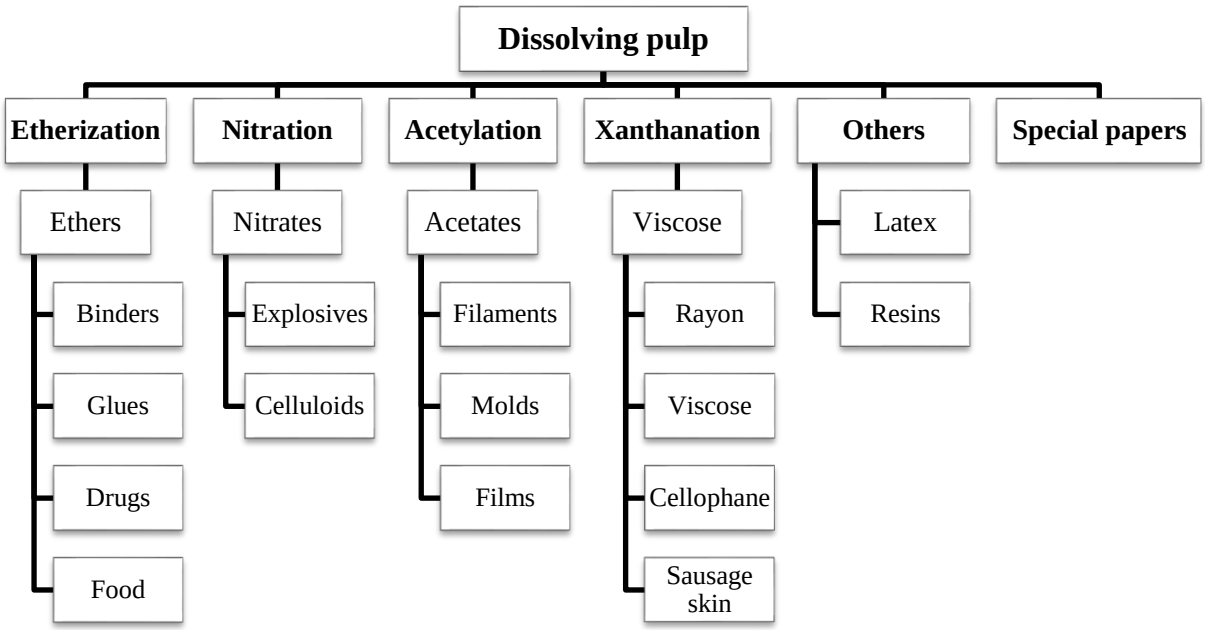

Figure 1 Products and by-products of dissolving pulp, and their respective derivation processes.
Adapted COLODETTE; GOMES, 2015.

Highly purified cellulose pulps also can be used to meet the demands of the food, textile and pharmaceutical industries. The dissolving pulp can be converted into products of several classes, including xanthates, esters and ethers of cellulose, microcrystalline cellulose, etc. These materials can be used to produce varnishes, enamels, emulsifiers, cellophane, sausage skin, pharmaceuticals, cosmetics, LCD (Liquid Crystal Display) screens, as well as it can be used for manufacture of nanofibrillated cellulose (NFC), a future precursor of advanced materials (SIXTA et al., 2013; COLODETTE, GOMES, 2015).

Nowadays, over 70 % of dissolving pulp is consumed in the production of viscose and is expected to increase global demand for dissolving pulp at the rate of 6 to 7 % per year to feed the rising global textile demand (KUMAR; CHRISTOPHER, 2017; YANG et al., 2019). It is expected that the global textile and apparel market will have a dynamic growth in the upcoming years, mainly due to increasing global population and income levels (SCHIER et al., 2021). A possible increase in per capita consumption of textile fibers could promote an increase of the global production from 72.5 million tons in 2010 to 133.5 million tons in 2030 (SIXTA et al., 2013). Despite the China being one of the largest consumers of viscose fiber, with a possible growth rate of 10% (KUMAR; CHRISTOPHER, 2017), the supply of dissolving pulp has always been less than demand (GONG et al., 2021).

According to Spectrum Magazine (2017), China is the largest producer of the dissolving pulp, and it is also largest consuming country, with estimated production of 1.9 million tons (25% of world output). Africa is the second largest producing region with all the production concentrated in South Africa, where the biggest dissolving pulp mill in the world is also located. The North America is the second-largest supplying region for the same product, with an estimated 1.8 million tons of production in 2017. The USA account for 1.2 million tons, and Canada account for the remainder. In Europe, the production has double since 2010 mainly due to conversions from paper-grade to viscose pulp on existing pulp mills.

The prices of dissolving pulp have been erratic and frequently affected by the price of chemical pulp (CHEN et al., 2019) and among the main world markets. The USA recorded the average price export of dissolving pulp of the US$ 1,147/ton in 2021, increasing 21% over the previous year. The highest prices of this product were US$ 1,431/ton and US$ 1,302 registered by Japan and China respectively, on the other hand, the lowest prices were registered by Indonesia and Belgium, US$ 962/ton and US$ 999/ton respectively (INDEXBOX, 2022).

Brazil, Canada and South Africa are the main dissolving pulp suppliers to the USA. The first was the biggest supplier of dissolving pulp from wood, providing 177 thousand tons in 2021, which corresponds to 72% of total imports. Canada and South Africa correspond to 5%, providing 32 and 12 thousand tons respectively (INDEXBOX, 2022).

Two new mills were installed in Brazil to produce dissolving pulp from wood, Bracell in Lençóis Paulista (SP), and another called LD Celulose, a joint venture between Dexco and Lenzing which is an Austrian company. This last one is located in the Triângulo Mineiro region (IBA, 2021). The LD Celulose S.A. has a production capacity of 500 thousand tons of dissolving pulp per year. The dissolving pulp produced from eucalypt wood is destined for production of viscose, Lyocell and non-textiles such as face masks, wet wipes, diapers, etc. The Bracell S.A. produces special dissolving pulp of two basic types, rayon-grade and specialty-grade, from wood. These materials are destined to produce Lyocell fibers, cellophane, cigarette filters, pharmaceuticals, etc. Furthermore, the Star Project is a major project by Bracell to expand its production capacity for 1.5 million tons/year of dissolving pulp or up to 3 million tons/year of eucalypt Kraft market pulp.

2.2 Raw material for dissolving pulp production

Dissolving pulp is made of cotton linters or wood however, the first has great requirements for water, soil fertility and nutrients compared to wood. Moreover, despite the high cellulose content, the higher price of cotton linters limiting their use for dissolving pulp production (KUMAR; CHRISTOPHER, 2017).

Eucalyptus species in particular are seen to increasingly dominate the world hardwood market (KUMAR; CHRISTOPHER, 2017), due to low price of production, high forestry productivity, adaptation to different environmental conditions, drought conditions and disease, high pulping yield and fiber quality (MAGATON et al., 2009; NEIVA et al., 2015; CUNICO et al., 2021). Furthermore, hardwoods, including eucalypt, have been incorporated in the production of dissolving pulp due to the advancement of wood cooking and hemicelluloses removal technologies (COLODETTE; GOMES, 2015). Approximately 90% of dissolving pulp is produced from wood by a low yield (30–35% of wood) pulping process (KUMAR; CHRISTOPHER, 2017).

Other raw materials, such as sisal, corn stalk, bamboo, elephant grass, birchwood, aspen, pine, spruce, rice and wheat straws, jute stick, etc., were also reported for dissolving pulp production (BEHIN et al. 2008; BATALHA et al., 2012; GOMES et al., 2013; HAURU et al. 2013; IBARRA et al. 2010a; KUMAR; CHRISTOPHER, 2017; DYUNYASHEVA, 2017; SARKAR et al., 2020). It is estimated that 40% or more of the dissolving pulp produced in China is from cotton, bamboo and chemical pulps (CHEN et al., 2019).

Batalha et al. (2012) report that the bamboo pulp is of slightly lower quality and more costly to produce when compared to eucalypt dissolving pulp. Gomes et al. (2013) report that due to high fibers production and chemical characteristics, mainly the low lignin content, possibly the elephant grass has high pulpability, however more investigation is required comparing its potential with the eucalypt wood.

Considering that the Brazil has 9.55 million of hectares planted destined for industrial purposes and the estimated of the gross revenue for the production of tree sector in 2020 was R$ 116,6 billion, 17,6% growth over 2019, cultivated trees put the Brazil as a world reference in production of pulp and other wood derivatives (IBA, 2020). Therefore, the large production of planted forests destined for the wood production, mainly eucalypt wood, can make the country a major player in the in the global dissolving pulp market.

The wood is a three-dimensional biopolymer composed mainly by 65-75% carbohydrates (cellulose and hemicelluloses), 18-35% lignin and in minor amounts, organic extractives and inorganic minerals (4-10%) (PETTERSEN, 1984; ROWEL, 2005). The composition and percentages of these polymers vary from between hardwood and softwood (KLOCK et al., 2005), age, stage of growth, and other conditions (PÉREZ et al., 2002).

Cellulose is a linear biopolymer of high molecular weight and structural material in cell wall composed for d-glucose subunits linked by glycosidic bonds (β-1,4) (KLOCK et al., 2005; SHARMA et al., 2019). The long polysaccharide chains are arranged parallelly to form cellulose microfibrils, which are linked by inter and intramolecular hydrogen bonds, forming the crystalline and amorphous structure of cellulose (SHARMA et al., 2019) (Figure 2). Due to fiber structure, the cellulose has high tensile strength and is insoluble in most solvents (KLOCK, 2013).

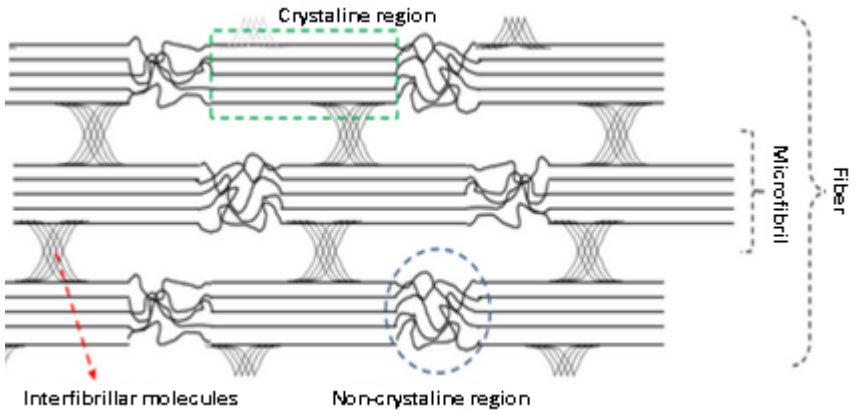

Figure 2 Crystalline and amorphous region of cellulose.
Adapted FATRIASARI; HERMIATI, 2016.

Lignin is a complex, amorphous hetero-biopolymer insoluble in water, consisting of an aromatic system composed of phenylpropane units linked by carbon–carbon (C-C) and aryl–ether (C-O-C) linkages (ROWELL, 2005; KLOCK et al., 2005; SHARMA et al., 2019), distributed in secondary wall with highest concentration on the middle lamella (ROWELL, 2005). It is formed by oxidative coupling of trans-p-coumaryl alcohol, transconiferyl alcohol and trans-sinapyl alcohol, resulting in phenylpropane units namely p-hydroxyphenyl, guaiacyl and syringyl units (Figure 3) (LEWIS; YAMAMOTO, 1990; CESARINO et al., 2012; SHARMA et al., 2019). The ratios of these monomeric moieties vary between species and between tissues, where structure of softwoods lignin predominately contains H (<5 %) and G (<95 %), and hardwood lignin contains 46–75 % S, 25–50 % G, and 0–8 % H (ZHU et al., 2018).

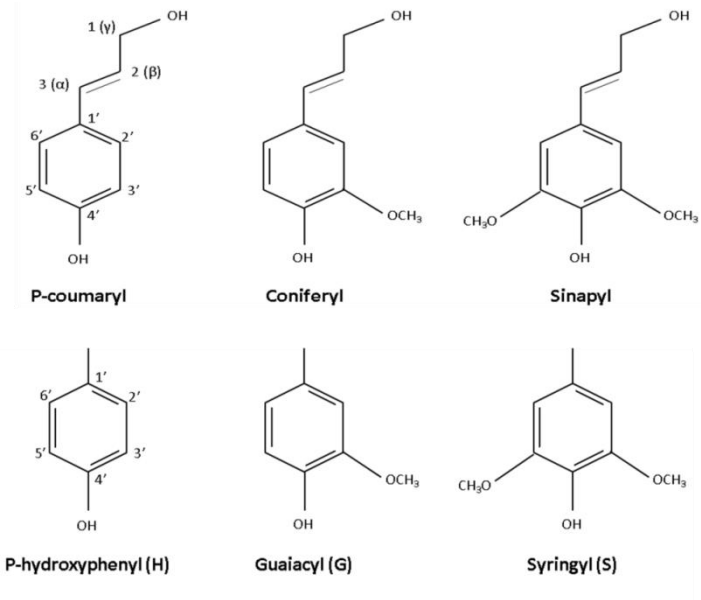

Figure 3 Lignin precursors and units phenylpropane.
LEWIS; YAMAMOTO, 1990.

Hemicelluloses are complex carbohydrates, that consist of different polymers like pentoses, hexoses, and sugar acids, linked by β-1,4-glycosidic and occasionally by β-1,3-glycosidic bonds (JOY et al., 2016; SHARMA et al., 2019). It is a branched and amorphous polysaccharide with a lower molecular weight, formed from D-xylose, D-mannose, D-galactose, D-glucose, L-arabinose, 4-O-methyl-glucuronic, galacturonic and glucuronic acids (JOY et al., 2016; SHARMA et al., 2019). Polymerization degree is variable, for example, the polymerization degree in hardwood is about 150-200 and, in softwood is about 70-130 (KULKARNI et al., 1999).

They are responsible for binding cellulose microfibrils, lignin and pectin to form a cross-linked of heterogeneous mixture in the cell walls (ZHANG et al., 2012; SHARMA et al., 2019), gives more rigidity (JOY et al., 2016). Hardwoods contain xylans and glucomannans and, softwood contain glucomannans, xylans, arabinogalactans, xyloglucans and glucans (SAHA, 2003; ZHANG et al., 2012). The principal hardwood hemicellulose is O-acetyl-4-O-methylglucuronoxylans, and in softwood is arabino-4-O-methylglucuronoxylans (KULKARNI et al., 1999; PÉREZ et al., 2002) (Figure 4).

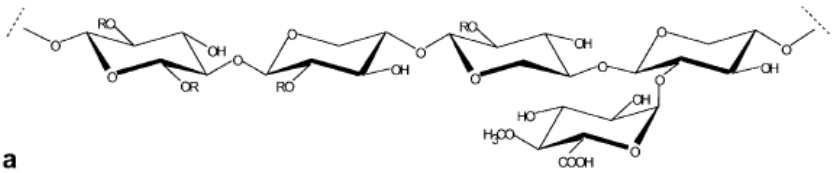

Figure 4 O-acetyl-4-O-methylglucuronoxylan hemicellulose structure from angiosperms.
Adapted PÉREZ et al., 2002.

Hemicelluloses and degraded cellulose can cause problems for the production of dissolving pulp derivatives however the end product defines the limits for the impurities (SAKA; MATSUMURA, 2004; ROSELLI et al., 2014). For viscose production, for example, low hemicellulose contents are required because they react with process solvents and reduce the quality of viscose fibers, derivatives filterability, control the degree polymerization and

substitution, reducing de quality of viscose fibers. Furthermore, they can precipitate during the conversion processes and fill the spinners (COLODETTE; GOMES, 2015).

For acetate production, they can produce low quality acetate-grade pulp and reduce cellulose reactivity. The purity requirements are more stringent (about 0.2-1.2 wt% anhydromannose and 1-1.3 wt% anhydroxylose). Residual hemicelluloses may hinder the acetylation process of the cellulose hydroxyl groups due to competition between hemicelluloses and cellulose during acetylation process. Methylglucuronoxylan can have negative impact mainly on the color, glucomannan are a contributor to cellulose acetate haze, false viscosity, and decrease in filterability, while Kraft xylan and arabinoxylan form color, haze, and the latter is also deleterious to filterability (SAKA; MATSUMURA, 2004; STEINMEIER, 2004; SIXTA, 2006; ROSELLI et al., 2014).

2.3 Dissolving pulp production

Typically, dissolving pulp is produced from cotton linters via soda pulping, and from wood (softwood and hardwood) via pre-hydrolysis Kraft (PHK) and acid sulfite (AS) pulping process (BATALHA et al., 2012), being necessary an additional purification stages in these last processes (SIXTA, 2006). However, the current high costs of raw material associated with environment constraints standard bleaching have caused a significant increase in the cost of dissolving pulp (BATALHA et al., 2012). The dissolving pulp produced by AS and PHK methods accounts 85-88% of the total dissolving pulp production all over the world (CHEN et al., 2019).

Wood pulps, especially those derived from sulfite process require a subsequent hemicellulose removal step that is performed during the bleaching operation (BATALHA et al., 2012). In the Kraft pulps, subsequently pre-hydrolysis and caustic extraction processes are responsible to remove hemicellulose and decrease cellulose molecular weight to promote pulp reactivity (DOU; TANG, 2017; KUMAR et al., 2017; LI et al., 2018a; FRIEBEL et al., 2019). High amounts of hemicellulose in dissolving pulp causes problems in its further processing to end-uses (KUMAR; CHRISTOPHER, 2017). The dissolving pulp production technologies were discussed below.

2.3.1 Acid sulfite (AS)

Sulfite pulping process involves cooking wood chips at high temperature and pressure in a digester with an aqueous solution of sulfur dioxide and calcium, sodium, magnesium or ammonium base. It is distinguished into three categories according to their pH, that is, acid sulfite, bisulfite, and alkaline sulfite (MBOOWA, 2021). These cationic base chemicals are used to prevent pulp discoloration (BALKISSOON et al., 2022). It shows the disadvantages such as low pulp strength, long cooking cycles, chemical recovery is nearly impossible, and only softwood species can be pulped (MBOOWA, 2021).

Dissolving sulfite pulp process is similar to production of sulfite paper-grade pulp, with some differences in parameters of the cooking and bleaching processes. In the AS process uses calcium as a base, where the cooking is carried out under the pressure at 135-150 °C for 4-12 hours and using a strongly acidic cooking liquor (pH 1,5-2,5) to avoid liming up conditions in the cooking digester (DYUNYASHEVA, 2017; MBOOWA, 2021).

It produces pulp with cellulose content to 90-92%, lignin content between 0.15-0.25% pentosan content 1.8-4% and small amount of ash (COLODETTE; GOMES, 2015; DYUNYASHEVA, 2017; BAJPAI, 2018). However subsequently purification by alkali extraction or multi-bleaching steps (KUMAR, 2021) can yield even higher cellulose levels-up to 96% (BAJPAI, 2018).

AS is used mostly to make viscose rayon for textiles and cellophane (BAJPAI, 2018). Only several companies in Europe which manufacture dissolving sulfite pulp (DYUNYASHEVA, 2017). However, this process has been replaced by pre-hydrolysis process because the second has higher yield from wood, better bleachability and optical properties.

2.3.2 Pre-hydrolysis Kraft (PHK)

The PHK step is used to extract most of the hemicelluloses, followed by Kraft pulping to remove most of the lignin, and a bleaching step (KUMAR; CHRISTOPHER, 2017). This process can be done hot water, auto-hydrolysis, acidic or alkaline medium, and steaming. Acid hydrolysis may cause undesirable corrosive effects, extensive lignin condensation and low yield, thus the auto-hydrolysis is commonly used in industries (MATEOS-ESPEJEL et al. 2013; SIXTA et al., 2006; LIU et al., 2011; KUMAR; CHRISTOPHER, 2017). This process is a well-known commercial practice for production of dissolving pulp from hardwood and it is performed for approximately 80-110 min (KUMAR; CHRISTOPHER, 2017).

During auto-hydrolysis the water at high temperature promote release of organic acids from the wood, which hydrolyzes hemicellulose to soluble sugars. (MBOOWA, 2021). High temperatures (150–180 °C) forms acetic acid due to the cleavage of the acetyl groups from hemicelluloses, which reduce the pH to about 4, and it acts as a catalyst to hydrolyze the glycosidic bonds in the hemicellulose resulting in hydrolysis of greater than 60% of these polysaccharides and in the dissolving pulp production with a high cellulose content (>90%) (SIXTA et al., 2006; MATEOS-ESPEJEL et al. 2013; LUO et al., 2014; TESTOVA et al., 2014; DOU; TANG, 2017; KUMAR; CHRISTOPHER, 2017). Generally, this process produces dissolving pulp with alfa-cellulose content between 94-96% (COLODETTE; GOMES, 2015). The pre-hydrolysis liquor contains approximately 50% of hemicelluloses and 10% of lignin dissolved.

After PHK, the pulp is submitted to Kraft pulp process, where the wood chips are cooked in a solution of sodium hydroxide (NaOH) and sodium sulphide (Na_2S), following bleaching stages to remove the lignin and hemicelluloses residual (BALKISSOON et al., 2022).

This process has intrinsic advantages such as capital investment, operation, and environmental compatibility (KUMAR, 2021) However, it shows some limitations such as increase in the total dissolving pulp production time due to the additional steps, and reduction in the dissolving pulp yield (on average 38%) as compared to 48% for the conventional Kraft pulping (MATEOS-ESPEJEL et al. 2013; KUMAR; CHRISTOPHER, 2017). Furthermore, the change from acid pH in PHK to alkaline pH in Kraft pulping can result problems, since acid pH also promotes the condensation of lignin, making it difficult to remove in the subsequent pulping process (DOU; TANG, 2017).

2.3.3 Bleaching stage

Bleaching is final delignification performed in multiple stages that aims to remove extractives and other substances containing chromophore groups, such as lignin, that make the pulp dark-colored (COLODETTE; GOMES, 2015; DYUNYASHEVA, 2017). The main objective is to improve the brightness, minimizing chemical and mechanical pulp damage, loos of yield, costs, carbohydrate oxidation and environmental impacts (COLODETTE; GOMES, 2015). However, this stage also increases the purity, removing lignin and hemicelluloses, adjusting the viscosity and molecular weight distribution of the cellulose (ARCE et al., 2020). In the dissolving pulp, this stage must also remove hemicelluloses and

reduce the viscosity (COLODETTE; GOMES, 2015). This step is responsible to remove about 5-10% of residual lignin to the pulp after the pulping process, since it cannot be removed by prolonged pulp without degrading the polysaccharides.

The stage is the most expensive and polluting stage of the pulp mill, being carried out in several steps with compounds containing chlorine or oxygen and alkaline extractions (FERDOUS et al., 2020). Therefore, several environmental friendly bleaching sequences have been reported (SHARMA et al., 2020b). The main bleaching sequences are Elemental Chlorine (EC), Elemental Chlorine Free (ECF) and Totally Chlorine Free (TCF) (ARCE et al., 2020; TRIPATHI et al., 2020). ECF pulp bleached corresponds to more than 93% of the world market with approximate production of 94 million tons, and TCF pulp is less than 5% (SHARMA et al., 2020a).

Despite the advantages of EC, such as selectivity towards lignin elimination and low cost (ARCE et al., 2020), sequences that use elemental chlorine have been eliminated from the mill due to the impacts caused by the toxic chemicals (SHARMA et al., 2020b) such as dioxins, furans, and adsorbable organic halides (AOX) (BOUIRI; AMRANI, 2010). These organochlorines formed cause genetic disorders in aquatic and terrestrial animals, including humans. In the Brazil the use of chlorine in the bleaching was banned.

The ECF sequence is carried out with chlorine dioxide (ClO_2) but without chlorine gas or hypochlorite (DYUNYASHEVA, 2017), where the biggest challenge is the reduction of the applied ClO_2 charge (ARCE et al., 2020). The TCF sequence replaces all chlorine-based compounds with oxygen-based (oxygen, hydrogen peroxide and ozone) (DYUNYASHEVA, 2017; ARCE et al., 2020; TRIPATHI et al., 2020).

The D-(EP)-D bleaching sequence has gained significant interest to produce quality ECF pulp and has been implemented to bleach various types of pulps from different raw materials (SHARMA et al., 2020a). However, the typical bleaching sequence for dissolving pulp is based on a five-stage bleaching process. The first stage is the oxygen stage (O_2) followed by the chlorination stage (D_0) that uses chlorine dioxide, extraction stage (E) that uses NaOH solution, the second chlorination stage (D_1), and lastly the hypochlorite stage (H) that uses sodium or calcium hypochlorite (CHUNILAL, 2009; COLODETTE; GOMES, 2015; BALKISSOON et al., 2022). These stages are responsible to oxidize, decolorize and solubilize lignin and to removal hemicelluloses that could not readily be removed during the pulping process, without compromising the integrity of the cellulose pulp (COLODETTE; GOMES, 2015; BALKISSOON et al., 2022).

Peroxide treatment is generally used in bleaching sequences and needed a previous metal removal step from the pulp (KUNZ et al., 2021). The chelation step is carried out to management of pulp metal ions, which may affect the selectivity and efficiency of bleaching with oxygen-based chemicals due to its decomposing effect through peroxide, resulting in quality-impaired products, colorization of pulp and catalytic decomposition (GRANHOLM et al., 2010; COLODETTE; GOMES, 2015; SHATALOV, 2017; KUNZ et al., 2021). Normally, it is operated in acidic conditions due to the better performance of chelating agents (AREA et al., 2010), where the metal ions were bonded to chelant and consequently blocked from undesired interaction (ASEMAVE, 2017).

The chelating agents are used to limit the effect of transition metals on alkaline decomposition of peroxide (SHATALOV, 2017). Cations such as Ca^{2+}, Mg^{2+} and Ba^{2+} form insoluble precipitates with carbonates, sulfates and phosphates, furthermore the presence of transition metal ions (copper, iron, zinc and manganese) may cause corrosion, catalytic degradation, polymerization inhibition, redox reactivity and changes in the coloring of products (OVIEDO; RODRÍGUEZ, 2003).

The classical chelating agents are aminopolycarboxylates (APCs), aminophosphonates and phosphates. Traditional phosphonate agents include: diethylenetriaminepentakis

(methylenephosphonic acid), DTPMP; 1,2 –diaminoethanetetrakis (methylenephosphonic acid), EDTMP; 1-hydroxy ethane (1,1-diylbis-phosphonic acid), HEDP; phosphonobutanetricarboxylic acid, PBTC; nitrilotris (methylenephosphonic acid), NTMP; N-phosphonomethylgycine, PMG. The APCs mostly used are ethylenediamine tetraacetic acid, EDTA; nitrilotriacetic acid, NTA; β-alanine diacetic acid, ADA; diethylenetriaminepentaacetic acid, DTPA; ethylenediaminedi(ohydroxyphenylacetic acid, EDDHA; N- (hydroxylethyl) – EDTA, HEDTA (ASEMAVE, 2017).

The EDTA is one of the most used chelating agents and is responsible to control the brightness restricting and reversion effects of iron salts and other heavy metals in the pulp (BALKISSOON et al., 2022). The metal removal process with EDTA is directly related to the strength of the metal–EDTA complex formed as well as to the strength that the metal ions are bound to the pulp functional groups present (KUNZ et al., 2021). This sequestering agent has 6 coordinating sites which contain functional groups (such as –COOH and $–NH_2$), that forms a ring structure chelate around the metal ion (GRANHOLM et al., 2010).

Studies have been proposed replacers to EDTA in the pulp industry. Greener alternative chelating agents include ethylenediamineN,N'-disuccinic acid (EDDS), iminodisuccinic acid (IDS), pyridine-2,6-dicarboxylic acid (PDA), methylglycinediacetic acid (MGDA) and siderophores like desferrioxamine B (DFOB), polyaspartic acid (PASA), desferrioxamine E (DFOE), glutamic diacetic acid (L-GLDA), citrate, gluconic acid, amino acids, plant extracts (PINTO et al. 2015; ASEMAVE, 2017; KUNZ et al., 2021).

2.4 New technologies for dissolving pulp production

2.4.1 Ionic liquids

Ionic liquids (ILs) are versatile materials that can be used fundamentally as solvents and catalysts for synthetic chemical reactions and other applications, such as engineering fluids, pre-treatment agents for wood grinding/biomass extraction, chemical separation, chemical fixation of carbon dioxide, nanoparticle formation, metal extraction, electro-chemistry applications, biological aid, etc. (CLOUGH et al. 2013; VEKARIYA, 2017; SINGH; SAVOY, 2020). They can be used as solvents due to their better selectivity when compared with that of other conventional organic solvents, low melting point (COTA et al., 2007) and their ability to modify cellulose structures, lose the rigid plant fiber structure, and remove lignin compounds (PENG et al., 2019).

ILs are non-volatile solvents compound for cations and anions, also referred to as "green" solvents, characterized by low melting point (usually below 100 °C), thermic and chemical stability, recyclability, low vapor pressures and not flammability. (MARSZALL et al., 2006; ZHU et al., 2006; LI et al., 2012; ADELEYE et al., 2019). They can be divided according to chemical behavior into two groups: aprotic (AIL), considered "classic" ionic liquids, and protic (PIL) ionic liquids, where the potential environmental impact of new PILs is expected to be smaller due to their simpler structure.

AILs are formed mainly on bulky organic cations (e.g. imidazolium, pyridinium) with long alkyl chain substituents and large variety of anions (e.g. $Cl^–$, $Br^–$, $BF^{4–}$, $PF^{6–}$, $N(CN)^{2–}$). PILs make up the recent family of short aliphatics formed by amines and organic acids with relatively low molecular weight, where cations are amine-based compounds substituted (monoethanolamine, diethanolamine or triethanolamine) and anions are organic acids compounds with different numbers of carbon atoms (formic, propionic, butanoic, isobutanoic pentanoic acid) (COTA et al., 2007; PERIC et al., 2013). PILs are the subset that functions

through proton transfer from Brønsted acid−base chemistry while inheriting many of the properties of the aprotic class (DAVIDOWSKI et al., 2016).

From a safety and environmental point of view, ILs have no significant vapor pressure, which means a strong interaction between their ions, they do not emit potentially hazardous organic compounds during use, handling, and transportation (COTA et al., 2007; ABUSHAMMALA; MAO, 2020). They reduce the risk of explosions due to their low flammability (STARK, 2011), as well as they also allow an easy separation of organic molecules by direct distillation without loss of the ionic liquid (COTA et al., 2007). However, their thermal stability is limited by the strength of their heteroatom-carbon and their heteroatom-hydrogen bonds, respectively (WASSERSCHEI; KEIM, 2000).

The hydrophilic/hydrophobic chemistry during ionic liquid synthesis affects their solvation properties (ADELEYE et al., 2019). ILs can be of hydrophobic or hydrophilic nature depending on the structures of ions (COTA et al., 2007). Often, the anion determines the solvation chemistry and the cation having a secondary effect (BRANDT-TALBOT et al., 2017). The anion influence in the ionic liquid ability in dissolution of cellulose, since some IL contain anions that may form hydrogen bonds with different groups, such as hydroxyl groups, carboxylates dialkyl phosphates, among others (ADELEYE et al., 2019). The cations may also indirectly influence the through impacting IL physical properties, such as the melting point, density and viscosity (HOU et al., 2017).

Firstly, the imidazolium-based ILs were reported to dissolve cellulose through their strong H-bond effect (PENG et al., 2019). These ionic liquids contain halides or carboxylates which are effective cellulose solvents, however, depending on the imidazolium ring and the chemical nature of the anion, can induce cellulose degradation at high temperatures (>90 °C) (MICHUD et al., 2016). Furthermore, due to ILs characteristics with thermal instability and ability of halides to corrode metal equipment, alternative anions were implemented (HUMMEL et al., 2015).

On the other hand, PILs are synthesized by one-step protonation reaction of organic amine, without any by-products, and have been explored for various applications (SUN et al. 2017; YANG et al., 2018). They reduce the cost for multi-ton IL production due to their costs saving and clean way to obtain and their performance to dissolve biomass components selectively (CLOUGH et al. 2013; HALLETT; WELTON 2011; YANG et al., 2018). Therefore, PIL have a potential for application in biomass pretreatment, dissolving pulp production, bleaching pulp, among others.

ILs have been shown to be able to promote disturbances in the hydrogen bonds of plant fibers (PENG et al., 2019). ILs are effective in the de-crystallization of cellulose and in the cleavage of lignin–hemicellulose linkages (BHAUMIK; DHEPE, 2015). They can promote selective cleavage of glycosidic, ester, and b-O-4 ether bonds (STARK, 2011; YOO et al., 2012), and they can compete with the lignocellulose components for hydrogen bonding, thus disrupting its three-dimensional network, due to their chemical interactions such as ionic interactions, and π-π interactions and hydrogen bonds (ZAVREL et al., 2009) (Figure 6). Strong H-bonds between IL and lignocellulosic components contribute to the biomass fractionation (MORA-PALE et al. 2011; YANG et al., 2018). The dissolving strength can be attributed to strong hydrogen-bonding interactions between the anions and equatorial hydroxyl groups on the cellulose (ADELEYE et al., 2019).

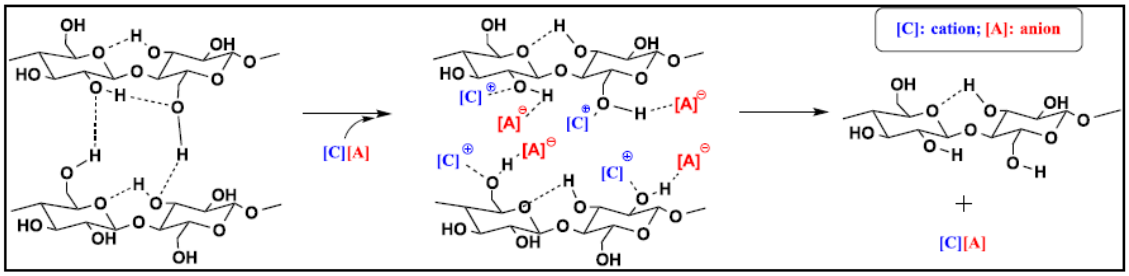

Figure 5 Dissolution of cellulose in IL.
YOO et al., 2017.

ILs have attracted interest in various research fields, for example its application direct solvents for lignocellulosic materials (MICHUD et al., 2016). ILs are useful for the production of high added value cellulose products such as glucose esters, films and carbon nanotubes (LI et al., 2012).

The only commercialized direct solvent process to dissolve cellulose uses the monohydrate of N-methylmorpholine N-oxide (NMMO), however it is cyclic ether that has thermal instability, a redox-active moiety and is prone to dangerous runaway decomposition and, requires high temperatures for the dissolution process. Therefore, suitable ILs could potentially replace NMMO·H2O (HAURU et al., 2012; MOHD et al., 2017).

The dissolving pulp (or regenerated cellulose fiber) based on NMMO/H_2O dissolution system in industrial and commercial scale involves Newcell (Akzo Nobel of Nether-lands) and Tencel (Lenzing of Austria). This last one is the largest producer of lyocell fiber in the world, with annual production about 220 thousand ton. In China, the mainly limited companies are Shanghai Leo, Baoding Swan, Xinxiang Bailu and Shandong Yingli (JIANG et al., 2020).

2.4.2 Caustic extraction

Several studies have reported that direct conversion of paper-grade Kraft pulps into dissolving pulp, aiming to replace the conventional process (sulfite and PHK), may be economically viable (SIXTA et al., 2006; ARNOUL-JARRIAULT et al. 2015; KUMAR; CHRISTOPHER, 2017). Wood chips are submitted to the Kraft or Sulfite pulping process, and subsequently to a sequence of bleaching stages to achieve the dissolving pulp characteristics (KUMAR et al., 2017; LI et al., 2018a; FRIEBEL et al., 2019) (Figure 5). Bleaching stages have at least one stage that is aimed at hemicellulose removal (SCHLESINGER et al., 2005; FRIEBEL et al., 2019). Generally, acid or alkaline treatments are applied to the pulp to remove hemicelluloses, such as caustic extractions (FRIEBEL et al., 2019).

Figure 6 Direct conversion of paper-grade Kraft pulps into dissolving pulp.
Adapted KUMAR; CHRISTOPHER, 2017.

Caustic extraction is an alkaline purification stage that can be carried out either as a cold or a hot stage (CCE and HCE respectively) which aims to remove short chain hemicellulose and amorphous cellulose in dissolving pulps (SYED et al., 2013). CCE is an alternative method to PHK, since the use alkaline conditions facilitates chemical recovery in the Kraft mill, does not require extra digester capacity prior to pulping and decrease loss of pulp yield (DOU; TANG, 2017).

HCE is carried out at higher temperatures 70-120 °C (SIXTA, 2006), higher pulp consistency (10-15%), a lower NaOH concentration, and with retention time between 1-2 hours. This stage usually indicated for sulfite pulps because the carbohydrates are not stabilized via peeling reactions during cooking at low pH. On the other hand, in a prehydrolysed Kraft pulp a new hot alkaline treatment is not efficient because the carbohydrates are stabilized during the cooking (SYED et al., 2013).

CCE usually takes place at 20-50 °C in 10-20% alkaline solution (SIXTA et al. 2013; GONG et al., 2021), a low pulp consistency, high NaOH concentration and the short retention time (SYED et al., 2013). Unlike HCE, the CCE depends on physical effects such as swelling, while the second utilizes chemical reactions for the removal of short chain hemicelluloses and amorphous cellulose (SYED et al., 2013).

In CCE step, the alkali promotes the dissolution of hemicelluloses and short chain carbohydrates is preceded by inter- and intra-crystalline swelling (SIXTA et al. 2013; ROSELLI et al., 2014; GONG et al., 2021). In inter-crystalline swelling occurs penetration into the accessible space between the microfibrils and the amorphous zones. At sodium hydroxide concentrations exceeding 8–9 wt% also intra-crystalline swelling occurs, where the solvent enters the highly organized crystalline regions of the cellulose (ROSELLI et al., 2014).

The pulp yield of CCE is higher than HCE due to side reactions, such as acid or alkaline cellulose degradation, due to higher temperatures. In the sulfite pulp, the caustic extraction is applied in total chlorine free bleaching sequences and with the goal to improve metal removal (FRIEBEL et al., 2019). However, the CCE process can compromise the cellulose reactivity (GEHMAYR et al., 2012; DOU; TANG, 2017). The potential reasons for reduced cellulose reactivity are: a) the cellulose “fibril aggregation” due to removal of residual hemicellulose and low molecular weight cellulose or; b) the conversion of cellulose I to cellulose II due to alkali induction, resulting more severe inter and intra molecular hydrogen bonding (GEHMAYR; SIXTA, 2012; DOU; TANG, 2017).

CCE and pre-hydrolysis produce pulps that vary in properties, such as pore size, accessible surface area and microfibril aggregation that profoundly impact cellulose accessibility and reactivity (DOU; TANG, 2017). The first can be used for dissolving pulp production due to ability to selectively remove hemicelluloses and others short chain carbohydrates (SIXTA et al. 2013; GONG et al., 2021). However, there are limiting factors in relation to recovery from high alkali concentration and the presence of hemicelluloses in the CCE filtrate (GONG et al., 2021).

2.4.3 Enzymatic hydrolysis

Currently, the application of enzymes on an industrial scale is increasing due to their environmental advantages such as ecofriendly, nontoxic and biodegradable nature, as well as their high selectivity (KUMAR; CHRISTOPHER, 2017). Several studies have been made to enzymatically convert pulps to dissolving pulp (IBARRA et al., 2010a,b; AMBJÖRNSSON et al., 2014; DUAN et al., 2015; WANG et al., 2016; KAUR et al., 2016; ZHAO et al. 2017;

BAJPAI, 2018; YANG et al., 2019). Enzymatic treatments also have been reported to improve dissolving pulp properties (LI et al., 2018a).

The accessibility of the residual hemicellulose in dissolving pulp may limit the direct use of enzymes in the purification of this type of pulp (KUMAR; CHRISTOPHER, 2017). Therefore, treatments such as mechanical refining, alkaline, cellulase and ionic liquid have been applied together with the xylanase treatment (DUAN et al., 2016; MA et al., 2017; YANG et al., 2019).

Kaur et al. (2016) explored an adequate dose of enzyme prior to alkali extraction to hemicelluloses removal for the efficient conversion of paper-grade pulp to dissolving pulp. Zhao et al. (2017) report the feasibility of combining refining and xylanase treatment to produce high quality bamboo dissolving pulp, since the refining improved enzymatic xylan removal with a concomitant increase in the alpha-cellulose content. Similar results were observed by Duan et al. (2015) that investigated the efficiency of mechanical refining, followed by CCE and endoglucanase treatment for upgrading paper-grade pulp to dissolving pulp.

Ma et al. (2017) report the use of an ionic liquid/water (IL/w) system to separate hemicelluloses from the chemical pulp with xylanase treatment to increase the efficiency and selectivity of the process. These authors concluded that pretreatment could increase hemicelluloses removal from 71 to 78% and increase the separation selectivity from 11 to 43.8. Moreover, the application of xylanase pretreatment resulted in decreased IL consumption, making the process more economical.

According to Duan et al. (2016), the upgrading paper-grade pulp to dissolving pulp can be done through a process that combines an initial mechanical refining followed by cold caustic extraction and endoglucanase treatment. They report that a synergic effect of refining, low alkali concentration and enzymatic activation increased the xylan removal and reactivity of resulting dissolving pulp.

2.4.4 Other processes

Currently alternative pulping technologies for dissolving pulp production have been explored (SIXTA et al., 2013; NAYEEM et al., 2017; KUMAR; CHRISTOPHER, 2017; SARKAR et al., 2020). Studies also have been focused on the upgrading of paper-grade pulp into dissolving pulp, such as organosolv extraction, mechanical refine, combination between enzymatic treatment and caustic extraction, among others (CHEN et al., 2016). These novel processes can serve as basis for the advanced biorefinery concept (SIXTA et al., 2013).

A recent study investigated the dissolving pulp production from non-wood through water pre-hydrolysis followed by potassium hydroxide (KOH) pulping process and bleaching sequence. The results showed that the further purification with cold KOH extraction increased the purity by 1-3% therefore the dissolving pulp produced can meet the criteria for rayon-grade pulp. Furthermore, this process can be related to the concept of biorefinary because after the pulping process the cooking liquor enriched with nutrients, such as potassium and nitrogen, can be used as fertilizer (SARKAR et al., 2020).

Organic electrolyte solutions (OES) also reported to dissolving pulp production. Yang et al. (2021) produced dissolving pulp from hardwood bleached Kraft pulp through application of ionic liquid (1-ethyl-3-methylimidazolium acetate) and a polar organic solvent c-valerolactone (GVL) solution. The hemicelluloses removal was effective, the yield was 76% and cellulose content was close to 95%. Cheng et al. (2017) also used an OES/ionic liquid system (1-ethyl-3-methylimidazolium acetate and dimethyl sulfoxide) to dissolve cotton linter at room temperature.

Extractions with metal-based complexes, such as nitren and cuen, have been reported to converted paper-grade pulp to dissolving pulp. The first is a strongly alkaline solution (tris (2-aminoethyl)-amine and nickel(II)-hydroxide) that can dissolve xylan and cellulose through interactions with hydroxyl group, and it can increase the cellulose content to 96%, but it is ineffective against softwood pulps. The second (copper ethylendiamine complex) is cellulose removal and it has less selective in xylan removal (KUMAR; CHRISTOPHER, 2017).

The use of formic acid process to produce dissolving pulp was also cited. Nayeem et al. (2017) investigated the dissolving pulp production by formic acid process (FA) followed by caustic extraction. These authors concluded that FA process with CCE is suitable for producing high purity dissolving pulp furthermore the FA process also fractionates lignin and hemicelluloses for biofuel, biochemicals and biomaterials. Jahan et al. (2016) aimed to use old corrugated cardboard (OCC) for production of dissolving pulp by formic acid pulping followed alkaline extraction, and bleaching.

The SO_2–ethanol–water (SEW) is a potential process to replace the acid sulphite process for the production of rayon-grade pulps due to lower cooking times, higher flexibility in the selection of the raw material, and low sugar degradation products (SIXTA et al., 2013).

Furthermore, the Deep Eutectic Solvent (DES) is reported in the literature as a promising process for efficient biomass utilization in dissolving pulp production. Chen et al. (2021) reported the use of the DES treatment process combined with pulping and bleaching processes to produce high-quality dissolving pulp. These authors found the Kraft pulp (DES-KP) produced showed a higher alfa-cellulose (94.02%) and a higher Fock reactivity (98.94%).

3. FINAL CONSIDERATIONS

Dissolving pulp is high value-added product that can be produced from numerous lignocellulosic materials and through different processes. It is a material with characteristics that allow the production of different cellulose derivatives to meet the global market demands.

Global demand for the dissolving pulp continues to grow, so the discovery and improvement of alternative production processes that combine high yields, costs reduction and environmental friendly processes will contribute to the technological advance in this area.

The existing dissolving pulp processes, AS and PHK, constitute the commercially and economically methods however, the new technologies such as ionic liquid, enzymatic hydrolysis, caustic extraction, etc. are promising for future industrial application aiming to replace conventional means of production. There is no doubt that these novel concepts can serve as basis for the advanced biorefinery concept. Ionic liquids for instance permits the production of high-purity dissolving pulps and could be the breakthrough for a new generation of dissolving pulp processes, provided that they can be recycled in an economically feasible way.

CHAPTER II: IMPROVING THE EUCALYPT KRAFT PULP MILL THROUGHPUT BY USING BIOREFINERY CONCEPT

RESUMO

ALMEIDA, Sabrina Mayer de. **Improving the eucalypt Kraft pulp mill throughput by using biorefinery concept.** 2022. 22p. Capítulo II Dissertação (Mestrado em Ciências Ambientais e Florestais). Instituto de Florestas, Departamento de Produtos Florestais, Universidade Federal Rural do Rio de Janeiro, Seropédica, RJ, 2022.

Plataformas de biorrefinaria têm emergido como uma estratégia alternativa para ser aplicada nas indústrias tradicionais de celulose. A estratégia de Biorrefinaria Florestal Integrada é um conceito crescente que tem potencial de substituir os meios de produção convencionais. Biorrefinarias baseadas em líquidos iônicos também são um conceito inovador que pode ser considerado uma alternativa futura economicamente viável e ambientalmente amigável para produção de biocombustíveis, químicos de alto valor agregado e outros bioprodutos. A conversão de polpas químicas em polpa solúvel é uma tecnologia atrativa que pode ser realizada por métodos químicos, físicos, físico-químicos e biológicos ou sua combinação. Portanto, a associação entre extração alcalina e líquidos iônicos pode ser uma alternativa e um potencial método para promover o upgrade de polpas químicas e produzir bioprodutos. Desta forma, o objetivo deste capítulo foi avaliar uma estratégia de aprimoramento dos usos de polpa Kraft comercial através do uso da tecnologia de extração alcalina a frio (CCE) e da aplicação do líquido iônico [2-HTEAF]mesy para produzir produtos de celulose de alto valor agregado. A polpa Kraft de eucalipto foi submetida ao tratamento alcalino (630, 765 and 900 $kg.ton^{-1}$) a 30 °C e subsequentemente à aplicação do líquido iônico (proporção polpa/LI 1:1, 1:2 e 1:6) a 120 °C. A polpa solúvel produzida foi avaliada pelo teor de xilanas e o biomaterial obtido do licor do LI, através de MEV, morfologia e Potencial Zeta. Os resultados mostraram que o estágio CCE produziu polpa solúvel com teor de xilanas entre 2.94-5.53% e que o tratamento 1:6 com LI resultou em um aumento na remoção desses polímeros na polpa solúvel em até 1,05%. Além disso, este solvente mostrou grande potencial para produção de biomateriais, que podem ser usados para produção de nanocelulose, por exemplo. Portanto, este estudo revelou que o uso de LI de baixo custo é um método alternativo que tem potencial para produzir polpa solúvel e outros produtos derivados de celulose.

Palavras chave: [2-HTEAF]mesy; extração alcalina a frio; teor de xilanas; polpa solúvel.

ABSTRACT

ALMEIDA, Sabrina Mayer de. **Improving the eucalypt Kraft pulp mill throughput by using biorefinery concept.** 2022. 22p. Chapter II Dissertation (Master Science in Environmental and Forestry). Institute of Forests, Department of Forest Products, Federal Rural University of Rio de Janeiro, Seropédica, RJ, 2022.

Biorefinery platforms have emerged as an attractive strategy for being applied to the traditional pulp mill. The Integrated Forest Biorefinery strategy is the growing concept that has potential to replace conventional means of production. Ionic liquids based biorefinery is also innovation concept that may be considered an economically viable and environmental friendly future alternative to produces biofuels, valuable chemicals and other bio-products. The upgrading chemical pulps to dissolving grade-pulp are attractive technology, which may be carried out by chemical, physical, physiochemical and biological methods or their combination. Therefore, the association between caustic extraction and ionic liquids may be an alternative and potential method to promotes chemical pulp upgrade and to produces bioproducts. Thus, the objective of this chapter was evaluates a strategy for improving the uses of the commercial Kraft pulp through the use of cold caustic extraction (CCE) technology and application of the [2-HTEAF]mesy ionic liquid to produce high value-added cellulose products. The eucalypt Kraft pulp was submitted to the alkaline treatment (630, 765 and 900 $kg.ton^{-1}$) at 30 °C, and subsequently ionic liquid application (pulp/IL proportion of 1:1, 1:2 and 1:6) at 120 °C. The dissolving pulp produced was evaluated by xylan content and the biomaterial obtained from the IL liquor, by SEM micrograph, morphology and zeta potential. The results showed that CCE stage produced dissolving pulp with xylan content between 2.94-5.53% and that the further 1:6 treatment with IL resulted in an increase in the removal of polymers in the dissolving pulp up to 1.05%. Furthermore, this solvent showed a good potential for biomaterials production that could be useful for nanocellulose production, for instance. Therefore, its study revealed the use of low-cost [2-HTEAF]mesy ionic liquid is alternative method that has a potential to produce dissolving pulp and others cellulose derivatives.

Key words: [2-HTEAF]mesy; cold caustic extraction; xylan content; dissolving pulp.

1 INTRODUCTION

New production technologies, which aim at the full use of raw material for the production of several products, have been considered important alternatives to replace conventional means of production. Biorefinery platforms have emerged as an attractive strategy for being applied to the traditional pulp mill (LUNDBERG et al., 2014). The integrated biorefinery strategy is the growing concept that has potential to respond to these concerns. Integrated Forest Biorefinery (IFBR) may be defined as a biorefinery that may process forest-based biomass, such as wood and forestry residues, for simultaneous production of fibers for paper products, chemicals and bioenergy (CHRISTOPHER, 2013; BAJPAI, 2018b). IFBR implementation of a biorefinery plant into a receptor Kraft pulp mill is the most investigated type (AJAO et al., 2018).

Ionic liquids based biorefinery is also innovation concept that may be considered an economically viable and environmental friendly future alternative to produces biofuels, valuable chemicals and other bio-products (NAZ; UROOS, 2020). The application of inexpensive and non-toxic reagents which have the ability to recover and reuse and mild reaction conditions are very important parameters that must be considered when designing a chemical process (BRZĘCZEK-SZAFRAN et al., 2021). Ionic liquids (ILs) may be called as the next-generation reagents (MOHD et al., 2017), and be used fundamentally as solvents and catalysts for synthetic chemical reactions and other applications (KOSAN et al., 2008; CLOUGH et al. 2013; ADELEYE et al., 2019).

ILs, also referred to as “green” solvents, are versatile materials which can be applied as engineering fluids, pre-treatment agents for wood grinding/biomass extraction, chemical separation, electro-chemistry applications, biological aid, etc. (CLOUGH et al. 2013; VEKARIYA, 2017; ADELEYE et al., 2019; SINGH; SAVOY, 2020). They may be used as solvents due to their better selectivity when compared with that of other conventional organic solvents (COTA et al., 2007) and their ability to modify cellulose structures, lose the rigid plant fiber structure, and remove lignin compounds (PENG et al., 2019). They reduce the cost for multi-ton IL production due to their costs saving and clean way to obtain and their performance to dissolve selectively lignocellulosic components (CLOUGH et al. 2013; HALLETT; WELTON 2011; YANG et al., 2018). The costs of the ILs recently cited in the literature are between \$0.78-5.88 kg^{-1} (BRZĘCZEK-SZAFRAN et al., 2021).

Chemical, physical, physiochemical and biological methods or their combination have been exploited for the production of bioproducts (NAZ; UROOS, 2020). The upgrading chemical pulps to dissolving grade-pulp are also attractive technology, which has the basic principle to remove hemicelluloses impurities selectively in the pulp via post-treatment (CHEN et al., 2019). Generally, acid or alkaline treatments are applied to the pulp (FRIEBEL et al., 2019). Cold caustic extraction (CCE) for example is an alternative method to pre-hydrolysis Kraft to remove short chain hemicellulose and amorphous cellulose to produce dissolving pulp (DOU; TANG, 2017; GONG et al., 2021). It is an alkaline purification stage usually takes place at low temperatures (20-50 °C) with high NaOH concentration, which aims to remove short chain hemicellulose and amorphous cellulose in the pulp (SYED et al., 2013; SIXTA et al. 2013; GONG et al., 2021), to produce cellulose products without much energy expenditure and with easy recovery of the reagent used in the process. Therefore, the association between alkaline treatments and ILs may be an alternative and potential method to promotes chemical pulp upgrade and to produces high value-added cellulose products.

High value bio-products such as biopharmaceuticals, biocosmetics, bionutrients, biochemical, biofertilizers, biomaterials, and biofuels may be produced into biorefinery (RESHMY et al., 2022). Dissolving pulp process, for example, may be considered a prototype

of forest biorefinery due to quantitative separation and cost-effective utilization of the main components of wood (cellulose, hemicelluloses and lignin) (YANG et al., 2019). It is characterized for high cellulose content, trace amount of lignin, extractives and minerals, low hemicellulose and degraded cellulose contents (SIXTA, 2006; SIXTA et al., 2013; DUAN et al., 2015; GONG et al., 2017; YANG et al., 2019). It may be used to produces cellulose esters (sulfonate, nitrate and acetate), cellulose ethers (carboxymethyl, ethyl-, methyl-celluloses), fibers or films (e.g., Viscose, Lyocell) and other new cellulose-based products (SIXTA, 2006; SIXTA et al., 2013; DUAN et al., 2015; YANG et al., 2019).

Furthermore, studies have been reported the use of the ILs aiming lignocellulosic materials fractionation, production of others cellulose derivatives, such as nanocellulose for example (PENG et al., 2019; YANG et al. 2018; CHOI et al., 2019; HAKKAK et al., 2019; BRZĘCZEK-SZAFRAN et al., 2021; SILVA et al., 2021; BABICKA et al., 2021; HARON et al., 2021). Nanocellulose (NC) is a cellulosic material with a last one of its dimensions on the nanometer scale, which may be classified into three subcategories: cellulose nanocrystals (CNC), nanofibrilated cellulose (NFC) and bacterial nanocellulose (BNC) (KHALIL et al., 2014; HARON et al., 2021). They have been used in potential applications such as pulp and paper, automotive, food industry, nanocomposites, drug delivery, medical applications, cosmetic, and implants (HARON et al., 2021). Currently, around 10 companies are producing NC at a commercial scale (50 ton.year^{-1}) (HARON et al., 2021).

Tris(2-hydroxyethyl)ammonium methanesulfonate ([2-HTEAF]mesy) ionic liquid is an emerging solvent used for biomass fractionation which has great selectivity lignin and hemicelulloses and great development potential in the industrial application because it is novel eco-friendly and it has a low cost of synthesis (YANG et al. 2018). Therefore, the use of this IL to obtain cellulose-based bioproducts can be an alternative for the mill, since it can reduce expenses with reagents and processes and possible structural changes in the industry, and consequently to meet other demands of the global market. Thus, the objective of this chapter was evaluates a strategy for improving the uses of the commercial Kraft pulp minimizing material loss by the generation of the potential biomaterials, through the use of cold caustic extraction technology and application of the [2-HTEAF]mesy ionic liquid to produce high value-added cellulose products.

2 MATERIAL AND METHODS

2.1 Methodology organizational chart

The following diagram outlines the steps performed in this research. It comprises synthesis, characterization and recovery of ionic liquid, cold caustic extraction, chelation and ionic liquid stages and cellulose derivatives characterization (Figure 7).

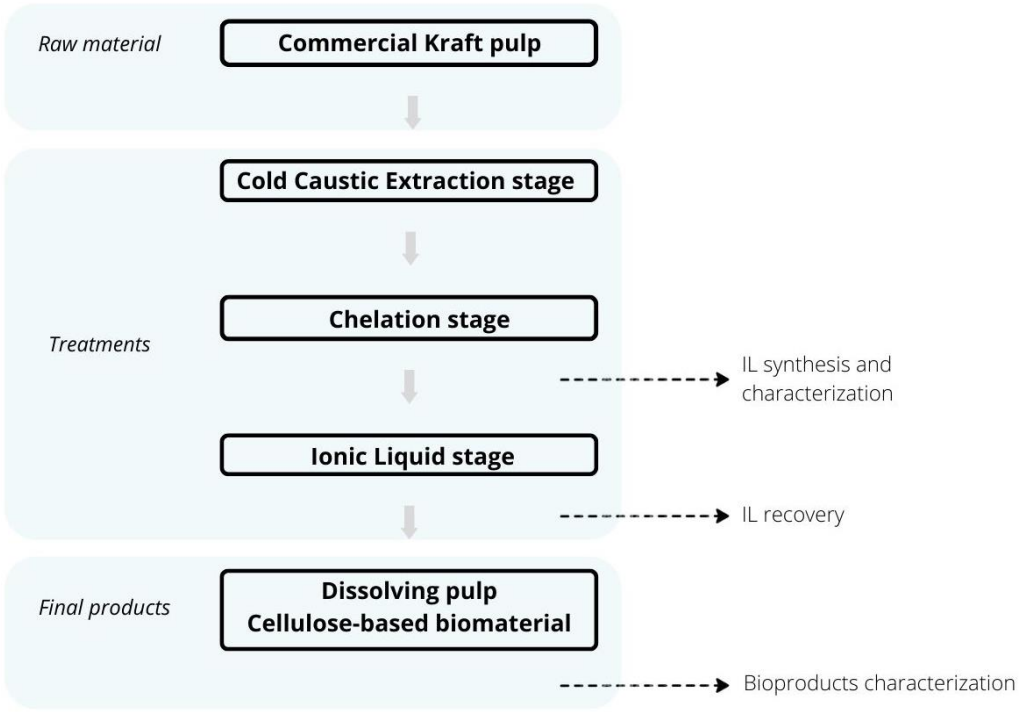

Figure 7 Methodology organizational chart of the steps performed in this study.

2.2 Material

Bleached commercial eucalypt Kraft pulp (*Eucalyptus sp.*) from a Brazilian pulp mill was homogenized and stored in a sealed polyethylene bag for conservation of moisture content. The chemical characteristics of the pulp used as starting raw-material were 91.21% alfa-cellulose content (TAPPI T203 cm-99), 15.28% xylan content (TAPPI T223 cm-84), 0.4 lignin content (TAPPI UM 251), 897.97 $dm^3.kg^{-1}$ viscosity (TAPPI T230 om-08), 0.18% ash content and silicates were not detected (TAPPI T211 om-02). The metals content (TAPPI T266 om-02) is exposed in the Table 1.

Table 1 Bleached commercial eucalypt Kraft pulp Metals content.

Metals content, $mg.kg^{-1}$							
Cu	**Fe**	**Mn**	**Mg**	**Ni**	**Cr**	**Zn**	**Pb**
0.5	13.8	0.9	63.2	0.1	nd	0.7	0.3

nd: not detected.

2.3 Cold caustic extraction and chelation stages

The cold caustic extraction (CCE) and chelation (Q) stages were performed in sequence, following the conditions established in preliminary study according to Table 2.

The CCE treatments of the bleached hardwood Kraft pulp was performed in duplicate at 30 °C and 10% consistency. The alkali charges applied were 630, 765 and 900 $kg.ton^{-1}$. The treatments were carried out in polyethylene bags heated in a water bath for 30 min. The pulp was previously homogenized in order to ensure that all the pulp was in contact with alkaline solution. After the samples were washed 4 times with 9 $m^3.ton^{-1}$ and residence time of 10 min, totalizing 36 $m^3.ton^{-1}$.

The Q stage was performed in duplicate by using 20 kg.ton^{-1} of EDTA, 10% consistency, at 90 °C for 30 minutes. After, the still hot samples were washed with 9 m³.ton^{-1} and residence time of 10 min.

Table 2 Conditions used in CCE and chelation stages.

		Temperature, °C	Time, min	Consistency, %
NaOH charge, kg.ton^{-1}	630 765 900	30	30	10
EDTA charge, kg.ton^{-1}	20	90	30	10

2.4 Synthesis and recovery of ionic liquid

The synthesis and recovery of [2-HTEAF]mesy ionic liquid were performed according the procedures previously described by Yang et al. (2018; 2020). The first was carried out in two steps: synthesis and purification and the second were carried out by extraction with organic solvents, as described below.

In the synthesis, 2 mol of methanesulfonic acid was added drop by drop into the triethanolamine in equal molar ratio, in an ice bath at 0 °C, using 100 ml of methanol as dispersant. The reaction remained active at room temperature for 48 h. At the end of process, the methanol excess was removed by vacuum filtration. In the purification, the salt formed was washed by using 100 ml ethyl acetate and 100 ml diethyl ether in this order. After the washing, these organic solvents were removed by filtration and IL was dried in greenhouse at 45 °C for 72 h.

The ionic liquid recovery was performed after the treatments by using different organic solvents. The derivatives of lignin and hemicelluloses were extracted by using diethyl ether, methylene chloride and ethyl acetate in turn, in three times of extraction for each organic solvent. The recovered ionic liquid was dried at 50 °C under high vacuum for three days and characterized according to Item 2.5.

2.5 Ionic liquid characterization

The [2-HTEAF]mesy ionic liquid was characterized by ^{1}H NMR Spectroscopy, melting point, pH and yield, according to described by Yang et al. (2018) in order to ensure the nature of the synthetized substance.

The ^{1}H NMR Spectroscopy was carried out before and after IL treatment in order to identify the solvent and possible lignocellulosic residues. The spectra were obtained by the BRUKER-500 MHz, with relaxation time of 1 second and 16 scans. 20 mg of IL sample was dissolved in 600 µl of dimethylsulfoxide (DMSO) at room temperature without stirring. Subsequently, the sample was transferred to the 5 mm NMR tube and the spectrum was generated.

The melting point was determined from the slow and gradual heating of the sample in capillary tube recording the start and the end of the melting of the sample. The pH was determined by diluting 5 wt% of IL in deionized water at room temperature, by PHMETRO QUIMIS Q400AS.

The yield was determined through the relationship between the amount of methanesulfonic acid and triethanolamine added for the synthesis and the amount of ionic liquid produced at the end of the reaction, according to the following equation:

$$\mathbf{Y_{IL}} = \frac{\mathbf{M_{synthesis}}}{\mathbf{M_{Acide+Amine}}} * \mathbf{100} \qquad \text{Equation 1}$$

Y_{IL}: yield of [2-HTEAF]mesy ionic liquid, %.
$M_{synthesis}$: mass of ionic liquid after synthesis, g.
$M_{Acide+Amine}$: mass of methanesulfonic acid and triethanolamine used in the synthesis, g.

2.6 Ionic liquid stage

The ionic liquid stage was performed after alkaline stage, according to the procedures previously described by Yang et al. (2018). This step was carried out in duplicate in glass flask heated in autoclave at 120 °C, and 10% consistency. The pulp/IL proportions were 1:1, 1:2 and 1:6, the reaction times were 10 and 30 min, according to Table 3. The heating and cooling times of the autoclave were 25 min each.

The pulp was previously homogenized in order to ensure that all the pulp was in contact with IL solution. In the end of heating water was added to the flask to stop the reaction. After IL treatment the liquor was collected for subsequent characterization of cellulose derivative according to Item 2.6. Posteriorly the pulp was washing with ethanol and water in three times of extraction, with 9 $m^3.ton^{-1}$ each.

Table 3 Ionic liquid stage conditions.

CCE, kg.ton^{-1}	**IL stage**			
	Pulp/IL proportion	**Time, min**	**Temperature, °C**	**Consistency, %**
630	1:1	10 30	120	10
	1:2	10 30		
	1:6	10 30		
765	1:1	10 30	120	10
	1:2	10 30		
	1:6	10 30		
900	1:1	10 30	120	10
	1:2	10 30		
	1:6	10 30		

2.7 Cellulose derivatives characterization

After IL treatments the dissolving pulp was collected and evaluated by measuring pentosan content according TAPPI T223 cm-84 standard procedure. The residual materials

collected by filtration from the IL liquor was characterized by Optical Microscopy, SEM Micrograph (Scanning Electron Microscope), Morphology, and Zeta Potential, aiming to identify the characteristics of the cellulose derivative. The SEM Micrograph analysis was carried out in the Scanning Electron Microscope, model HITACHI TM3000 the, where the samples previously prepared with agar-agar solution (50 g/L) was put on stubs to obtain the images. The optical images were analyzed by Optical Microscope, model LEICA DMi8, and the samples were previously homogenized and inserted in glass slides. The morphological characteristics were obtained by Morfi Neo TECHPAP to the samples previously diluted. The Zeta Potential was evaluated by Litesizer TM500, at 25 °C, where the filtrates were diluted to 0.1 $mg.ml^{-1}$, homogenized for approximately 15 minutes, after 350 µL of the sample were added to the cuvette for analysis.

2.8 Feasibility

The cost of [2-HTEAF]mesy ionic liquid synthesis was estimated by using the Equation 2 previously reported to Hallett et al. (2011). The prices of reagents were obtained in the Alibaba website (ALIBABA, 2022).

$$\textbf{IL price} = \frac{\mathbf{M_1 * P_1 + M_2 * P_2 + M_3 * P_3 + M_4 * P_4}}{\mathbf{M_1 + M_2 + M_3 + M_4}} * \mathbf{1.25} \qquad \text{Equation 2}$$

M_1, M_2, M_3, M_4, M_5: molecular weights of triethanolamine, methanesulfonic acid, methanol, ethyl acetate and diethyl ether, $g.mol^{-1}$.
P_1, P_2, P_3, P_4, P_5: prices of triethanolamine, methanesulfonic acid, methanol, ethyl acetate and diethyl ether, $.

3 RESULTS AND DISCUSSION

3.1 Ionic liquid characterization

The [2-HTEAF]mesy IL was characterized by ^{1}H NMR spectroscopy, melting point, pH and yield to ensure the nature of the substance obtained as previously described in the methodology. According to the physical characteristics, [2-HTEAF]mesy IL was described as white and hygroscopic solid soluble in water, whose pH was 2.69, melting point 85 °C and yield 92.27% (Table 4), which corroborates with Yang et al. (2018).

Table 4 Characterization of [2-HTEAF]mesy IL.

Ionic Liquid	Melting Point, °C	pH	Yield, %
[2-HTEAF]mesy	85	2.69	92.3

IL synthesis occurred by adding methanesulfonic acid drop by drop into the triethanolamine in ice bath to removes the excess heat released from the exothermic reaction. Studies report that generally protic ionic liquids (PILs) are synthesized by one-step protonation of organic amine without any by-products (SUN et al. 2017; YANG et al., 2018) however, this reaction releases extreme heat and typically is very fast, making it difficult to control (CHEN et al., 2014). The yield (92.3%) obtained in the synthesis step may be considered satisfactory since that values closer to 100% demonstrate that practically all the reagents consumed in the synthesis, there are not losses for the production of by-products and consequently, the lower chemical costs. It is one the most important parameter to enable de use of IL on an industrial scale because are related with the production costs.

Melting point is associated with structure and chemical composition of IL (WASSERSCHEI; KEIM, 2000; FABRE; MURSHED, 2021) and it is of key importance in different applications (NASIRPOUR et al., 2020). The [2-HTEAF]mesy IL showed a low melting point, 85 °C, a fact that may be related with to the ions size. Generally, salts with large and asymmetrical ions and greater alkyl chains interaction usually have low melting points (WASSERSCHEID; KEIM, 2000; WANG et al., 2014; NASIRPOUR et al., 2020). Plechkova; Seddon (2008) report that 1-butyl-3- methylimidazolium cation (with has only C1 symmetry) has only one methyl substituent and larger asymmetry, therefore it has a melting point about 100 °C. McFarlane et al. (2000) observed that ammonium, pyrrolidinium and phosphonium cations had melting points below room temperature when had asymmetric radicals.

The Figure 7 shows the ^{1}H NMR spectra of the [2-HTEAF]mesy IL, where it was seen that the peaks are in accordance with was previously reported by Yang et al. (2018). The chemical shifts 3.30 and 3.75 ppm correspond to the resonance of the hydrogens indicated as 2 and 3, which are associated with the triethanolamine (cation) (Figure 8). Peak 5 is related to the hydrogens of methanesulfonic acid (anion) and has chemical shifts of 2.39 ppm. Peak 1 indicates the resonance associated with the exchangeable proton (N-H) of IL, with chemical shifts of 8.65 ppm. The hydrogens indicated as 4 did not show resonance. Exchangeable protons are understood to be hydrogens linked to oxygen (OH) and hydrogens linked to nitrogen (N-H).

Analyzing different ILs, Davidowski et al. (2016) observed that the tendency is that as the strength of the acid increases, the chemical shift of the exchangeable proton is shifted to lower ppm values, therefore, the change of this proton has information about how strong is the association between it and the base. When comparing them with the spectrum generated in this research, it appears that the more unshielded proton (δ between 8 and 9 ppm) have a lower chemical shift, thus possibly they show a stronger association between the acid and the amine.

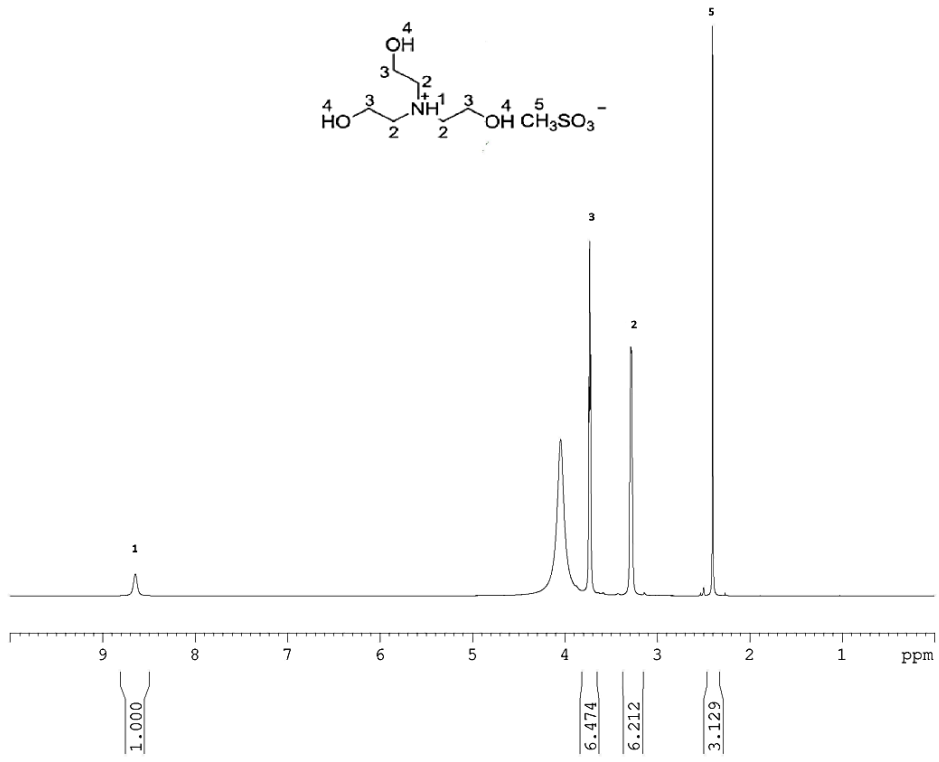

Figure 8 ¹H NMR spectrum of [2-HTEAF]mesy ionic liquid. 1H NMR (DMSO) δ in ppm 2.39 (s; 3H), 3.30 (m; 6H), 3.75 (m; 6H), 8.65 (s; 1H).

The knowledge of these characteristics contributes significantly when aiming to use ILs in industrial processes. The characteristics of [2-HTEAF]mesy IL, such as melting point below 100 °C and solubility in water allows to adjust the process temperature according to final use, reducing process costs. Several ILs with miscibility gap in water have been considered interesting candidates for separation process by ionic liquid extraction (WASSERSCHEID; KEIM, 2000).

3.2 Cold caustic extraction and chelation stages

The CCE and Q stages were performed in order to remove hemicelluloses and transition metal ions, respectively. The performances of these stages were evaluated by measuring xylan, ash, metals and silicates contents following the procedures previously described in the methodology. The Table 5 shows the results obtained in the alkaline stage.

Table 5 Cold caustic extraction results.

	Sample	**Xylan content, %**	**Removal efficiency, %**	**Yield, %**
	Pulp*	15.28	-	-
CCE, kg.ton^{-1}	630	5.53	63.83	91.73
	765	3.88	74.63	91.59
	900	2.94	80.77	92.75

*Untreated bleached eucalypt Kraft pulp

It was observed that the CCE yields were greater than 90% and yield losses were around 9% which may be related with to the removal of short cellulose chains and hemicelluloses. Friebel et al. (2019) report that the pulp yield did not significantly decrease at low temperature, due to alkaline peeling, as cellulose alkaline degradation including hydrolysis begins only at temperatures exceeding 140 °C. Roselli et al. (2014) observed that the high purity pulps generate higher yield losses.

Furthermore, with the improving alkaline charges there was a good performance in the xylan removal and consequently efficiency removal, being the best performance obtained when using CCE treatment of 900 kg.ton^{-1}. This behavior may be related to the greater fiber swelling that may have improved the accessibility of the xylans associated with the microfibrils. Some authors report that the CCE step depends on physical effects such as swelling (inter- and intra-crystalline) to remove short chain hemicelluloses and amorphous cellulose (SIXTA et al. 2013; SYED et al., 2013; ROSELLI et al., 2014; GONG et al., 2021).

The hemicelluloses are mainly located in the inter-crystalline areas (ROSELLI et al., 2014), therefore strong alkaline environment promotes the swelling of cellulose skeleton (GONG et al., 2021) and consequently allows the penetration into the accessible space between the microfibrils and the amorphous zones (ROSELLI et al., 2014) resulting in the removal of these carbohydrates during CCE extraction (GONG et al., 2021). Li et al. (2018b) found that high NaOH concentration may be effective to cleave linkages of the hemicelluloses embedded firmly in the cell wall. Friebel et al. (2019) observed that at lower temperatures (0–40 °C) xylan content of has significantly reduced. The same authors also report that the higher the NaOH concentration more intensive was the swelling and consequently, more hemicellulose was extracted.

Considering that dissolving pulp is purified bleached pulp with low content of hemicelluloses (3-6%) (DUAN et al., 2015; YANG et al., 2019) and that the CCE is

alternative method to PHK for dissolving pulp production (DOU; TANG, 2017), all alkaline treatments produced dissolving-grade pulp due to a drastic drop in the xylan content.

The hemicelluloses are undesirable because they react with the reagents of the derivatization process, can compete with the cellulose hydroxyl groups and promote defects in the quality of the products dissolving pulp based. They can promote color and haze formation, an increase in false viscosity and, reduced filterability and cellulose reactivity (SAKA; MATSUMURA, 2004; ROSELLI et al., 2014; COLODETTE; GOMES, 2015).

Furthermore, the management of pulp metal ions, ash and silicates must be carried out in order to minimize these possible inconveniences in the pulp quality. The Table 6 shows the ash and silicates contents and the Table 7 presented metals content, obtained in the stages CCE and CCE-Q. It was possible to observe that the chelation stage works well, removing a high content of minerals from the dissolving pulp.

Table 6 Ash and silicates contents obtained before and after the Q stage.

Sample	CCE, kg.ton^{-1}	Ash content, mg.kg^{-1}	Silicates, mg.kg^{-1}
Pulp	-	36.2	nd
CCE	630	75.2	0.8
	765	74.6	0.3
	900	170.0	nd
CCE-Q	630	51.8	0.5
	765	34.4	nd
	900	25.8	nd

nd: not detected / Pulp: untreated bleached eucalypt Kraft pulp

Table 7 Metals content before and after Q stage

Sample	CCE, kg.ton^{-1}	Metal content, mg.kg^{-1}							
		Cu	Fe	Mn	Mg	Ni	Cr	Zn	Pb
Pulp*	-	0.5	13.8	0.9	63.2	0.1	nd	0.7	0.3
CCE	630	0.6	19.0	1.8	114.6	0.4	0.2	6.4	2.9
	765	20.9	107.2	2.6	74.9	4.1	4.8	82.1	11.0
	900	1.5	201.6	11.9	1016.1	0.6	0.6	6.1	2.5
CCE-Q	630	1.6	14.3	0.8	19.6	0.6	nd	2.5	0.5
	765	2.1	12.9	0.5	20.9	0.3	nd	3.2	3.1
	900	0.4	6.9	0.3	5.6	0.1	nd	1.8	0.6

nd: not detected.
Pulp: untreated bleached eucalypt Kraft pulp.

In the CCE stage was observed the increase in the ash and silicates contents due to applied alkaline charge however the chelation step promoted a significant reduction in this parameters, with the best performance obtained when using CCE treatment of 900 kg.ton^{-1}. The final pH of Q step for 630, 765 and 900 kg.ton^{-1} was 5.61, 5.56 and 6.16 respectively, where can be seen that after chelation there was a tendency to reduce metal ions in the pulp. Normally, the Q stage is operated in acidic conditions, pH 4-7, due to the better performance of chelating agents (AREA et al., 2010; PINTO et al., 2015) and depends on how strongly these are bound to the pulp (GRANHOLM et al., 2010).

The iron (Fe) and magnesium (Mg) were the mainly metal ions observed in the pulp as they are related to the physiological demands of the tree. After chelation these contents were significantly reduced because chelating agent functional groups (such as –COOH and $–NH_2$) form a ring structure chelate around the metal ion and due to the high-stability of the Fe-EDTA complex in acid environments (GRANHOLM et al., 2010; PINTO et al., 2015). The low content of the others metal ions observed in the CCE-Q sequence show that they have a greater affinity to chelating agent and were removed with high efficiency.

A recent study report the previous application of EDTA-based neutral detergent solvent in the treatment of corn straw biomass with [2-HTEAF]mesy IL, to wash away most of the cellular contents including fat, sugar, starch and protein from raw material. (YANG et al., 2018). This biomass also has approximately 25% ash in its composition (DAUD et al., 2014), therefore this washing with EDTA solvent possibly also contributed to the removal of these minerals.

High inorganic materials content is a challenge to dissolving pulp production (BATALHA, 2011). They may also interfere in the subsequent derivatization process, in the quality of products causing colorization of pulp and catalytic decomposition, as well as in the process efficiency because can promote incrustation and corrosion of equipment in unscheduled plant shutdown (GRANHOLM et al., 2010; COLODETTE; GOMES, 2015). Reyes et al. (2019) report that the ILs in the presence of some residual ions from the synthesis might result in pulp color changes. According to Colodette and Gomes (2015) the acetate-grade dissolving pulp has 0.05% ash content.

3.3 Ionic liquid stage

The pulp obtained after CCE-Q treatment was submitted to the IL stage aiming to remove even more hemicelluloses of dissolving pulp produced. The performance of this stage was evaluated by measuring xylan content following the procedures previously described in the methodology.

In general it was observed that the [2-HTEAF]mesy IL has the ability to reduce the xylan content after alkaline treatment. The Tables 8 and 9 show the results obtained in treatments with 1:1 and 1:2 IL proportions, where it is seen that the higher alkaline charge (900 $kg.ton^{-1}$) favored the IL action in the removal of the residual xylan to dissolving pulp. In the first proportion, the best scenario was observed in the reaction time of 30 min and in the second, in the treatment with 10 min, where the xylan content reduced 0.34 and 0.38% respectively, when compared to CCE. In spite of small removal, this purity increase may be relevant, since in the next sessions it will be demonstrated that the IL may be recovered and used again. It is also important to note that other reference has showed a better performance of the evaluated IL in this study (YANG et al., 2018).

Table 8 Variables observed in the treatment 1:1 IL proportion of [2-HTEAF]mesy IL.

	Sample	Time, min	Xylan content, %		Removal efficiency, %	Yield, %
			CCE	CCE-IL		
CCE, $kg.ton^{-1}$	630	30	5.53	5.53	nd	98.44
	765		3.88	3.88	nd	98.06
	900		2.94	2.60	11.49	97.31
	630	10	5.53	5.53	nd	99.08
	765		3.88	3.88	nd	96.61
	900		2.94	2.83	3.83	98.78

nd: not detected.

Table 9 Variables observed in the treatment 1:2 IL proportion of [2-HTEAF]mesy IL

	Sample	Time, min	Xylan content, %		Removal efficiency, %	Yield, %
			CCE	CCE-IL		
CCE, kg.ton^{-1}	630	30	5.53	5.53	nd	99.94
	765		3.88	3.88	nd	99.30
	900		2.94	2.64	10.21	99.10
	630	10	5.53	5.30	4.07	98.93
	765		3.88	3.88	nd	98.95
	900		2.94	2.56	12.77	98.56

nd: not detected.

In the Table 10 was observed that the higher IL proportion associated with longer reaction time, 1:6 and 30 min respectively, promoted a drastic drop in the yield and in the removal efficiency. In the 900 kg.ton^{-1} CCE, it was not possible to determine xylan content and removal efficiency, because all material was leached during the washing of the pulp, being observed 42.73% of yield.

On the other hand, when the time was reduced to 10 min, there was increase in the xylan removal and consequently in the other parameters. The best scenario was obtained in the treatment with 1:6 IL proportion, reaction time of 10 min and CCE charge of 630 kg.ton^{-1}, being observed a decrease of 1.05% in the xylan content compared to CCE. Despite the alkaline charge of 765 kg.ton^{-1} has shown the higher removal efficiency, the xylan was lower than in the first case, there was a decrease of 0.83%.

These treatment conditions proved to be efficient to remove xylan possible more strongly linked with cellulose. The cellulose swelling promoted by previous alkaline environment may be improved the accessibility of the xylans associated with the microfibrils, favoring the subsequent IL action. Further, it is possible that the IL can also improve the fiber swelling. LI et al. (2018b) suggest that the ILs with a strong penetrating ability can conducive to the swelling of the cell walls, resulting in the solubilization of hemicelluloses with high molecular weights in subsequently treatments. The IL may be diffused into amorphous domains of the cellulosic fibers and then it gradually deteriorated its crystalline network (GHASEMI et al., 2018), resulting in greater accessibility the hemicelluloses.

Table 10 Variables observed in the treatment 1:6 IL proportion of [2-HTEAF]mesy IL

	Sample	Time, min	Xylan content, %		Removal efficiency, %	Yield, %
			CCE	CCE-IL		
CCE, kg.ton^{-1}	630	30	5.53	5.04	8.82	73.98
	765		3.88	3.43	11.61	66.26
	900		2.94	nd	nd	42.73
	630	10	5.53	4.48	19.00	90.31
	765		3.88	3.05	21.29	90.13
	900		2.94	2.49	15.32	89.52

nd: not detected.

The yield loss observed mainly in the treatments with higher IL proportion (1:6) and time (30 min) at 120 °C may be related to dissolution of hemicelluloses and cellulose from

dissolving pulp, due to break of bonds in its structure. IL may degrade the glucan fraction, which is more evident at higher temperatures (MALARET et al., 2020) due to destabilization of the hydrogen bonding (QASIM et al., 2021). In the environment with high temperatures the O(2)H-O(6) intra-molecular H-bonds disrupting at the first place (WEI et al., 2018; QASIM et al., 2021). The breakdown of this polymer occurs due to interaction between cellulose hydroxyl groups and anion (electron-pair donors) and cation (acceptors) of IL, which form a complex of electron-donating and electron-accepting molecules that interacts with each other (QASIM et al., 2021).

The [2-HTEAFF]mesy IL was previously used for corn straw fractionation, and show the great selectivity to remove lignin and hemicelluloses at 140 °C (YANG et al., 2018). This biomass had approximately 31.35% of hemicelluloses (YANG et al., 2018) being composed mainly xylan (22.9%) and arabinan (2.9%) (MONIZ et al., 2013), consequently this solvent has selectivity for xylan.

Yang et al. (2018) observed the hemicelluloses extraction efficiency between 30-50% however in this study it was found the low removal efficiency. The corn straw has higher hemicelloses content than from eucalypt dissolving pulp, consequently these polymers are more available in the first material, favoring their removal. Furthermore, it is possible that the difference between chemical structure and molecular masses of hemicelluloses of hardwood and biomass have contributed to the difference in selectivity of the [2-HTEAFF]mesy IL.

Studies report that the limiting factor in the optimization of hemicellulose removal is the chemical and macromolecular nature of the pulp polymers and not their amount (ROSELLI et al., 2015). The selectivity of hemicelluloses dissolution is based on the difference in molar mass between this polymer and cellulose, where low molar mass hemicelluloses are dissolved in less powerful solvent mixtures than cellulose, further their OH-groups are readily accessible (ROSELLI et al., 2017). The molecule sizes of the hemicellulose and cellulose can overlap slightly (ROSELLI et al., 2012; FROSCHAUER et al. 2013), thus losses of smaller cellulose chains with sizes similar to hemicelluloses may occur.

Recent study shows that in the IONCELL-P process the birch pulp was the most suitable substrate compared to eucalypt because its hemicelluloses have a higher molecular mass than that the first. The authors also report that the pine pulp could not be purified as efficiently as the eucalypt pulp because of the larger moiety of hemicelluloses with higher molar masses, which are overlapping severely with the molar mass region of the cellulose fraction (ROSELLI et al., 2015).

In solvation process, there was an interaction between anion-polymer-cation, where the anion form strong H-bonds with the OH groups of the polymer, while the cation interacts with the anion and is gradually moving between the dissolving polymer strand and the solid bulk of the substrate, acting as a lever, pushing the dissolving strand into the solution (ROSELLI et al., 2017). Roselli et al. (2015) observed that the Ioncell-P extraction in the eucalypt pulp results in the decrease of hemicelluloses content (xylan and mannan) from 16.6 to 2.4%, but less cellulose was dissolved. Malaret et al. (2020) investigate pretreatment efficacy of the IonoSolv pretreatment of eucalypt and found the complete hemicellulose removal at 120 °C and times equal to or longer than 240 min, and for 150°C at times longer than 60 min.

On the other hand, it is believed that water content in the IL stage may be reduced the efficiency of the solvent. Some authors report that the dissolution capacity of ILs and hemicelluloses solvation depends strongly on the water content of the solvent system (HAURU et al., 2012; ROSELLI et al., 2014). IL-water system at moderate temperatures can extract hemicelluloses with high selectivity and efficiency (ROSELLI et al., 2012; FROSCHAUER et al. 2013; SIXTA et al. 2013; ROSELLI et al., 2015), because water

content can reduce drastically the cellulose solubility (HAURU et al., 2012; ROSELLI et al., 2014; NASIRPOUR et al., 2020). Hemicelluloses with low molecular weight and polar side chains are more easily dissolved in presence of water (WOLLBOLDT ET al., 2017). The NMMO IL, for example, when completely hydrated is no longer a good for dissolution of cellulose (MOHD et al., 2017), therefore the selectivity by other lower molecular weight polysaccharides can be increase.

The IL-water system with optimum water concentration must balance the maximum hemicellulose and minimum cellulose dissolution (or degradation) (WOLLBOLDT ET al., 2017). Low water content increases the efficiency of the xylan removal but also promotes cellulose dissolution, due to polymers sizes (ROSELLI et al., 2012; FROSCHAUER et al. 2013; ROSELLI et al., 2015; ROSELLI et al., 2017). The cellulose is insoluble in water at moderate temperatures because the intra- and intermolecular hydrogen are stronger than bonds to water (HAURU et al., 2012). Rabideau and Ismail (2015) observed that the IL anion ability to form hydrogen bonds with cellulose decreases dramatically when water is added to the system.

Despite adding water at the end of the LI application process to precipitate the cellulose, it is possible that during the process the amount of water used (to reach 10 % consistency) may have been small to maintain the integrity of the cellulose chains and selectively remove the hemicelluloses to the dissolving pulp. Therefore, the use of IL-water system, in adequate amounts, could promote cellulose precipitation, increase of selectivity of IL on hemicelluloses, decrease the intense yield loss observed mainly in the most drastic treatments and consequently reduce application costs.

The system consistency and the type of solvent may be influence the xylan removal. Systems with IL with high molar mass has lowest molar ratio between anion-pulp, evidently the consistency applied must be low (that is less amount of solid material) enough to ensure a sufficient amount of anions to solvate the polymers. Furthermore, high pulp consistencies reduce the IL strength due to the increasing amount of accessible hydroxyl groups in the pulp (ROSELLI et al., 2017). Thus, it can be considered that this is an initial study, but that an improvement of the operational conditions should be considered to improve the potential of this ionic liquid for its application in a pulp mill.

In addition to the production of dissolving pulp, the formation of a biomaterial was observed. This pulp derivative was produced in the treatments with 1:6 IL proportion, reaction time of 30 min and CCE charges of 630, 765 and 900 $kg.ton^{-1}$. These biomaterials were collected in the filtrate obtained from the IL liquor and they were characterized by Optical Microscopy, SEM Micrograph, Morphology, and Zeta Potential following the procedures previously described in the methodology.

In order to further study the structural changes of the fiber, optical and SEM pictures were taken and shown in the Figures 8 and 9. The fibers analyzed were obtained of treatment of the 1:6 IL proportion with 900 $kg.ton^{-1}$, where it is seen that the IL action promoted the structural alterations of the fibers, being observed that the surface area of fibers was fragmented, the fiber walls were deconstructed and the size was intensely reduced, possibly because the [2-HTEAF]mesy broke the stable interaction among different lignocellulosic components (YANG et al., 2018). Similar results were obtained by Yang et al. (2018) a when analyzing the fibers of the biomass treated with IL.

These characteristics may be related to the nanocellulose production, which it has at least one of its dimensions on the nanometer scale and can be classified into three subcategories: cellulose nanocrystals (CNC), nanofibrillated cellulose (NFC) and bacterial nanocellulose (BNC), which varies according to their dimensions, their functions and their synthesis (KHALIL et al., 2014; HARON et al., 2021). Reyes et al. (2019) found that the

eucalypt Kraft pulp treated with ILs can be dissolved and that the dissolution can be evolves to partial hydrolysis appearing cellulose nanocrystals (CNC).

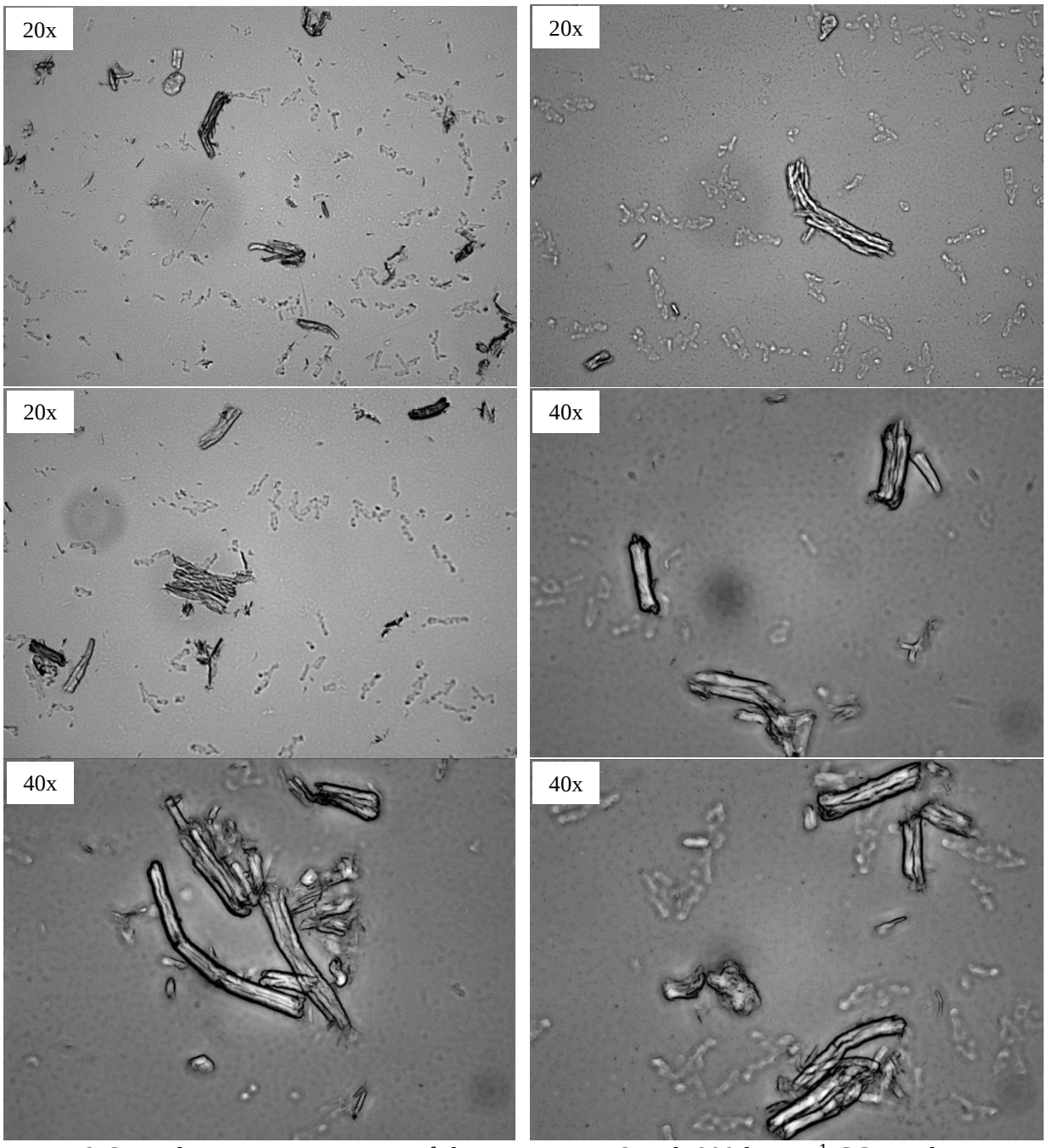

Figure 9 Optical microscopy images of the treatment 1:6 with 900 kg.ton^{-1} CCE and reaction time of 30 min.

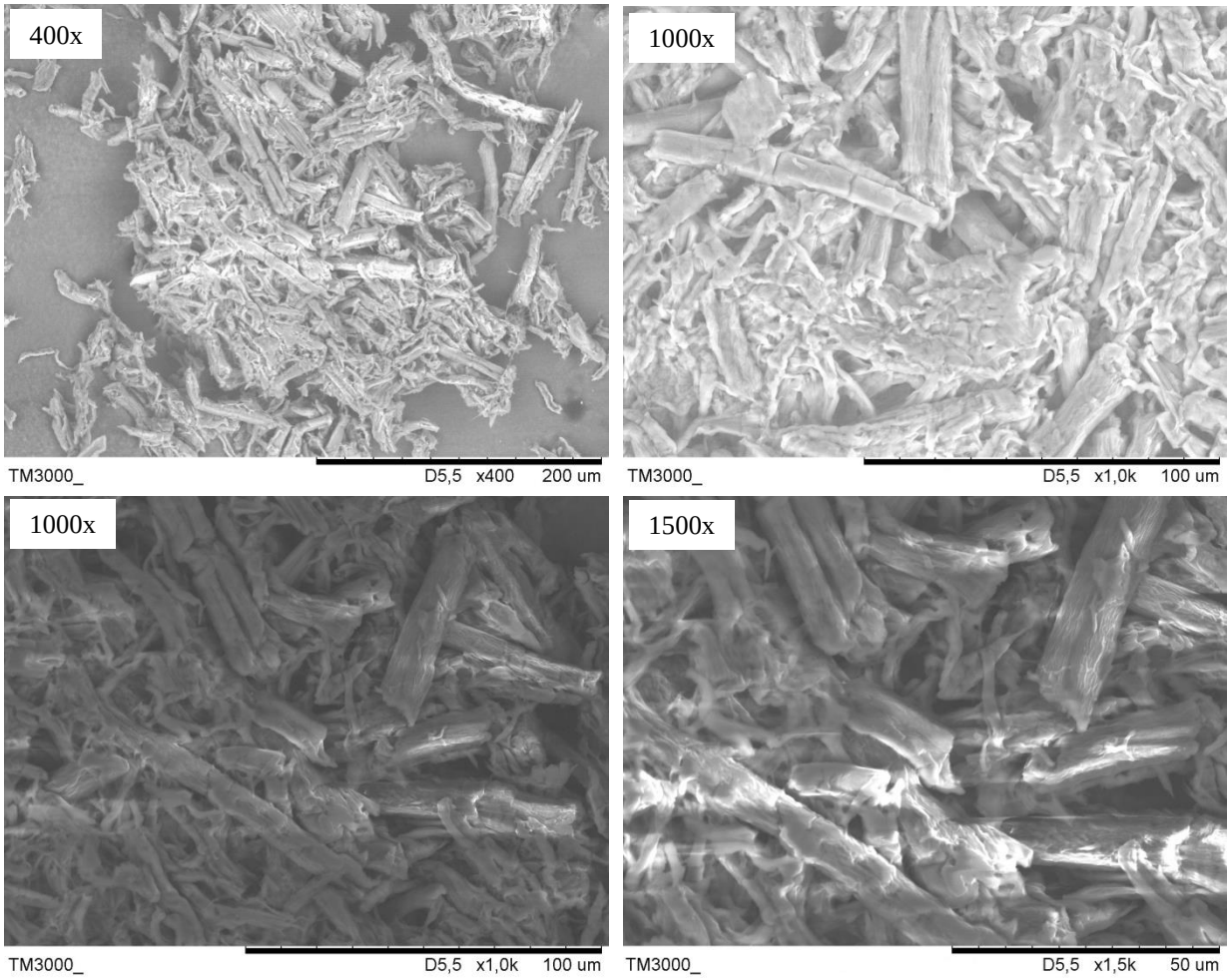

Figure 10 SEM micrograph images of the filtrate obtained from the treatment 1:6 with 900 kg/ton CCE charge and reaction time of 30 min.

The Table 11 shows the results of the morphology analysis of the treatments 1:6 IL proportion, reaction time of 30 min and three CCE charges (630, 765 and 900 kg.ton^{-1}), where the fiber was considered the material greater than 200 µm and fines, less 200 µm. It was observed that the mean length of the fiber and fines reduced according to the increase in the charge of the treatments, where to the first the values were around 297-340 µm and to the second, 20-31 µm, which on the nanometer scale represent values 1000x larger.

The lengths obtained in this research are below that normally eucalyptus pulp fibers have, 0.6-0.85 mm (or 600-850 µm) (NEIVA et al., 2015), on the other hand, they are above the expected for nanocellulose. Generally, NFC has diameter between 5-70 nm and several micrometers length, and CNC has typical diameter of 5–30 nm and the length of 100-500 nm (HARON et al., 2021). Reyes et al. (2019) verified that ILs are capable to produce cellulose nanocrystals in the form of spherical aggregates with a diameter of 40–120. Damasio (2015) obtained nanocrystals with mean widths and length of 10.32 and 85.48 nm respectively. Demuner (2017) produced eucalypt nanofibrillated lignocellulose and found mean fibril widths around 23.7 and 38.9 nm.

It was evident that all samples were predominantly composed by fines, the percentages varying between 86-98% approximately. Obviously, the IL treatments with the higher NaOH concentration showed higher fines content, due to the intense fragmentation of the cellulose fibers due to the action of LI-CCE. The samples with the higher alkaline charge showed a

greater broken fiber content, being 24.65, 38.48 and 40.51% to the 630, 765 and 900 kg.ton^{-1}, respectively.

Table 11 Morphology parameters obtained from treatments 1:6 IL proportion, reaction time of 30 min and 630, 765 and 900 kg.ton^{-1} CCE charges.

	Parameter	**CCE, kg.ton^{-1}**		
		630	**765**	**900**
Fibers	Mean length, µm	340	300	297
	Mean width, µm	16.8	17.4	19.9
	Broken fiber content, %	24.65	38.48	40.51
Fines	Mean length, µm	31	32	29
	Mean area, µm	539	571	466

The Zeta measures the speed of the particles in the presence of an electric field. How fast the particles move depends on the surface charge (or zeta potential) of the particles. In general, the greater the magnitude of the zeta potential the more stable the colloid. The Table 12 shows the Zeta potential, where it seen that the values are close, 0.1, 0.5 and 0.2 mV to 630, 765 and 900 kg.ton^{-1} respectively.

The results indicate that the particles do not have high stability, showing Zeta Potential below the expected for nanocellulose. Values with zero charge have a high tendency to agglomerate (REYES et al., 2019), thus with low stability. High zeta indicate high dispersion capacity in water and lower tendency to agglomerate and precipitate, while lower values indicate low dispersion stability (TONOLI et al., 2012; LU et al., 2014; DEMUNER, 2017; REYES et al., 2019). Demuner (2017) obtained -45.0 mV for eucalyptus NFC considering the materials the stable suspensions, while Damasio (2015) obtained -26.86 mV to long fiber NFC. Reyes et al. (2019) observed zeta potential of -24 and -12 mV to the CNC produced from Kraft pulp treated with [bmim][HSO4] and [emim][Cl] ILs.

According to Reyes et al. (2019) the electrical environment of the CNC particles has a direct influence on morphology, where the unstable CNC suspensions resulting in more agglomeration, consequently making it difficult to visualize the individual nanocrystals (REYES et al., 2019).

Table 12 Zeta Potential obtained from the treatment 1:6 with reaction time of 30 min in the three CCE charges.

CCE, kg/ton	**Zeta Potential, mV**
630	0.1
765	0.5
900	0.2

Despite having physical similarities with nanocellulose, it is not possible to consider that the fibers contained in the IL liquors correspond to this product. However, it is verified that the IL has potential for nanocellulose production, therefore more studies is needed to obtain information about the process optimization (time, temperature, NaOH and IL concentration), aiming at the expansion of the possibilities for IL application to produce different products in only process.

3.4 Ionic liquid recovery

Generally, ILs are expensive material, therefore their recycling is necessary to make their application economically feasible (NASIRPOUR et al., 2020). In order to realize the

environmentally friendly processing, the IL should be able to completely recyclable and keep high separation efficiency (YANG et al., 2018). Thus, [2-HTEAF]mesy IL recovered was analyzed by ^{1}H NMR spectroscopy to evaluate the efficiency of the recovery process and identify the possible impurities.

It was observed that the [2-HTEAF]mesy returned to solid state after recovery process. The Figure 11 shows the ^{1}H NMR spectrum of the solvent recovered which corroborates with Yang et al. (2018). It can be seen the chemical shifts 3.29 and 3.74 ppm, which correspond to the resonance of the hydrogens indicated as 2 and 3 respectively associated with the triethanolamine (cation). Peak 5 is related to the hydrogens of methanesulfonic acid (anion) and has chemical shifts of 2.42 ppm. Peak 1 indicates the resonance associated with the exchangeable proton (N-H) of IL, with chemical shifts of 8.68 ppm. The hydrogens indicated as 4 did not show resonance. Furthermore, it was also observed the presence of some new protons localized in the 1.89, 2.43 and 4.69 chemical shifts, but its intensity was very weak, which means that the recycled IL contained little impurities. Also observed slight color change which can probably be attributed to the traces of thermal degradation products of dissolving pulp (YANG et al., 2018). Therefore, this solvent shows the recovery ability, favoring its reutilization in the mill and consequently reducing the production costs.

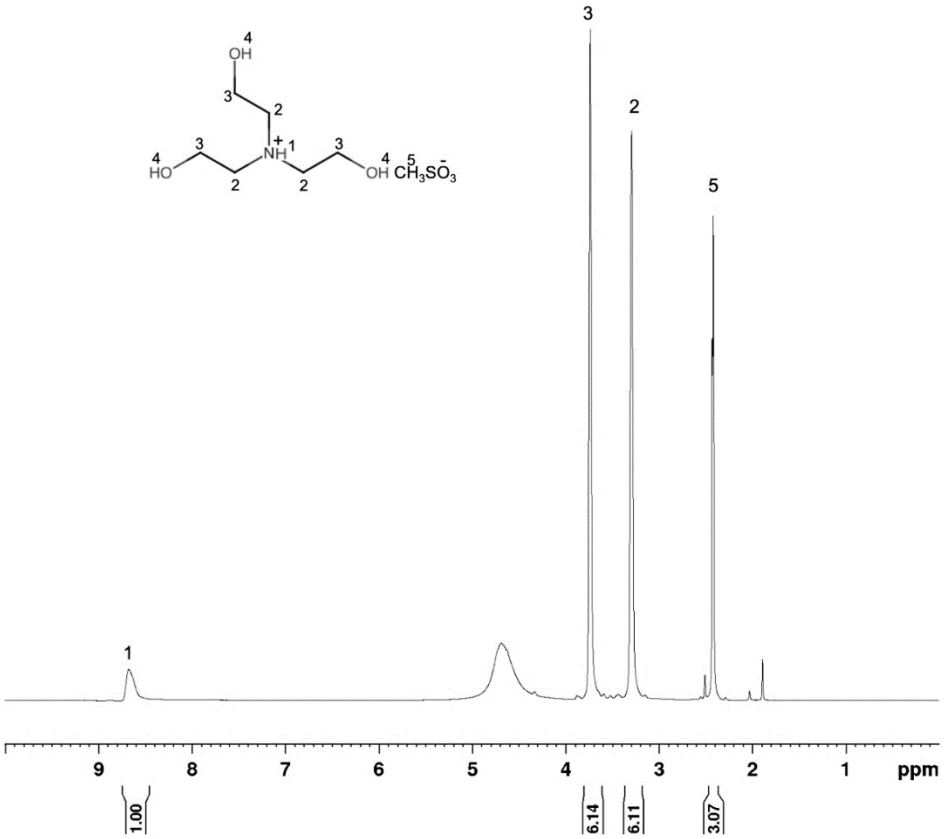

Figure 11 ¹H NMR spectrum of the [2-HTEAF]mesy ionic liquid recovered. ^{1}H NMR (DMSO) δ in ppm 2.42 (s; 3H), 3.29 (m; 6H), 3.74 (m; 6H), 8.68 (s; 1H).

3.5 Feasibility

Current IL process has environmental disadvantages and high-cost, therefore design novel eco-friendly and cheap ILs designing novel ILs has been a great possibility for the application of these solvents on an industrial scale (YANG et al., 2018). ILs have exhibited

significant potential for application in different areas of research at laboratory scales as well as have been arousing interest for applications in ILs-based industrial process, but the high costs of most laboratory-synthesized ILs are considered the limiting factor (CHEN et al., 2014).

Three key-points must be considered when trying to make ILs-based treatment process a practical reality: reducing IL cost, reducing IL charge and increasing IL recycling. These last two are also directly related with the IL costs. Therefore, if the price of ILs is reduced, this process can be placed in a competitive position with other conventional process (KLEIN-MARCUSCHAMER et al., 2011; CHEN et al., 2014). To economically evaluate the cost of production of the IL, the total annualized cost (TAC) of the scaled-up processes must be taken into account, comprising of the operating expenses (OPEX) and the annualized capital expenses (CAPEX) (BAAQEL et al., 2020; BRZĘCZEK-SZAFRAN et al., 2021).

However in this research was applied a simplified methodology reported by some authors that does not determine the absolute price of industrial process, but which provides important information about costs (CHEN et al., 2014; YANG et al., 2018; BRZĘCZEK-SZAFRAN et al., 2021). These authors used an equation proposed by Hallett et al. (2011) reported in Item 2.7 which the IL cost is estimated by using the molecular weight and prices of reagents. The prices available on the Alibaba website (ALIBABA, 2022) were used to estimate the IL cost and provides a reasonable comparison (Table 13).

Table 13 [2-HTEAF]mesy IL synthesis costs.

Reagent	**Price, US$.kg^{-1}**	**Molecular weight, g.mol^{-1}**	**Final cost, US $.kg^{-1}**
Methanesulfonic Acid	1.00	96.11	
Triethanolamine	0.08	149.19	
Methanol	0.38	32.04	0.93
Ethyl Acetate	0.20	88.11	
Diethyl Ether	2.57	74.12	

The cost of synthesis of the [2-HTEAF]mesy LI was US$ 0.93 kg^{-1}, whose value is well below the cost of NMMO IL ($2.00 kg^{-1}) (ALIBABA, 2022) and others ionic liquids and organic solvents, such as acetonitrile ($1.54 kg^{-1}), and toluene ($1.03 kg^{-1}) (CHEN et al., 2014). Yang et al. (2018) reported the costs of polyhydric protic ammonium-salt ILs about $1.00 kg^{-1}. Chen et al. (2014) produced the triethylammonium hydrogen sulfate and 1-methylimidazolium hydrogen sulfate ILs with the costs estimated as $1.24 kg^{-1} and $2.96–5.88 kg^{-1}, respectively.

Chen et al. (2014) quotes the price of chloride-based and acetate-based ILs obtained in the Sigma-Aldrich website are around $300 and $700/kg respectively. However, even if it is not ideal to use small quantity pricing as a guide to commercial use, ILs are normally in the range of 5–20 times more expensive than molecular solvents (PLECHKOVA; SEDDON, 2008; CHEN et al., 2014). Therefore, the [2-HTEAF]mesy IL application may be economically viable in biorefineries, considering the reagents recovery and the possibility to produce dissolving pulp and other added-value cellulose products.

4 FINAL CONSIDERATIONS

This study revealed that the use of low-cost [2-HTEAF]mesy ionic liquid and cold caustic extraction is a method that has a potential to produce dissolving pulp due to its ability to remove xylan. The best scenarios of the treatments CCE-IL were obtained on reaction time

of 10 min, and 630-1:6 and 765-1:6, with a decrease of the xylan content of 1.05 and 0.83% respectively. Another relevant aspect is that the method of IL synthesis is efficient and allows obtaining solvent with high yield with a low cost, $\$0.93.kg^{-1}$.

Furthermore, there are future perspectives to produce others cellulose derivatives through IL application. However, further studies are necessary to obtain information about process optimization, such as the ideal ratio between LI, water and pulp in the system in order selectively remove hemicelluloses and preserve the cellulose chains, for application on an industrial scale. Therefore, the use of this solvent may be an alternative for the pulp mill, since it can reduce expenses with reagents and processes and possible structural changes in the industry, and consequently to meet other demands of the global market.

GENERAL CONCLUSION

Through the results obtained in this work, it was possible to observe that there are great opportunities for the production of dissolving pulp and biomaterials in the pulp mill. Biorefinery platforms have a synergy with the current pulp mill facilities, since their integration would be greatly facilitated by it already knowledge and equipment necessary to fractionate biomass components. Besides with the improvement of already commercial pre-treatments, the use of ionic liquids may be a strategy of interest for this industry (Chapter I).

In the Chapter II were presented insights on the association between cold caustic extraction and [2-HTEAF]mesy ionic liquid to produce dissolving pulp from a commercial eucalypt bleached Kraft pulp, as well as the possibility of its alternative use to produce biomaterials with high added-value.

Technical-economic analyzes are needed to obtain more information on cost, process optimization, industrial scale expansion, environmental issues, life cycle metrics, recycling and compatibility. The behavior of cellulose-IL system needs to be properly characterized prior to establishing a process even to a pilot-scale production.

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