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Coupling refining, chemical and enzymatic treatments for improved purification and dissolution of cellulose

Gloria Ifunanya Ngene

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THÈSE

Pour obtenir le grade de

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Présentée par

Gloria Ifunanya NGENE

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préparée au sein du **Laboratoire Laboratoire de Génie des Procédés Papetiers**
dans l'**École Doctorale I-MEP2 - Ingénierie - Matériaux, Mécanique, Environnement, Energétique, Procédés, Production**

Couplage raffinage, traitements chimiques et enzymatiques pour une meilleure purification et dissolution de la cellulose

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Couplage raffinage, traitements chimiques et enzymatiques pour une meilleure purification et dissolution de la cellulose

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Dedication

Nrara nye nne na nna m, Mazi Jerome N. NGENE na Oriaku
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List of Abbreviations

CCE: Cold Caustic Extraction

CI: Crystallinity Index

CUEN: Cupri-ethylenediamine

Da: Dalton

DMAc: Dimethyl acetamide

DMSO: Dimethyl Sulfoxide

DP: Degree of polymerization

DP_v: viscosity Degree of polymerization

DP_n: number average Degree of Polymerization

DP_w: weight average degree of polymerization

dRI: differential Refractive Index

GPC: Gel Permeation Chromatography

HCE: Hot Caustic Extraction

HexA: Hexenuronic Acid

HPAEC-PAD: High Performance Anion Exchange Chromatography with Pulsed Amperometric Detection

LCC: Lignin-Carbohydrate Complexes

LS: Light Scattering detector

M_n: Number average Molecular weight

M_w: Weight average Molecular weight

MALDI-TOF: Matrix-Assisted Laser Desorption/Ionization - Time Of Flight

MeGlcA: 4-O-methylglucuronic acid

MWD: Molecular Weight Distribution

o.d.p: oven-dried pulp

PDI: Poly Dispersity Index

PHK: Pre-Hydrolysis Kraft

RI: Refractive Index

S1, S2, and S3: Secondary cell wall layers

SEM: Scanning Electron Microscopy

SR: Schopper Riegler

SSA: Specific Surface Area

UR: Unrefined pulp

UV: Ultra violet

VB: Valley beater

WRV: Water Retention Value

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General Introduction

Biorefineries are a perfect model of the circular bioeconomy, and the pulp and paper industry is a front runner. The demand for materials and energy from renewable raw materials has risen sharply over the years. Rapid population growth, the depletion of fossil resources, and the apparent link between fossil consumption and climate change are the main driving forces. In several developed countries, policies are already in place to limit the exploitation and use of fossil resources. To offset the gap that would be created by the reduction in fossil resource consumption, scientists have been studying lignocellulosic biomass, mainly cellulose. Cellulose has potential for several applications in polymer, chemical, and textile industries. Textile production, which already exists, is certainly one of the fastest growing sectors for cellulose, and still the most promising application. However, the challenge remains the laborious extraction process and resistance to dissolution in conventional solvents. Several fractionation methods have been developed to extract high purity cellulose (dissolving pulp) (>95% purity) like the acid sulfite process associated with hot alkaline extraction and the pre-hydrolyzed kraft process (PHK) combined with cold caustic extraction. The typical feedstock is woody biomass. Simpler techniques are regularly proposed such as organosolv processes, ionic liquid extraction, but without any industrial development so far.

The acid sulfite process accounts for about 65% of the total dissolving pulp produced, while the prehydrolysis kraft accounts for about 25% and cotton linters 10%. The decline in cotton cultivation due to irrigation demands, pollution by fertilizers and pesticides and the competition with food for arable lands has drastically boosted the dissolving pulp market. As a result, other lignocellulosic raw materials, such as bamboo, have been investigated for their potential in dissolving pulp production.

Between 2013 and 2015, global dissolving pulp production increased by 25% and is expected to continue to grow in the future. In contrast, the paper pulp market has shrunk over the years due to the replacement of printed media, a major application of paper, with electronic media. Since around 90% of the paper pulp is made from the kraft process, it is imperative to find methods compatible with the kraft mill for upgrading paper pulp into dissolving pulp. Dissolving pulp is high purity cellulose

with less than 5% hemicellulose content, narrow molecular weight distribution, and reactive to chemical transformations, like xanthation which is the basic reaction required for the dissolution of cellulose in the viscose process (the most popular process to produce cellulosic textiles from wood). The challenge is how to extract the 20-25% hemicellulose present in paper pulp in order to upgrade it to dissolving pulp. Cold caustic extraction and enzymatic hydrolysis of the hemicellulose have been suggested in the literature. Still, individually, these hemicellulose extraction processes do not achieve complete removal of the hemicellulose. Moreover, if the CCE is performed at high caustic soda concentrations, which would be necessary for efficient hemicellulose removal, cellulose may lose its reactivity upon drying because of the presence of the cellulose II formed during the CCE.

To improve the extraction performance of the CCE and xylanase treatment, it is necessary to increase the accessibility of the chemical and enzymatic agents to the active site. Mechanical refining, cellulase or xylanase pretreatments prior to CCE have been proposed in the literature, and promising results have been obtained. Mechanical refining looks particularly interesting since it is a common operation for papermaking. While the influence of the refining mechanism on paper properties is well documented, its effect on hemicellulose extraction is not well understood.

In addition, for hardwood paper pulp, cold alkali extraction enables the recovery of relatively high quantity of xylans (around 20% in pulp) in the polymeric form with good purity, which is not the case with PHK or acid sulfite processes. Xylan has drawn considerable interest due to its potential in packaging films and coatings for food, as well as for its use in biomedical products. The effect of mechanical refining on the degree of polymerization of the extracted xylan is also not known.

The present study aims to find the best coupling strategy for mechanical refining, cold extraction, and xylanase treatment to upgrade paper pulp to dissolving pulp. To do this, some of the questions we hope to answer include:

- (i) What are the best conditions of refining that produce pulp with morphological changes that facilitate hemicellulose extraction?
- (ii) Does the refining technology affect the pulp's response to the extraction treatment?

- (iii) Might upscaling the refining treatment to the pilot-scale affect the extraction performance?
- (iv) Is mechanical refining a better pretreatment for hemicellulose extraction than cellulase hydrolysis?
- (v) Does the refining treatment improve the reactivity of the cellulose for its subsequent dissolution?
- (vi) Does the refining treatment affect the molecular mass of the extracted xylan?

Thus, the objectives of this study include;

- (i) To determine the best refining condition for hemicellulose extraction on the Valley beater, PFI and pilot disk refiner.
- (ii) To determine the most efficient sequence involving refining, cold caustic extraction and xylanase treatment, for quantitative hemicellulose extraction from paper pulp.
- (iii) To study the effect of refining on the swelling behavior of cellulose in an alkaline solution.
- (iv) To determine the effect of refining on the molecular weight of extracted xylan

The first chapter presents an in-depth literature review on the subject and the context required for the study. Chapters 2 and 3 show the results of the refining treatments used and the influence on the extraction of hemicelluloses; also, a study on a new approach to the extraction of hemicelluloses by simultaneously performing refining and CCE treatment. The effect of the hemicellulose extraction treatments on the molecular weight distribution and degree of polymerization of cellulose was also discussed. In chapter 4, the study of the extraction treatment on the swelling of cellulose in alkaline solution and its reactivity to xanthation are presented, while chapter 5 presents the results of the study of the effect of refining on the DP of the extracted hemicellulose. Finally, the last chapter describes the methodology applied.

Chapter 1: Literature review

1.1 Renewable resources

As the name suggests, renewable resources are materials of economic value that are "inexhaustible," that is, they are naturally replenished within a limited period. Products and processes involving renewable resources are considered as being sustainable. According to the United Nations world commission on Environment and Development, sustainability focuses on the ability of a resource, process, or system to provide or satisfy the needs of the present without compromising that of future generations (Keeble, 1988). The earth is endowed with numerous resources. Fossils are considered to be one of the most economically important because of their ability to be refined and converted into various chemicals, products, and fuels. However, the significant decline in fossil deposits prompted the search for alternative renewable carbon sources. In addition, environmental concerns due to greenhouse gases emissions from fossil consumption and the spike in population growth intensified these efforts. Figure 1 illustrates the growth of CO₂ emission during the last decades.

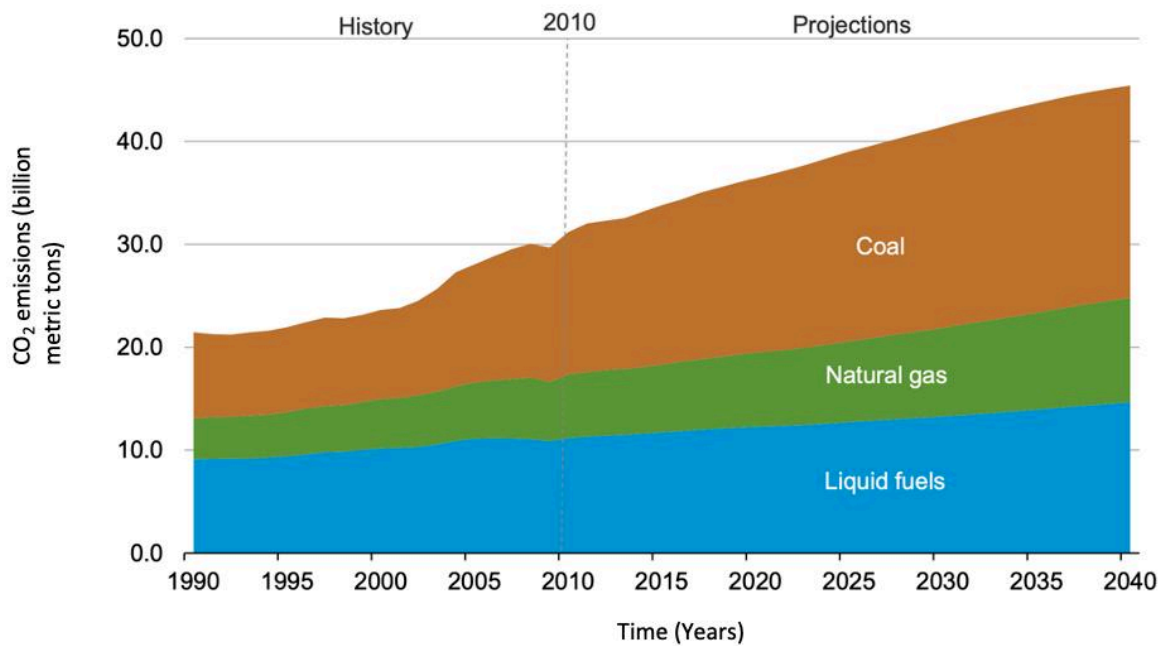


Figure 1. CO₂ emissions by fossil fuel 1990-2040 (Sieminsky, 2014).

1.1.1. Forest outlook

Biomass-sourced carbon is not only sustainable but leaves a significantly lower carbon footprint. The exploitation of lignocellulosic biomass is environmentally benign compared to fossil exploitation. Also, there is no fear of it running out if it is used sustainably. According to the global forest resources assessment report for 2020 (FAO, 2020), forest covers approximately 31% of the international land area. So that, the total forest area is at 4.06 billion hectares. Also, about 162 million hectares of wooded land not classified as forest were reported worldwide in 2020. Figure 2 shows the distribution of the global forest resources.

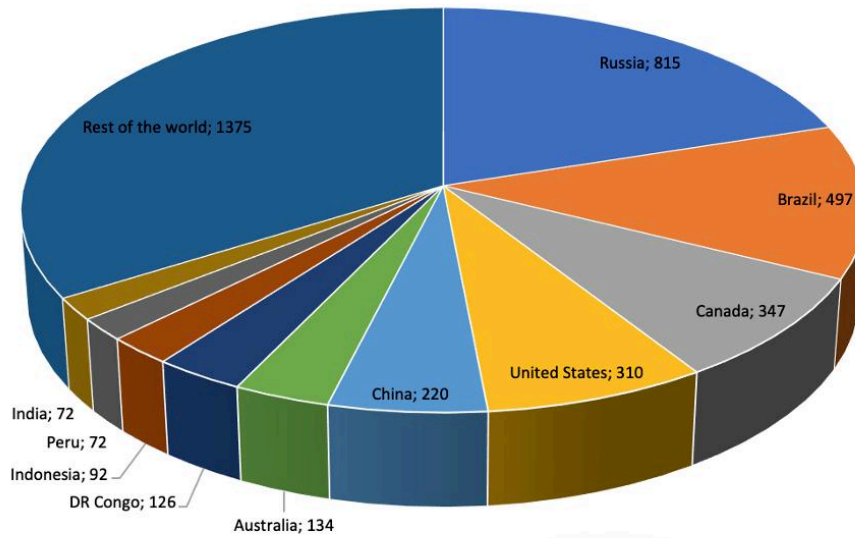


Figure 2. Global forest distribution 2020, showing countries with the largest forest areas (million hectares) (FAO, 2020).

1.1.2. The biorefinery concept

A biorefinery is similar to a petroleum refinery with the difference in the type of raw materials used. In the case of the biorefinery, the feedstock is biomass which is a renewable carbon-rich substrate with a significantly less carbon footprint than fossil carbon sources (Celiktaş & Alptekin, 2019; Yuan et al., 2017). The core principle of the biorefinery is that it processes biomass obtained sustainably into a spectrum of carbon-based products, chemicals, and energy with minimal pollution from the production of wastes as byproducts or undesired material (Jong et al., 2011).

In the integrated biorefinery system, the facility comprising of the feedstock, and processing technology are located nearby. Other subsidiaries that concentrate on the processing of recyclable materials are also situated in the vicinity of the parent plant. This ensures that the cost and environmental impact of resource transportation is reduced or eliminated. The biorefinery lays the foundation for a sustainable bio-based economy that satisfies the conditions of a circular economy and serves as a model for other sustainable production architecture (Jong et al.,

2011). It employs various fields and expertise to achieve its goals. Interestingly, five of the UN sustainable development goals (7,12,13,14,15) are executed in the biorefinery concept (Figure 3).

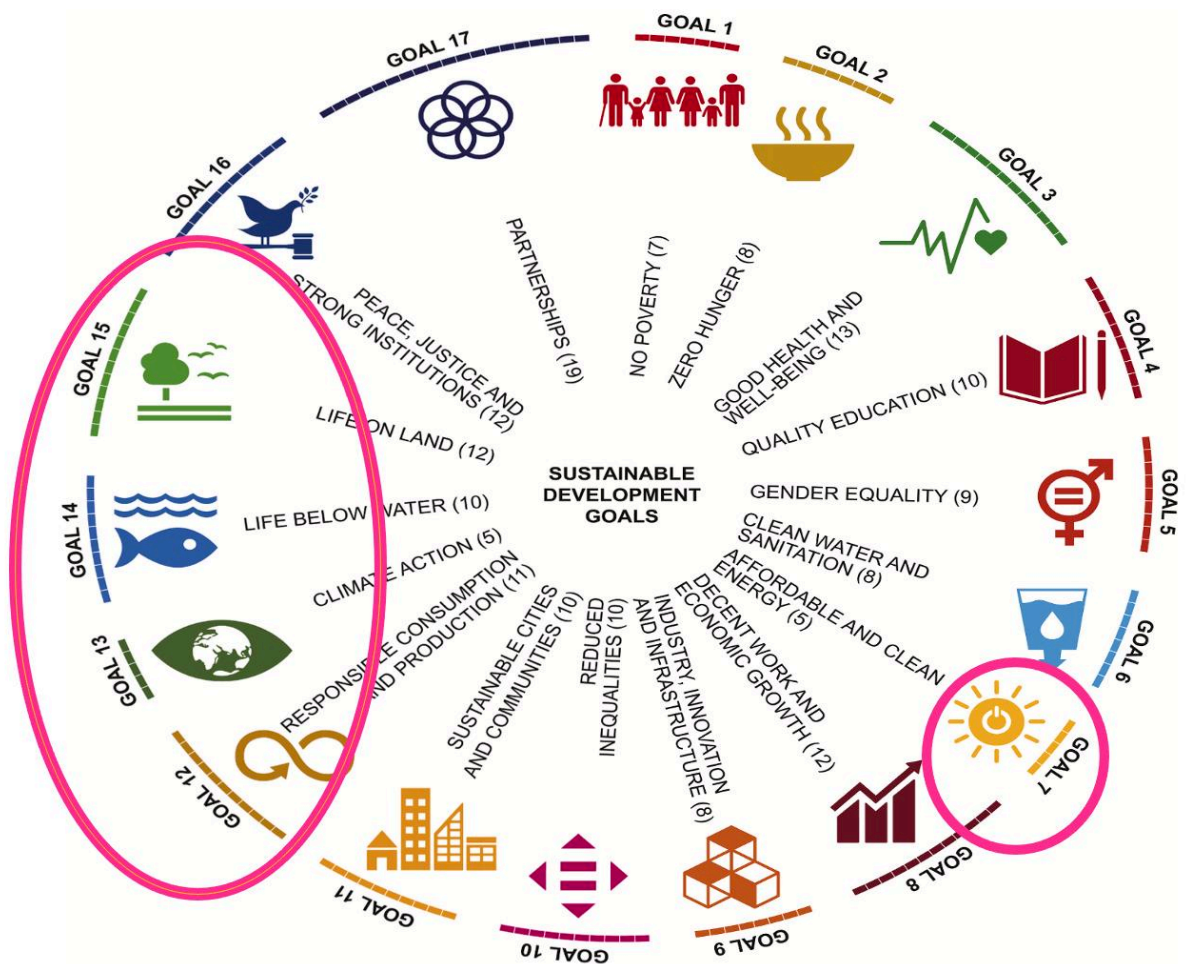


Figure 3. The United Nations 17 sustainable development goals (Carr et al., 2021).

Although forest resources are unevenly distributed worldwide (Figure 2), other carbon-rich biomass sources that can be processed into energy, chemicals, and materials abound in nature. A broad spectrum of biorefinery feedstocks is available. Biorefinery feedstocks can be grouped into three general classes; terrestrial biomass (agricultural residues and forests), marine biomass, industrial and household wastes (Figure 4) (Cherubini, 2010).

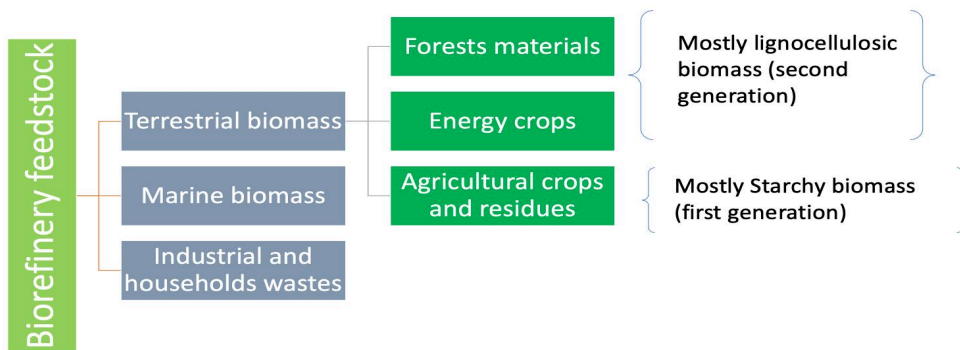


Figure 4. Classification of biorefinery biomass

1.1.3. Lignocellulose feedstock

The earth is endowed with an abundant supply of diverse lignocellulosic biomass, a sustainable feedstock for the bio-refinery industry. Lignocellulose feedstock is broadly classified into virgin biomass (forestry resources), agricultural residues, and energy crops. Of the more than 100 billion tons of biopolymer that is available in nature, forest resources provide the majority in the form of woody biomass.

The wood biorefinery industry has thrived for over a century, producing over 140 million tons of cellulose fibers annually (Chirat, 2017). Wood sourced cellulose has various applications ranging from food, pharmaceuticals, materials, chemicals, and energy. Most importantly, there is no competition with food as it is not sourced from edible biomass or cultivated on arable land. Although cotton is renewable and produces the purest form of cellulose, its use in the textile industry has shrunk over the years, and the trend is predicted to continue. The reason being that cotton competes with food for arable land, requires pesticides which contribute to cost and pollution, not to mention its high irrigation demand. Consequently, the fall in supply due to declined cotton cultivation has paved the way for wood dissolving pulp to become an essential raw material for producing several cellulose-based products.

1.2. Structure and chemical composition of wood

1.2.1. The cellular structure of wood

The cellular structure and chemical constituents of wood vary depending on the wood type and species. There are two types of wood, hardwood, and softwood and the difference in cellular structure between the wood types is presented in Figure 5. The four crucial wood cells are the fiber which provides support (cellulose-rich); the parenchyma, which stores nutrients; the tracheid, which transports water and sap (abundant in softwood); and the vessel, which transports sap (abundant in hardwood). The hardwood cell is more complex than the softwood cell, with smaller parenchyma and fiber cells. Hardwood is also known as porous wood (Figure 6), while softwood is described as nonporous wood because of the presence of vessels and lack of it in hardwood and softwood, respectively.

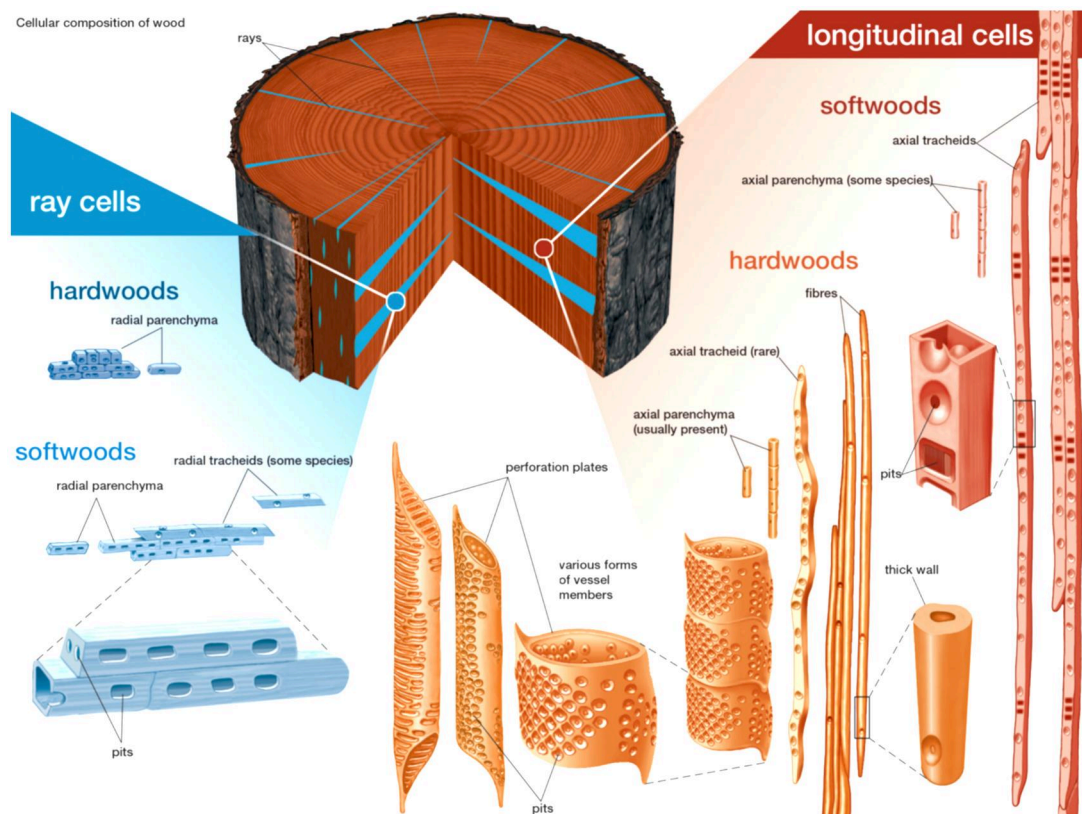


Figure 5. Cellular composition of wood ([Www.britannica.com](http://www.britannica.com), n.d.).

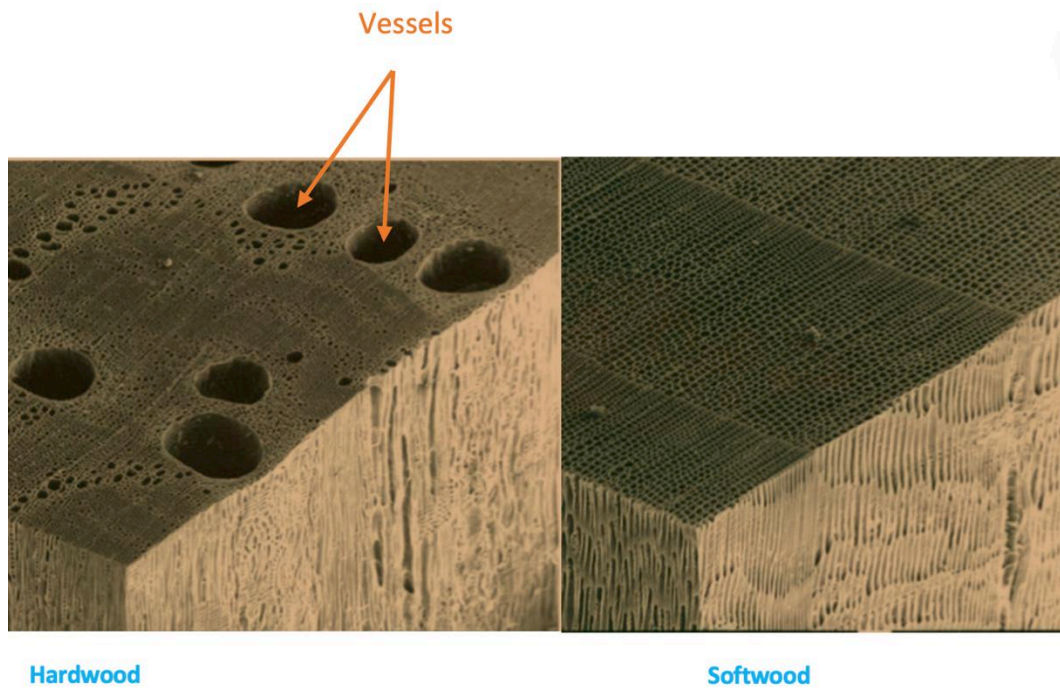


Figure 6. SEM image of hardwood and softwood showing the difference in cellular structure Adopted from ([Ansell, 2015](#)).

1.2.2. Wood cell wall

A schematic representation of the wood cell wall is shown in Figure 7. The cell wall consists of concentric layers called the middle lamella (ML), primary cell wall (P), a thin outer secondary layer (S1), a thick middle secondary layer (S2), and the thin inner secondary layer (S3). The middle lamella binds neighboring cells together and is rich in lignin and pectin. At the same time, the primary layer is a thin layer composed of pectin, hemicellulose, and irregularly aligned cellulose microfibrils. On the other hand, the secondary layers consist of regularly aligned cellulose microfibrils and hemicellulose embedded in a lignin matrix. Also, the lignin content in the secondary layer is lowest in the S3 layer, while the highest concentration and organization of cellulose microfibrils are obtained in the S2 layer ([Wiedenhoft, A. C., & Miller, 2005](#)).

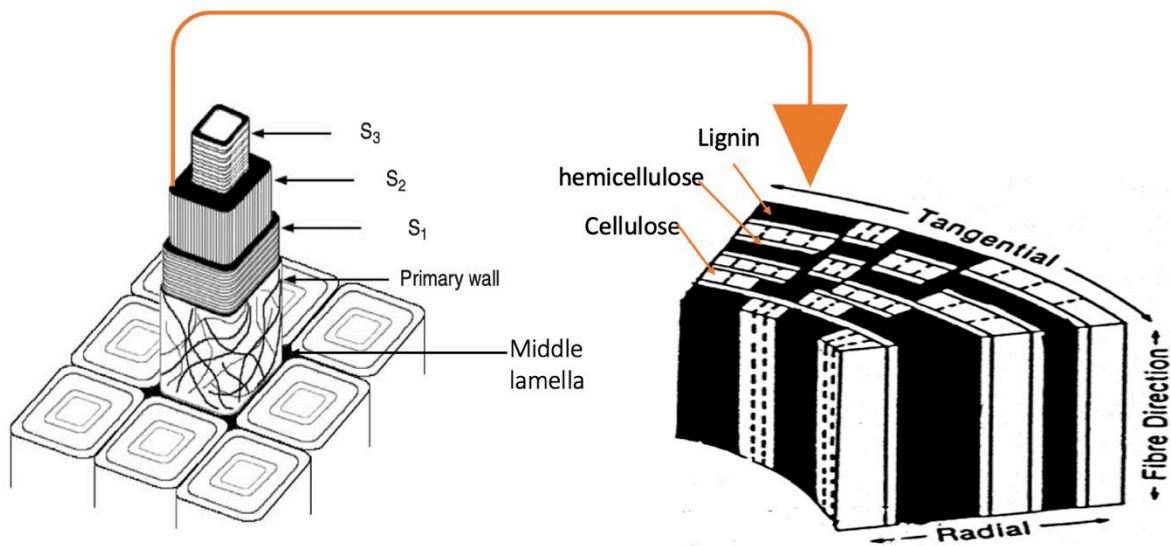


Figure 7. schematic representation of wood cell wall layers and the distribution of lignin, hemicellulose and cellulose adopted from (Kirk, 1988; Zink-Sharp, 2004).

1.2.3. Chemical composition of wood

Wood is composed of three major polymers: cellulose (40-50%), hemicellulose (20-30%), and lignin (20-30%). The proportion of these natural polymers depends on the wood type (hardwood or softwood). In terms of chemical composition, the major difference between hardwood and softwood is in the hemicellulose and lignin content. Table 1 presents an estimate of the chemical composition of hardwood and softwood.

Table 1 Chemical composition of wood (% dry matter)

Constituents	Hardwood	Softwood
Cellulose	40-45	40-45
Hemicellulose	25-35	20-30
Lignin	20-25	25-35
Extractives and minerals	< 5	< 5

1.2.4. Cellulose

Cellulose is the most abundant carbon-rich polymer in nature. Over 1 trillion tons of cellulose have been synthesized by nature (mostly in land plants and some algae) (M. Y. Ioelovich, 2016). On average, higher plant cells consist of 40-45% (wood) to 65% (energy crops) cellulose. Cotton, on the other hand, is composed of over 90% cellulose. Most of the cellulose is located in the secondary layer of the plant cell walls. Cellulose is a carbohydrate polymer consisting of glucose monomers linked by β -1,4- glycosidic bond. The basic unit of cellulose is the cellobiose molecule which is composed of two glucose monomers. It is essentially hydrophilic due to the abundance of hydroxyl groups it contains (Figure 8).

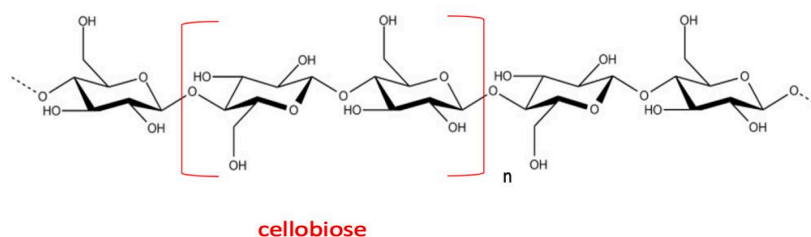


Figure 8. Molecular structure of cellulose showing the basic unit.

These hydroxyl groups form intra and inter hydrogen bonds between chains which aggregate to form the elemental fibril. Clusters of the microfibril bundles constitute the macrofibrils that aggregate to form the fibers (Figure 9). This results in a highly organized structure that is resistant to conventional solvents. The cellulose microfibril has a semi-crystalline lattice structure with a degree of polymerization ranging from 1500 (bleached wood) to 10000 (native wood) (S. Wang et al., 2016; N. Zhang et al., 2015). The predominant cellulose in nature is the Cellulose 1 β allomorph found in land plants.

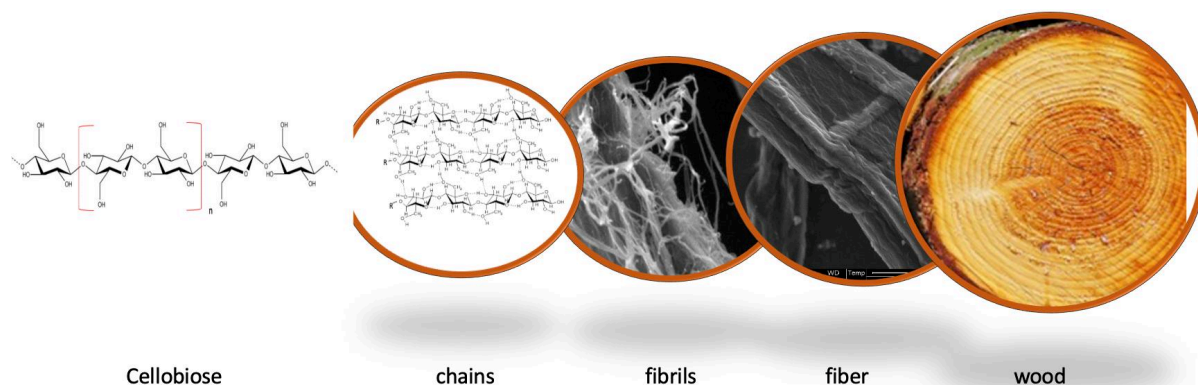


Figure 9. Levels of cellulose organization from wood to cellobiose.

2.2.2. Hemicellulose

Hemicelluloses are carbohydrate polymers of low molecular weight compared to cellulose. Unlike cellulose, hemicelluloses are amorphous and susceptible to hydrolysis. The ease of hydrolysis might be attributed to the branched nature of the backbone and the low DP (50-200). They are found in the primary and secondary layers of the plant cell wall. Hemicellulose contributes immensely to plant rigidity. These heteropolysaccharides consist of hexoses (glucose, mannose, galactose), pentoses (xylose, arabinose), and some modified sugars (4-O-methyl glucuronic acid) (Gehmayr et al., 2011; Pinto et al., 2005; Sixta, 2008a). The chemical structure and sugar composition of hemicellulose vary depending on the source. For instance, in hardwood, the predominant hemicellulose is the O-acetyl-(4-O-methylglucurono) xylan, while in softwood, the main hemicelluloses are the O-acetyl-galactoglucomannan and arabino-(4-O-methylglucurono) xylan.

1.2.5. Softwood hemicelluloses

Softwood has a lower hemicellulose content than hardwood, and the most important are the galactoglucomannan and arabinoglucuronoxylan. The

galactoglucomannan consists of a branched β -1-4 linked D-glucopyranose and mannopyranose backbone. A galactopyranose unit is linked to the backbone by an α -1-6 bond. The hydroxyl groups on (C2/C3) in the mannopyranose unit are substituted with O-acetyl groups. The arabinoglucuronoxylan is also branched but with no acetyl group at C2/C3 (Jacobs & Dahlman, 2001). Side groups of Methyl glucuronic acid and arabinofuranose are linked to the xylan backbone by α -1-2 and α -1-3 bonds, respectively (Figure 10 a and b).

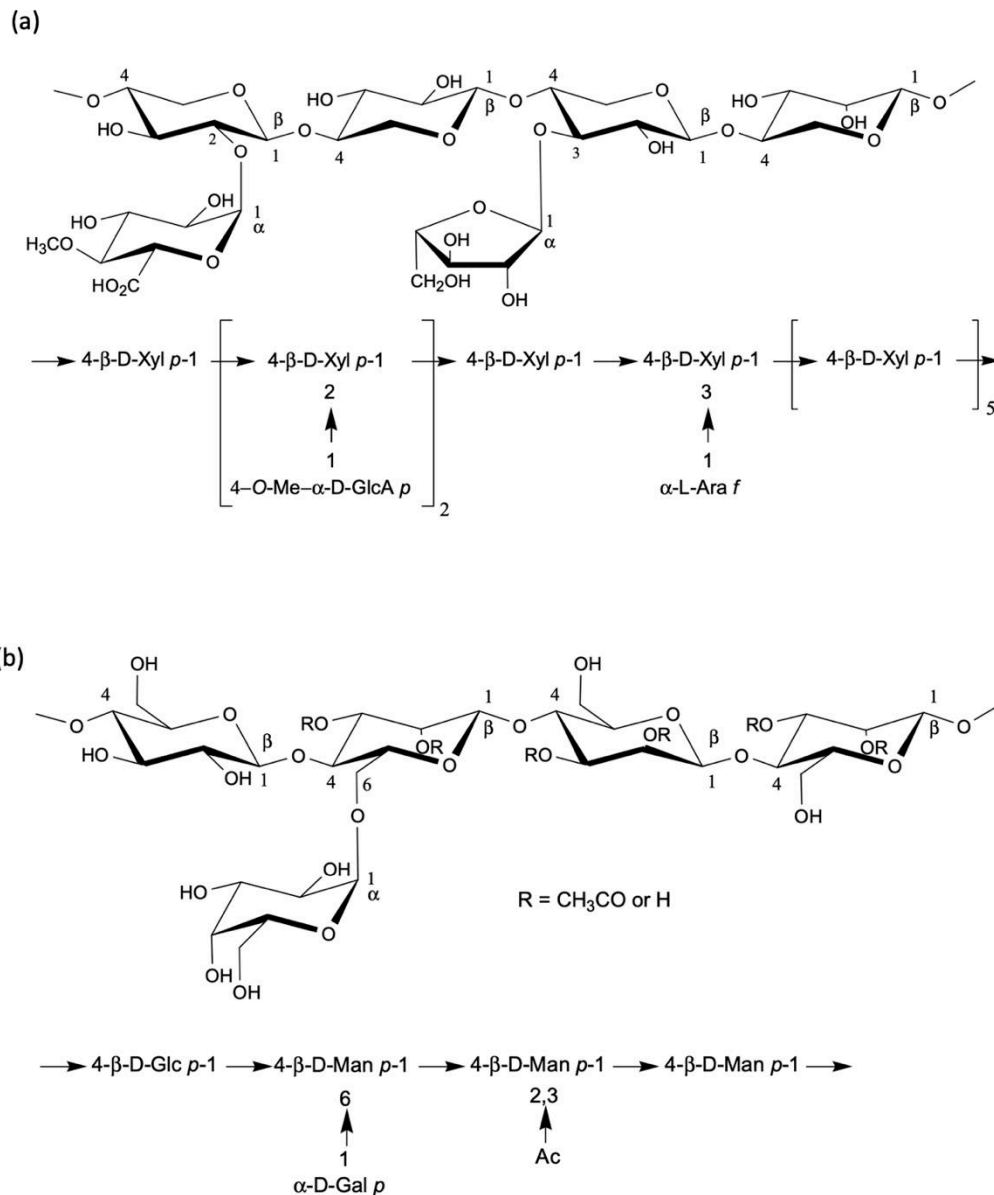
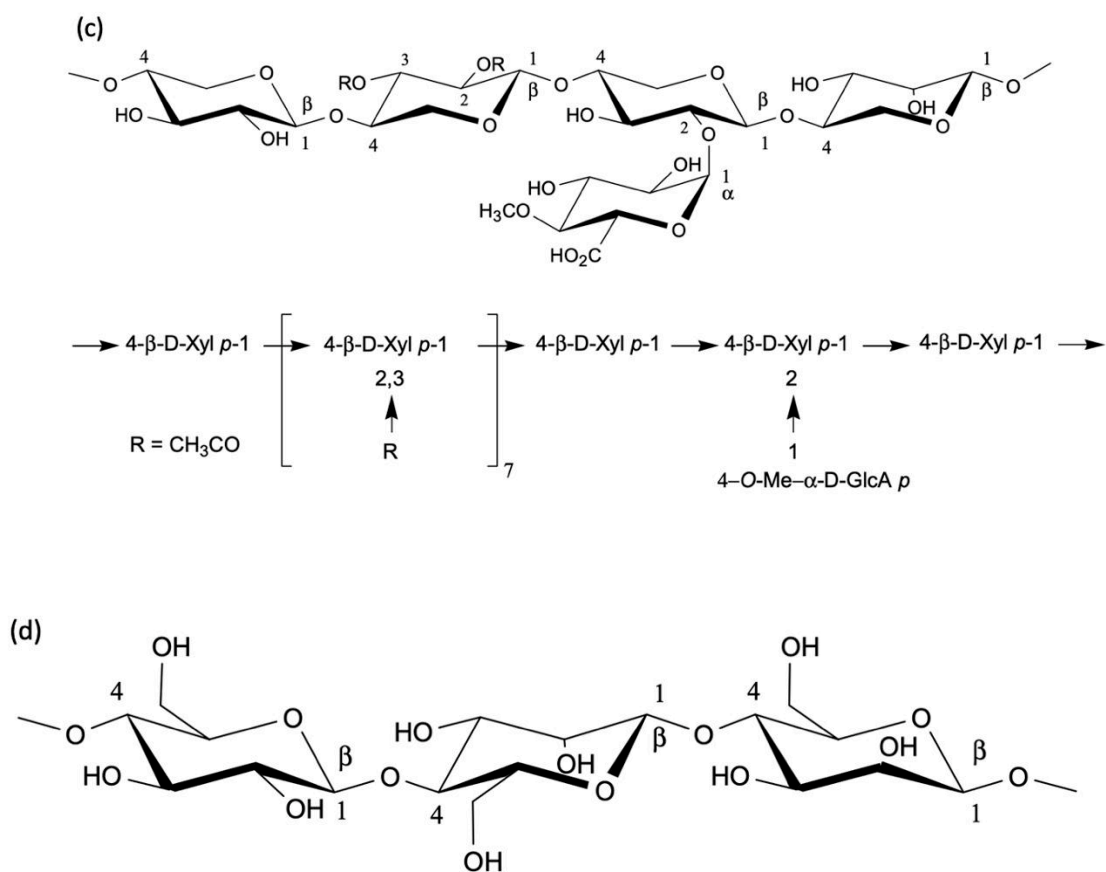


Figure 10. (a) Molecular structure of softwood arabinoxylan; (b) Molecular structure of softwood galacto-glucomannan (Laine, 2005).

1.2.6. Hardwood hemicelluloses

Hardwood hemicelluloses are the second most abundant component of wood. Glucuronoxylan accounts for about 90% of hemicellulose, while glucomannan accounts for about 10% (de Carvalho, 2015; Sharma, Khaire, et al., 2020). Xylan has a linear D- xylopyranose backbone made of xylose units linked by a β -1-4 xylosyl bond. The methyl glucuronic acid side group is attached to the xylan chain by an α -1-2 linkage. Also, the hydroxyl groups on C2/ C3 are substituted by O-acetyl groups. The glucomannan, on the other hand, consists of a linear β -1-4 linked D-glucopyranose and mannopyranose. Glucomannans are acetylated on the mannose units (Figure 10 c and d).



1.2.7. Lignin

Lignin is one of the main polymers in wood. Unlike cellulose and hemicellulose, it is not a carbohydrate but a rich aromatic compound. It occurs more in softwood than hardwood. It is found in all the layers of the cell wall, especially the middle lamella. It serves as a glue that binds other wood components together. Lignin is a nonlinear copolymer of phenylpropane units randomly linked together. The three main monomers of lignin are coumaryl alcohol, sinapyl alcohol, and coniferyl alcohol (Figure 11).

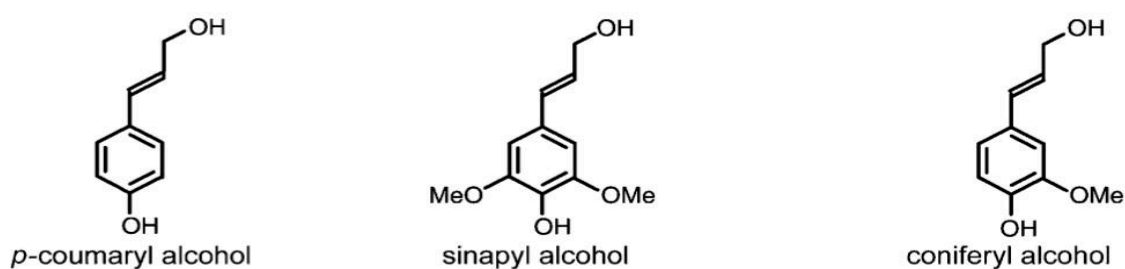


Figure 11. Lignin monomers (Vanholme et al., 2010).

The lignin precursor in hardwood is the coniferyl alcohol, while in softwood it is the coumaryl and sinapyl alcohols. The common linkages in lignin are the β -O-4 ether (50-60%) bonds, α -O-4 ether bonds (5-7%), and C-C bonds (7-10%). Various structural models are proposed for lignin, depending on the source (Figure 12).

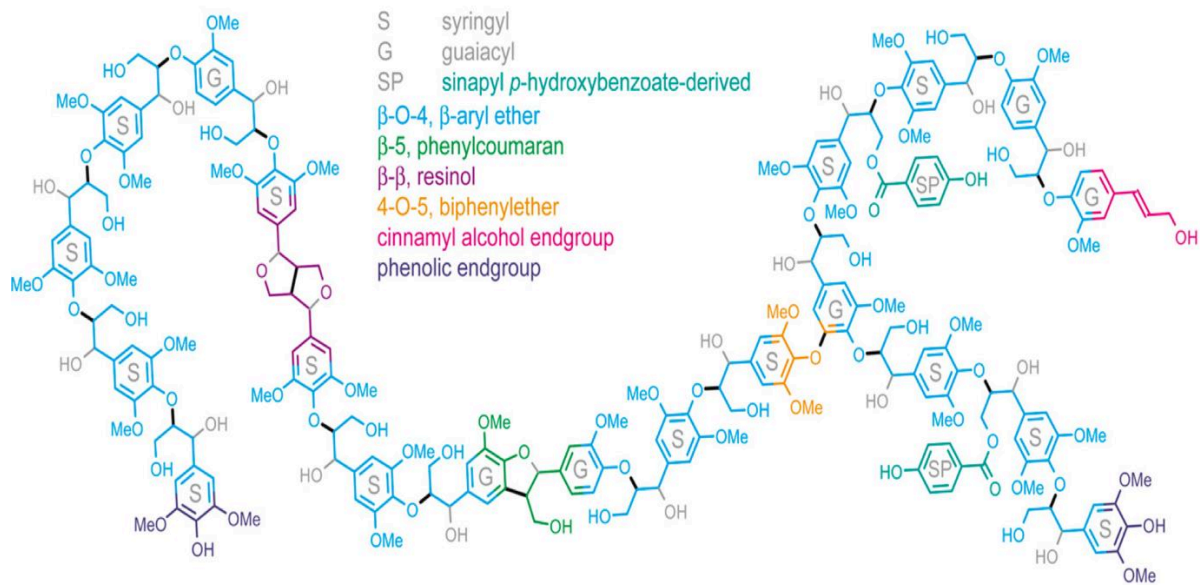


Figure 12. Proposed lignin structure (Vanholme et al., 2010).

1.3. Production of paper pulp from wood

There are typically two pulping processes employed in the papermaking industry, the chemical and mechanical pulping methods. The chemical process involves using chemical products at elevated temperatures and pressure to deconstruct the wood structure and extract the lignin fraction. In contrast, mechanical pulping involves using mechanical action (physical means) to disintegrate the wood chips to pulp.

1.3.1. Mechanical pulping process

Mechanical pulping is the oldest industrial pulping process (Kerekes, 2015). The preferred mechanical action that is currently employed is refining. Although chemical pulping has overtaken mechanical pulping, it is still in use, especially for

the production of newspapers and magazines. The strength properties of mechanical pulp fibers are diminished when compared to a chemical pulp. It also has a high energy demand. The pulp yield is usually high as lignin is retained in the pulp. It gives the pulp excellent printing properties but also limits the life span of the paper (yellowing).

1.3.2. Chemical pulping

The fractionation of lignocellulosic biomass dates back to the 19th century. Soda, sulfite, and kraft cooking were the predominant pulping processes at that time. Soda and kraft are both alkaline delignification processes, while the sulfite cooking process is acidic. The kraft process is a modification of the soda cooking achieved by adding sodium sulfide to the cooking liquor. The kraft process presented improved delignification of wood substrate compared to soda cooking. Even though sulfite cooking was preferred in the earlier part of the 20th century due to its brightness and low-cost chemicals, advancement in the development of efficient chemical recovery processes for kraft cooking resulted in a significant shift from sulfite to kraft pulping (Sixta, 2008a). The kraft process also has the advantage of not being partial to certain wood species; it is applied to all wood species, unlike the sulfite process, which is somewhat selective (cooking difficulty experienced in some pinewood species). A wide range of vegetal biomass is pulped by the kraft process, unlike the sulfite process.

In addition, kraft pulp had better mechanical properties than its counterpart (sulfite pulp). Consequently, about 90% of wood cellulose is fractionated by the kraft process (Sixta, 2008a). Other pulping processes such as ionic liquids, organosolv have been proposed, but they are still under development.

1.3.3. Sulfite pulping

Acid sulfite pulping, also known as bisulfite pulping, is a chemical pulping process that occurs in acid conditions. The process occurs at elevated temperatures (130-160 °C) with pH ranging from 2 to 5 depending on the salt used. The reaction time can vary between 4 and 14 hours. The cooking chemicals are

prepared by the action of SO_2 with a base. The hydroxides or carbonates of sodium, calcium, magnesium, potassium, and ammonium have been used as base. However, magnesium-based sulfite is preferred for its chemical recovery advantage. The lignocellulose fractionation process in sulfite pulping is accomplished by solubilization of the lignin polymer rather than depolymerization as obtained in kraft pulping. Sulfite pulp is easy to bleach as it is brighter than kraft pulp, but the fibers are weaker due to the harsh acidic conditions. Thus, acid sulfite pulping is preferred for dissolving pulp production, and the lignin byproduct (lignosulfonates) has potential in specific applications.

1.3.4. Kraft pulping

Kraft pulping is a type of alkaline pulping that includes sodium sulfide in the alkaline liquor to improve the lignocellulose fractionation process and limit lignin condensation reaction.

It is a chemical pulping technique that transforms the compact chunks of wood chips or other lignocellulosic biomass into pulp. It involves the depolymerization of lignin and the solubilization of lignin fragments, the separation of the volatile extractives, leaving behind cellulose and a bulk of the hemicelluloses. This operation is carried out by mixing white liquor ($\text{NaOH}/\text{Na}_2\text{S}$ solutions) with wood chips at elevated temperatures (160-170 °C) for 2 to 4h.

1.3.5. Chemical modification of carbohydrates in the kraft process

To understand how chemical pulps respond to subsequent chemical or enzymatic treatment, it is imperative to; first, understand the structural changes that occurred during the alkaline pulping process. Cellulose and hemicellulose are both affected by the peeling reaction and random hydrolysis of the 1- 4 glycosidic bond that takes place during alkaline pulping. At temperatures of 80-100 °C, the

polysaccharide component begins to degrade from the reducing ends by a mechanism known as the peeling reaction (Wetterling, 2012). The peeling reaction is the successive cleavage of the 1-4 glycosidic bond starting from the reducing end group, resulting in the liberation new reducing end group, which perpetuates the peeling action and a glucose monomer that is converted into a stable isosaccharinic acid through a series of rearrangement reactions (Figure 13).

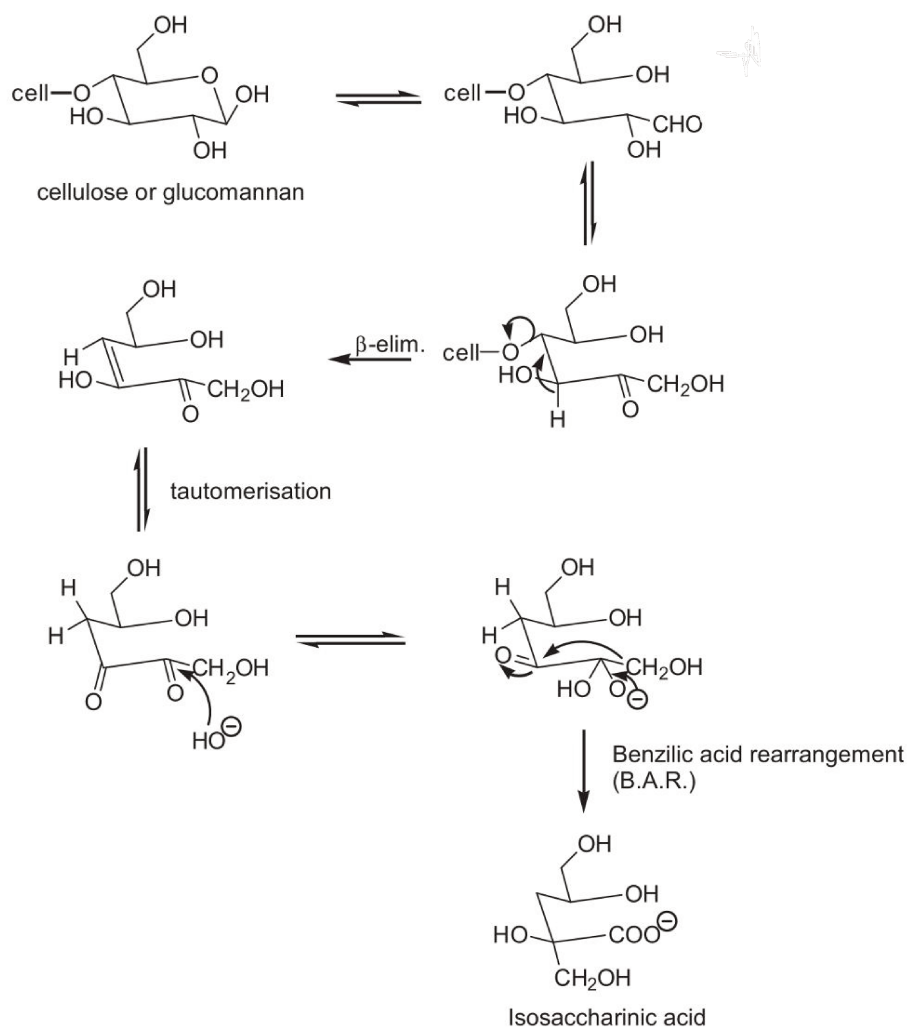


Figure 13. Mechanism of the peeling reaction occurring in cellulose (Monica Ek, Göran Gellerstedt, 1993).

The degradation is more pronounced in hemicelluloses with low DP (100 - 200) than in cellulose with high DP (10000). However, the peeling reaction is halted

in xylans because of the 4-O-methylglucouronic acid substituent attached at the C2 position, absent in cellulose and glucomannan. The presence of 4-O-methylglucouronic acid at the C2 position prevents the β -alkoxy elimination at C4. At the same time, the reducing end group is then transformed to a stable metasaccharinic acid, as shown in Figure 14. In cellulose and glucomannan, where there is no branching at C2 or C3, the peeling continues until about 50-70 monomers are released, after which a stabilization occurs with the commencement of the competing reaction (Wetterling, 2012).

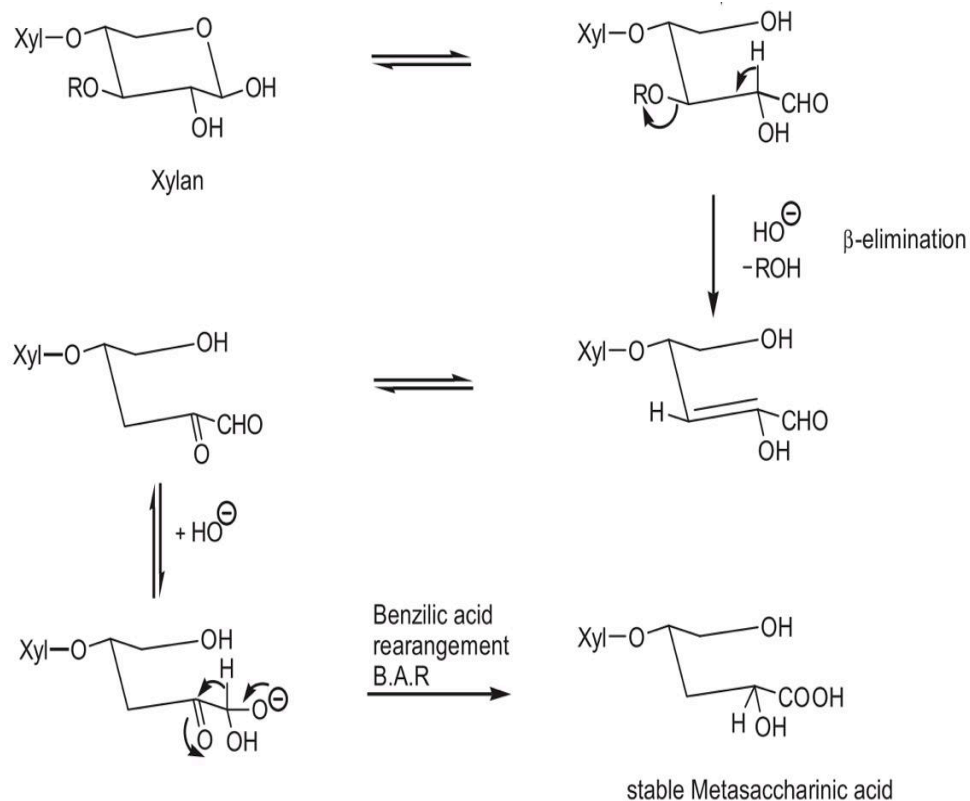


Figure 14. Mechanism of the competing reaction that prevents peeling in arabinoxylan (Monica Ek, Göran Gellerstedt, 1993).

Another important chemical modification that occurs during the high alkaline kraft pulping is the conversion of 4-O-methylglucouronic acid linked to the xylan backbone at C2 to hexenuronic acid (Figure 15). The process involves the

elimination of the methoxy group substituent of glucuronic acid. Hexenuronic acid is reported to be rather resistant to bleaching chemicals and contributes to the yellowing of pulp. According to (Pouyet et al., 2014) hexenuronic acid increased the chances of carbonyl group formation during ozonation through the generation of radicals, resulting in polysaccharide depolymerization during alkaline and peroxide treatment by β -alkoxy elimination .

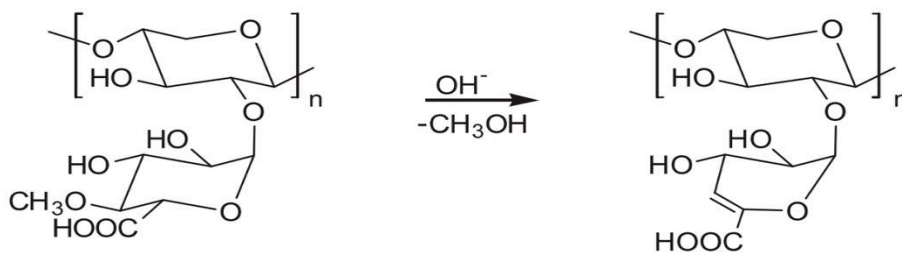


Figure 15. Conversion of 4-O-methylglucuronic acid to hexenuronic acid during kraft cooking (Monica Ek, Göran Gellerstedt, 1993).

The second polysaccharide degrading reaction that occurs during kraft pulping is alkaline hydrolysis (Figure 16). It occurs at higher temperatures of $> 130\text{ }^\circ\text{C}$, where the severe condition triggers the ionization of the hydroxy group on C2, which attacks C1 cleaving the β -1,4- glycosidic bond (Monica Ek, Göran Gellerstedt, 1993). This reaction occurs randomly around the polysaccharide chain generating new reducing end groups susceptible to the peeling reaction (secondary peeling). Thus, alkaline hydrolysis contributes more to DP loss.

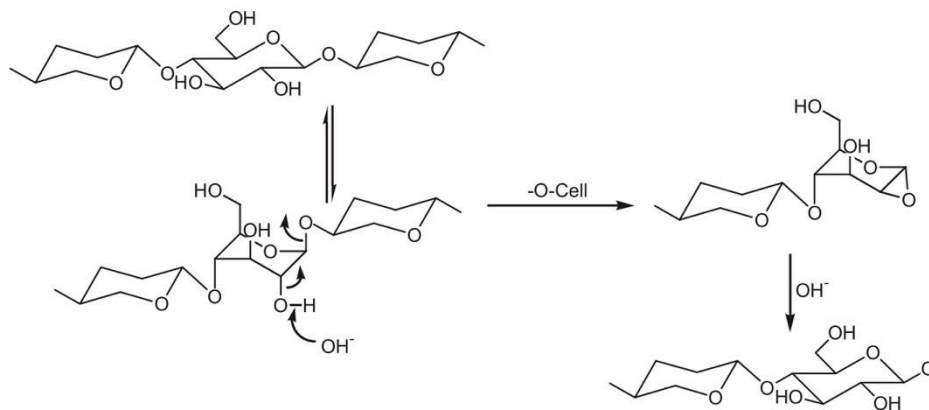


Figure 16 Mechanism of the alkaline hydrolysis in cellulose during the kraft cook (Monica Ek, Göran Gellerstedt, 1993).

1.3.6. Bleaching process

Pulp bleaching or whitening is the downstream delignification process carried out on pulp after cooking, washing, and screening. The aim is to eliminate the residual lignin in the pulp that accounts for its brown color because of the chromophoric groups in the lignin structure. It involves the treatment of the pulp at controlled pH and time with chemicals like chlorine, chlorine dioxide, oxygen, ozone, hydrogen peroxide, and sodium hypochlorite, which attack, oxidize, depolymerize the lignin structure and eventually make it soluble in aqueous medium. Residual lignin in the pulp is determined by the kappa number, which indicates the lignin content in the pulp. It is known that softwood has more lignin than hardwood, and hence the higher kappa number observed for unbleached softwood pulp (20-35) compared to unbleached hardwood pulp (15-20). Therefore, bleaching of softwood pulp must be more intense than that of hardwood pulp. The target of bleaching is residual lignin. However, cellulose and hemicellulose may be slightly depolymerized because of the occurrence of radical reactions with some of the bleaching chemicals (oxygen, ozone, hydrogen peroxide) Despite that there is no substantial solubilization of carbohydrates during bleaching.

1.4. Production of dissolving pulp from wood

The dissolving of cellulose for textiles application was first invented in 1884 by a French scientist using cellulose nitration to make cellulose soluble in water. The extreme flammability of the process and the cost are part of the challenges that led to the search for alternative solubilization and regeneration methods. British scientists invented the xanthation process from which the viscose rayon fibers were prepared in the 1890s (Floer, 2011). It was a much faster and safer alternative to the nitration process and therefore became very popular. About 80% of the dissolving pulp produced globally is used in the manufacture of viscose rayon fibers, most of which are used in the production of textiles. The great interest in viscose textiles is due to their specific properties of comfort, touch and visual appearance. Other considerations were added, linked to their plant and non-fossil origin and to the environmental problems posed by cotton cultivation. The growing world population, the fundamental need for clothing, and the fact that the regenerated cellulose may have numerous other applications will ensure the future of dissolving pulp. China is the world's largest producer and consumer of dissolving pulps, followed by other Asian countries, then Europe, and finally the Americas (Kumar & Christopher, 2017). There is no significant activity in Africa concerning dissolving pulp production except for South Africa.

Currently, dissolving pulp is produced from wood, cotton linter, and bamboo. Over 80% of the world's dissolving pulp is processed from wood, about 10% from cotton linter, and the rest from bamboo, especially in China. Apart from the viscose rayon fibers, the lyocell rayon fibers, cellulose acetates, and cellulose ethers are among other applications of the dissolving pulp (J. Chen, 2015; Kumar & Christopher, 2017; S. Wang et al., 2016).

Dissolving pulp is pure cellulose with a high alpha-cellulose content, less than 5% hemicellulose content, and uniform molecular weight distribution (Table 2). Other properties such as increased porosity, low crystallinity index, and high surface area are crucial to improving chemical accessibility, which leads to high reactivity towards direct dissolution or derivatization. Maintaining the cellulosic fibrous structure is of paramount importance in the manufacture of paper pulp, but as the name suggests, destruction of the ordered fibrous structure architecture is

required when processing pulp for dissolving applications. Dissolving pulp should be accessible to the solvent, which ultimately destroys the fibrous structure of the pulp and thus enables solubilization.

1.4.1. Processes of dissolving pulp production

Conventional routes to dissolving pulp manufacture are the so called prehydrolyzed Kraft process (PHK) and the acid sulfite process (AS) (C. Chen et al., 2016; Curmi et al., 2018; Duan, Li, et al., 2015), which respectively represent 65% and 25% of world production (Kumar & Christopher, 2017). PHK is actually a kraft process in which part of the hemicellulose is extracted prior to cooking by acid hydrolysis of the chips. This is performed usually at high temperature (150 °C) as a separate phase in the cooking reactor, which represents a significant change from the traditional kraft cooking operation. The recovery of the hydrolyzed hemicellulose is complicated and generally not performed. Acid Sulfite cooking used to be the traditional process to prepare dissolving pulp. By adapting the conditions, it is possible to obtain a pulp with a low content in hemicellulose. However, because of environmental and technical issues, no new installation with the sulfite process will be built in the future. Moreover, both processes (PHK and AS) deliver a pulp which may need further extraction of residual hemicellulose to comply with the specifications, depending on the application. Recent researches focus on upgrading paper pulp (kraft) to dissolving pulp by post-extraction of hemicelluloses (Arnoul-Jarriault et al., 2015; Janzon et al., 2006; Roselli et al., 2014; H. Wang et al., 2014). One of the most promising processes of hemicellulose extraction is cold caustic extraction (CCE). Other options do exist as it will be seen below (e.g. use of enzymes) (Christov et al., 1996; Gübitz et al., 1997). This approach (post-extraction of hemicellulose by CCE) offers the kraft mill the possibility of easily switching from the production of paper pulp to that of dissolving pulp, or the reverse, depending on the market situation, since the kraft process is not affected. Moreover, the degree of polymerization of the cellulose is higher than after PHK, which broadens the spectrum of applications of the dissolving pulp produced. Finally, the process ensures a higher yield compared to the PHK, but some disadvantages do exist like the difficulty to reach very low hemicellulose content and some lack of cellulose

reactivity when the cold caustic extraction is too strong. Despite its merits the upgrading of paper pulp to dissolving pulp is not an industrial reality yet (Figure 17).

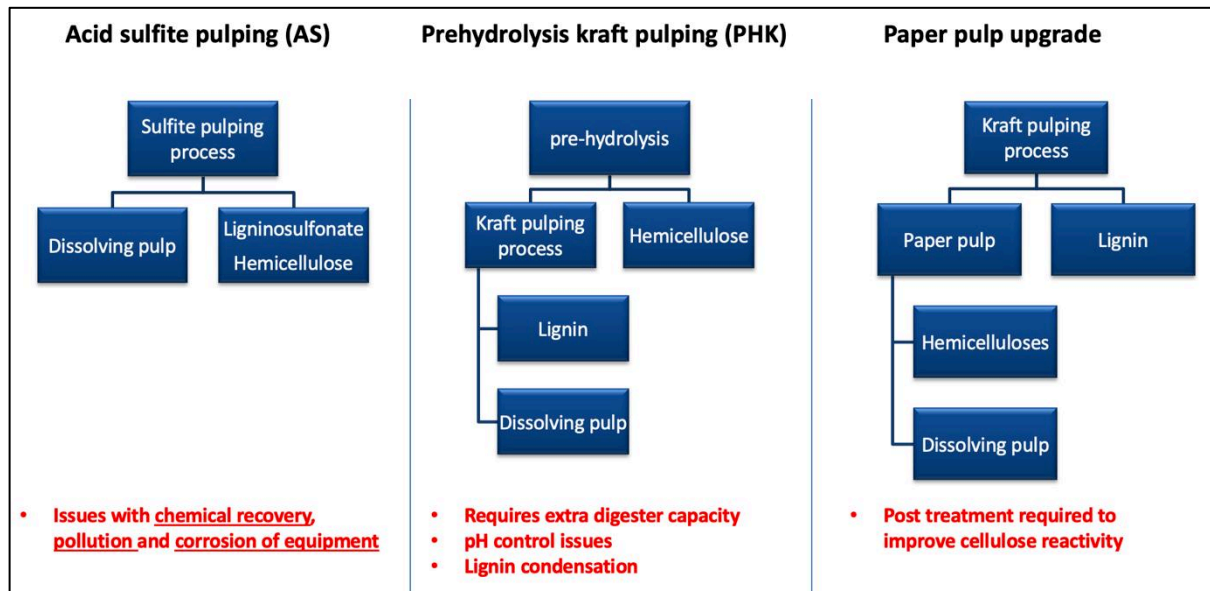


Figure 17. Processes of dissolving pulp production.

1.5. Hemicellulose extraction processes

In pulp production for papermaking purposes, the kraft process coupled with a series of bleaching steps that focus on lignin elimination is sufficient to achieve desired properties. A bulk of the hemicellulose content of the pulp is preserved ($\leq 25\%$) as removing it will compromise paper quality. In contrast to paper pulp, dissolving pulp has a high cellulose purity requirement (Table 2), with a hemicellulose content of about 5% or less depending on the application (Sixta, 2008b). This is because hemicellulose in dissolving pulp negatively affects the downstream processing of pulp into regenerated cellulose fibers. These low molecular weight polymers are solubilized during the mercerization process (highly alkaline pretreatment which opens the cellulose structure in the viscose process), consuming part of the NaOH reserved for cellulose swelling. They have also been associated with yellowing the final product and clogging the spinneret nozzle during the fiber spinning process (Kim et al., 2019). Also, inferior mechanical strength

properties of regenerated cellulose fiber with high hemicellulose content have been reported.

Table 2 difference between paper and dissolving-grade pulp.

paper pulp	dissolving pulp
high hemicellulose content (18-25%)	low hemicellulose content < 5%
moderately high alpha-cellulose (70-80%)	very high alpha-cellulose >95%
broad molecular weight distribution	narrow molecular weight distribution
not applicable	high cellulose reactivity (Fock index >60)

There are several processes for removing residual hemicellulose from kraft paper pulp depending on the pulp type and application. Some hemicellulose extraction processes compatible with kraft mills include hot water extraction, alkaline extraction, acid extraction, enzymatic extraction, and organic solvent extraction. The efficiency of the hemicellulose extraction could be improved by coupling two or more of the extraction methods mentioned above.

1.5.1. Alkaline extraction

In the context of removing the residual hemicellulose in paper pulp to upgrade it to dissolving pulp, two alkaline treatments are known. The cold caustic extraction (CCE) and hot caustic extraction (HCE).

The difference between the two treatments are:

- Reaction conditions: Soda concentration and temperature.
- Mechanism of the treatment: Physical swelling and dissolution for CCE and chemical peeling for HCE.
- Effect of the treatment of cellulose and hemicellulose chains: Substantial yield losses due to degradation for HCE and minor yield losses for CCE.
- Selectivity: CCE selectively solubilizes hemicelluloses while the HCE is less selective and acts on cellulose chains as well as hemicelluloses.

- Adaptability: The peeling mechanism exhibited by the HCE is suitable for the extraction of softwood hemicelluloses populated by glucomannan, provided they still have reducing end groups, while the CCE is well suited for COOH groups carrying xylan predominant in hardwood.

1.5.2. Cold caustic extraction (CCE)

Cold caustic extraction is an effective method of residual hemicellulose removal from kraft pulp because of the selective solubilization of hemicellulose, particularly those carrying COOH groups (xylans). The process is operated at high soda concentration (8-10 %) and low temperature (20-40 °C). Low yield losses have been reported, and the treatment allows for the recovery of the polymeric form of xylan that has potential application in pharmaceuticals, cosmetics, and food industries. (Sixta, 2008b) describes two sequential steps involved in the process of removing residual hemicellulose. The first step is a physical interaction between the cellulose fibers and a sodium hydroxide solution, which causes the fibers to swell. The second is the diffusion step, which involves the movement of the hemicellulose from the fiber's interior to the exterior. The transformation of native cellulose (cellulose I) to cellulose II occurs during the CCE treatment. According to (Arnoul-Jarriault et al., 2015), the CCE treatment temperature has no significant effect on the transformation of native cellulose to cellulose II polymorph as it depends more on the caustic concentration. Also, studies show that the CCE was more suitable for the extraction of hardwood hemicellulose rather than softwood hemicellulose likely because of the presence of COOH groups on the xylan molecules. From the reports of (Arnoul-Jarriault et al., 2015; Gehmayr et al., 2012; J. Li, Zhang, et al., 2015), applying the CCE on paper pulp at soda concentration of around 100 g/L may achieve a hemicellulose removal of up to 70%.

1.5.3. Hot caustic extraction

The hot caustic extraction (HCE) is operated at low soda concentrations and high temperatures (70-120 °C). It proceeds via the peeling reaction, which involves the cleavage of the terminal glycosidic bonds (β -alkoxy elimination). Some

carbohydrate degradation is observed due to the non-selective nature of the process. The HCE is reported to be particularly suitable for the extraction of residual hemicellulose in softwood sulfite pulp because it essentially consists of glucomannans with reducing end groups. In contrast PHK pulp responds poorly since the residual hemicelluloses have already seen the peeling and are stabilized against it ([Arnoul-Jarriault et al., 2015](#)).

1.5.4. Hot water extraction

The method is particularly interesting for the recovery of the hemicellulose (xylo-oligosaccharides), and it does not require the addition of chemical agents. Unbleached hardwood kraft pulp was subjected to the hot water extraction treatment at various temperatures, and over 50 % xylan removal was achieved when the temperature reached 240 °C ([Borrega & Sixta, 2013](#)), with a 12 % loss in cellulose yield. The authors identified two xylan fractions: the simple xylan fraction, which is easily removed during the prehydrolysis stage of the PHK process, and the recalcitrant xylan fraction, which remains after the kraft cook and is only removed by further treatments (cold caustic extraction, hot caustic extraction, etc.). Cellulose losses during the extraction were attributed to the removal of the recalcitrant xylan, which was closely associated with cellulose chains. Overall, the hot water extraction method was not efficient for quantitative hemicellulose removal.

1.5.5. Enzymatic extraction (xylanase)

Enzymatic hydrolysis of the hemicellulose component of lignocellulose biomass has been beneficial in paper pulp bleaching (bleaching boost) ([Bajpai, 2014](#); [Dhiman et al., 2008](#)). Interesting results have been recorded in pulp enzyme-aided refining (reduced resistance to refining ((energy saving)) ([Lyytikäinen & Backfolk, 2017](#); [Pere et al., 2020](#); [Viikari et al., 2000](#)) and in dissolving pulp manufacture ([Christov et al., 1996](#); [Gübitz et al., 1997](#); [Hutterer et al., 2017](#)). The most common hemicellulose extraction enzymes investigated in these applications are the xylanases. Mannanases have been much less studied. Although they do not achieve quantitative removal of hemicellulose, particularly in chemical pulp, they contribute to the overall reduction of the residual hemicellulose content ([Hutterer et](#)

al., 2017). The pretreatment of paper-grade pulp with xylanase prior to alkaline extraction was found to enhance xylan removal efficiency (Ibarra et al., 2010). The resistance of residual xylan in bleached pulp to xylanase treatment has been attributed to the structural modification of the xylan chain during the pulping and bleaching process resulting in a linearized xylan structure that interacts more with the cellulose molecules. The advantage of enzymes for pulp purification is that they are selective, non-toxic, bio-sourced, and biodegradable. However, enzymes are expensive, sensitive to handle, and produce degraded hemicellulose molecules (monomers and oligomers).

1.5.6. Solvent extraction

Several solvents have been proposed to extract hemicellulose from paper-grade pulp, including organic solvent (dimethyl sulfoxide (DMSO)) (Jacobs & Dahlman, 2001), metal complexes (nitren), a metal complex of tris(2-aminoethyl) amine and nickel (II)- hydroxide), and ionic liquids (Janzon et al., 2006; Janzon, Saake, et al., 2008). Of these solvents, the most promising are the ionic liquids which were reported to be efficient in hemicellulose removal without yield losses from degradation or occurrence of side reactions (Isik et al., 2014; Laine et al., 2016; Navard & Cuissinat, 2006; Roselli et al., 2016). DMSO is not as efficient in extracting hemicellulose and does not achieve quantitative hemicellulose removal from paper-grade pulp due to the chemical modifications that occur during the pulping and bleaching process. Actually, DMSO favors the extraction of acetylated hemicellulose, which is easily accessible and more susceptible to solubilization. These groups have disappeared almost completely during pulp preparation. Nitren was shown to give interesting results. However, its use is strongly compromised due to the toxicity of the complexing metal (Nickel), which is adsorbed onto the cellulose fiber (Janzon et al., 2006).

1.6. Pretreatments to enhance hemicellulose removal

The effectiveness of the hemicellulose extraction process from paper pulp is highly dependent on the structural disposition or morphological properties of the

pulp. Moreover, some components of the substrate (extractives) may impede the extraction process.

The common pretreatments applied to pulp to enhance hemicellulose removal include; mechanical refining, enzymatic hydrolysis, and acid treatment.

1.6.1. Enzymatic treatment

Cellulase pretreatment have been shown to improve the hemicellulose removal process. Actually, there are three main groups of cellulose-degrading enzymes based on their activity; endoglucanase (hydrolyses β -1-4 glycosidic bonds within the cellulose chain), cellobiohydrolase or exoglucanase (hydrolyses terminal β -1-4 glycosidic bonds cellulose chain to form cellobiose), and glucosidase (hydrolyses β -1-4 glycosidic bonds in cellobiose) (Hutterer et al., 2017; Sindhu et al., 2016). In most of the studies these three types are present in the cellulases cocktail applied to the pulp to weaken the structural barrier of the fiber walls. This is because cellulase randomly hydrolyses the β -1-4 glycosidic bonds of cellulose, creating new reducing ends, pores, depolymerizing the substrate, ultimately improving accessibility. Remarkable improvement in the reactivity of cellulase-treated pulp to xanthation has been reported (Duan et al., 2016b; Liu et al., 2019). Also, some studies where a coupling of endoglucanase with xylanase treatment or cold caustic extraction was carried out showed improved xylan removal (Gehmayr et al., 2011; J. Li et al., 2018).

1.6.2. Acid treatment

Unlike enzymatic hydrolysis of cellulose, which is specific, acids, are non-specific in their attack and cleavage of β -1-4 glycosidic bonds. Harsh conditions are required (temperature higher than 120 °C). This treatment depolymerizes the carbohydrates, a part of it is eventually dissolved, creating some porosity. Not only are some hemicelluloses removed but also those which remain in the pulp end up with new reducing end groups liable to subsequently undergo the peeling reaction (Arnoul-Jarriault et al., 2015). Depending on the severity of the treatment, some

sugar degradation products like furfural and hydroxymethyl furfural are formed (Jędrzejczyk et al., 2019). Another disadvantage of acid treatment is that special corrosion-resistant equipment is required for the operation.

1.6.3. Mechanical treatment

Mechanical treatment involves the physical modification of pulp properties by compression and shear forces. In the papermaking industry, the common mechanical treatment is the mechanical refining that occurs in wet conditions. The goal of the mechanical treatment of pulp depends on the desired application, but generally, it involves fiber cutting, fines generation, and an increased surface area. In the context of hemicellulose extraction, the expected refining outcome would be an increase in accessibility achieved by external fibrillation and swelling/internal fibrillation. The efficiency of mechanical treatment in improving accessibility of pulp to chemical (NaOH) and enzymatic (xylanase) agents in the extraction of hemicelluloses from pulp have been reported (Duan et al., 2016a; Gomes et al., 2020; Kim et al., 2019; J. Li, Liu, et al., 2015; Zhao et al., 2017). These studies attribute the improvement in xylan removal to the modification of the fiber structure with mechanical refining, which is characterized by increased specific surface area and water retention value, reduced degree of polymerization, shorter fiber length and increased fines content. The refining treatment in the above studies were all performed with the PFI refiner at different revolutions.

Description of pulp refining (or beating) will be reviewed in detail below since this thesis work will mainly concern the use of this pretreatment.

1.6.3.1. Mechanical refining

Mechanical refining is the treatment applied to pulp that alters the fiber morphology. Fiber suspension is treated between metallic bars (rotor and stator), which partially disrupt the fiber matrix, particularly on the surface. The refining mechanism progresses in three stages, as shown in Figure 18.

Fiber pick-up stage: In this stage, the fiber floc is formed and picked up by the edge of bars.

Edge to edge: It involves the compression of the fiber floc between the edges of the bar.

Edge to surface: in this stage, shear forces act upon the fibers while they are between the rotor edge and stator surface.

The fiber development (evolution of fiber morphology) during refining is not only influenced by the refining conditions but also by the type of fiber (long or short). According to (Lumiainen, 2000), the stapling of the fiber floc during the initial stage of the refining process was impacted by the fiber length. Long fibers form a more stable floc that is easily attached to the edge of bars, while short fibers form an easily dispersed floc that is difficult to secure on the bar edges.

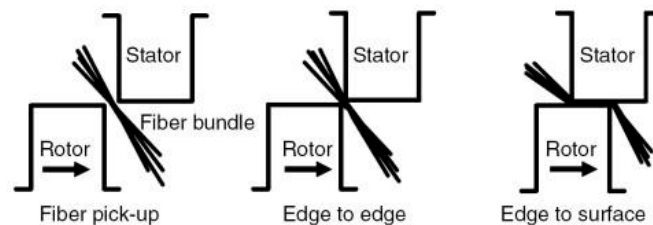


Figure 18. Mechanism of refining (Lumiainen, 2000).

1.6.3.2. Factors that influence fiber development during refining

There are two groups of factors that influence fiber development:

- (I) Initial fiber property: They are fiber-based factors unique to the fiber due to the source (hardwood, softwood, flax, cotton hemp) and chemical composition (unbleached or bleached pulp). The initial state of the pulp influences fiber development.
- (II) Refining condition: The refining condition applied to produce specific changes to fibers. Therefore, refining conditions can be controlled during the refining action to yield desired fiber/pulp properties.

1.6.3.3. Theories of refining

The refining theories help to predict changes in fiber morphology from the refining condition applied. It involves the use of mathematical models to describe and measure the refining action at various refining conditions. Refining action can be quantified by determining the refining energy or refining intensity. In this study the refining theory applied was the specific refining energy.

1.6.3.4. Specific refining energy

The energy applied to the fibers during refining determines the extent of fiber development. The total refining energy is defined as the sum of the no-load energy and the net refining energy. In this study, the specific refining energy was employed to assess the refining progress in the disk refiner pilot, while the refining time and revolutions were employed for Valley beater and PFI respectively.

$$E = \frac{P_{net}}{m} = \frac{P_{net}}{C \times V} \quad (1)$$

$$P_{net} = P_{total} - P_{no\ load} \quad (2)$$

Where, (m= dry mass flux, C = pulp consistency, V = flowrate)

The no-load energy, also known as idle energy, is the energy required to run the equipment (when the gap clearance is above the critical point required for refining action). The no-load energy does not bring about refining. The changes that occur with refining are brought by the net refining energy, which is the actual energy transferred to the fibers during refining. The specific refining energy required to achieve a given refining outcome depends on the refining technology and the fiber resistance to refining.

1.6.3.5. Important refining conditions to control

Pulp consistency: The consistency of pulp during refining significantly affects fiber development. Various refiners operate at specified consistency for efficiency. When the consistency is low or higher than required, it leads to fiber cutting, plate plugging, and overall poor fiber development (Lumiainen, 2000).

Plate material and design: Different refining technologies exist with unique plate material and design, which influences the refining action. Sometimes, even with the same refiner, different plate designs are used for various fibers sources. For instance, in the disc refiner, plates with broad bars and groves are adapted for softwood refining, while plates with narrow bars and groves are preferred for hardwood fibers (Lee et al., 2016). Also, selecting the appropriate plate material prevents bar breakage, bar edge rounding, and rapid bar wear. Therefore, employing the right plate material and design is vital for efficient refining.

Flow rate: The flow rate is a crucial refining parameter to ensure efficient fiber treatment. Applying the wrong flowrate could result in plate clashing due to poor fiber pick up, inefficient refining, increased fines generation, and short plate life.

Beating or refining degree: The extent of refining or beating degree of pulp can be determined by the dewatering or drainage resistance, which is measured by the Schopper-Riegler value (°SR) or Canadian standard freeness (CSF). The (°SR) increases with beating while the (CSF) decreases.

1.6.4. Refining effects

The changes that result from the mechanical treatment of pulp which can influence hemicellulose removal treatments are categorized as follows;

- Fiber cutting
- External fibrillation
- Swelling/internal fibrillation
- Redistribution of surface chemical composition (carbohydrate leaching)

- Fines generation

1.6.4.1. Fiber cutting

Irrespective of the refiner design and refining conditions, fiber shortening is an inevitable consequence of refining (Przybysz et al., 2020). However, the extent to which it occurs can be controlled. Depending on the pulp source or application, fiber cutting might be the predominant desired outcome of a refining action. Therefore, refining technologies or refining conditions that promote fiber cutting are applied. For instance, in the production of microfibrillated cellulose, severe fiber cutting is desired before the fibers are transferred to the homogenizer (Bossu et al., 2019). Also, in papermaking, fiber cutting has been shown to lower flocculation by reducing the crowding number, which leads to improved sheet formation and smoothness (Hua et al., 2005; Lumiainen, 2000). In biorefinery applications like enzymatic sugar conversion and hemicellulose extraction, an increased surface area created by refining due to the formation of new fiber ends through fiber cutting has been shown to enhance reagent accessibility and the overall improvement in the reactivity (Jones et al., 2017).

1.6.4.2. External fibrillation

Refining leads to the peeling off of fibrils from the exterior of the fiber wall exposing hidden regions of the fiber layers. In some instances, the peeling effect of the refining process produces fibrils that are still attached to the fiber wall (external fibrillated). In papermaking, external fibrillation increases fiber-fiber bonding and surface area, which contribute to the strength properties of the paper but in biorefinery processes, the exposure of the hidden surfaces and the gain in the specific surface area improve reagent accessibility to active sites (Hua et al., 2005).

1.6.4.3. Swelling/internal fibrillation

A delamination of the fiber wall layers occurs during mechanical refining, which results in swelling. The swelling is induced by the penetration of water molecules through the pores created during refining. It was reported that the

mechanism of swelling varied depending on the fiber source. Higher swelling has been recorded for hardwood compared to softwood pulp which resulted in a reduction in the lumen size. This was described as an inward swelling mechanism. In contrast to wood, bamboo was reported to swell outwardly due to its small-sized lumen (Gharehkhani et al., 2015). According to (Abitz, P., & Luner, 1989), internal fibrillation is the most critical refining effect because it enables increased fiber flexibility. Swelling in fiber can be measured by the change in water retention value (WRV) or the fiber saturation point (FSP).

1.6.4.4. Redistribution of surface chemical composition (carbohydrate leaching)

Mechanical refining has been associated with the leaching of colloidal substances, a redistribution of hemicelluloses from the interior of the fiber wall to the exterior (Lumiainen, 2000; Page, 1989). Likewise, a change in the distribution of chemical composition on the fiber surface during refining was also reported by (Gharehkhani et al., 2015)

1.6.4.5. Fines generation

Fines refer to fibrous particles severed from lignocellulosic biomass during the chemical pulping process or mechanical refining. They are described as fibers of length $\leq 200\mu\text{m}$ or particles that can pass through a 200-mesh wire (ISO 10376:2011) or a 75 μm diameter round hole (TAPPI 261 cm-94). Fines have unique properties that differ considerably from fibers, and in some cases, they are used as additives in the papermaking process. Fines increase paper strength properties, reduce porosity and improve fiber bonding ability (Motamedian et al., 2019; Seth, 2003). In chemical pulps, particularly bleached chemical pulp, two types of fines are defined. The primary fines are generated solely by the pulping process without mechanical refinement (Bäckström et al., 2008; Hult et al., 2002). They are composed of ray cells, parenchyma cells, vessels, and fiber fragments. On the other hand, secondary fines are a product of mechanical refining. These fines are of

particular interest in papermaking as they are composed of fibrils detached from the surface of fibrillated fibers. They are reported to exhibit high specific surface area, resulting in high swelling ability and high flexibility.

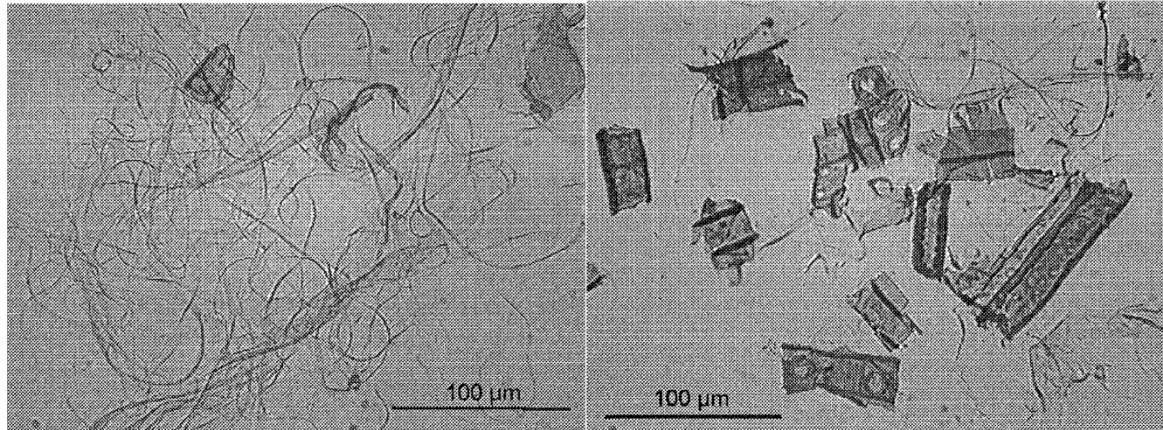
1.6.5.1. Fines generation processes

Fines are also produced during chemical or enzymatic activities, but the amount produced is marginal compared to mechanically generated fines. Mechanical pulping produces fines rich in lignin and hemicellulose, while refining of chemical pulps produces cellulose-rich fines. It has been reported that better swelling occurs in secondary fines compared to primary fines (Mayr et al., 2017; Olejnik et al., 2017). This observation was attributed to the presence of lignin in primary fines, particularly mechanical pulp fines. As lignin is hydrophobic and surrounds the cellulose microfibrils, restricting the swelling ability (Luukko & Maloney, 1999). Several studies have been done on the effect of various refining parameters on fines generation. Irrespective of the refining technology, increasing the specific energy consumption also increases the fines content (Gharehkhani et al., 2015; Olejnik et al., 2017). Other conditions that influence fines production include; refining consistency (high consistency refining limits fines production and low consistency refining increases it), pulp origin, and process history. (Olejnik et al., 2017) reported that fines generation was mainly influenced by the effective refining power and the rotational speed of the rotor. The study also showed that the swelling degree of fines vary with refining conditions applied, especially rotational speed and low pulp consistency

1.6.5.2. Properties of fines

Fines, in general, are structurally (size, shape) and chemically (composition) heterogeneous as they can be generated from various parts of the cell wall, for instance, from fractured fibers, fibrils, ray cells, and lamellae. Depending on the process history, they can be chunky particles (flakes) rich in lignin and hemicellulose or finer particles (fibrils) rich in cellulose as shown in Figure 19 (Luukko & Maloney, 1999). The finer cellulose-rich particles generated principally from mechanical

refining are preferred for papermaking, as they are more flexible, have a higher specific surface area with higher hydration (swelling), and are known to improve bonding properties and, consequently, strength properties of paper.



Finer particles (fibrils)

chunky particles (flakes)

Figure 19. Microscopic images of cellulose-rich fines and flakes (Luukko & Maloney, 1999).

1.6.5.3. Chemical composition of fines

The fiber wall of wood is organized in layers. In chemical pulps, these layers include an almost entirely damaged primary layer and the partially intact secondary layers (S1, S2, and S3). As fines are detached from the fiber's surface, their chemical composition and supramolecular structure vary from that of the fibers, particularly for unbleached pulp. This has been supported by various investigations reporting lower crystallinity index and higher lignin and hemicellulose content for fines compared to fibers of the same pulp (Asikainen et al., 2010; Duan et al., 2017; Hult et al., 2002). In the case of bleached pulp, the increased hemicellulose composition in the fines could be attributed to the precipitation of dissolved hemicellulose on the fiber surface during the pulping process.

1.6.5.4. Pulp modification by Valley beater refining

The Valley beater (Figure 20) is a laboratory beating or refining apparatus for pulp and papermaking processes. It improves pulp properties like fiber length, fines

content, internal and external fibrillation, density, and wet fiber flexibility, giving superior paper properties (Abitz, P., & Luner, 1989; Roux et al., 2017). The valley beater is operated at a low pulp consistency of $\leq 2\%$, and the energy applied can be adjusted by the loading level and the refining time. The refining action occurs between the bedplate and the rotor (Hua et al., 2005). The bedplate is fixed and has slightly inclined bars and grooves. The refining mechanism of the valley beater has been reported to favor fiber cutting and external fibrillation rather than internal fibrillation and swelling observed in the PFI mill (Kerekes, 2005).

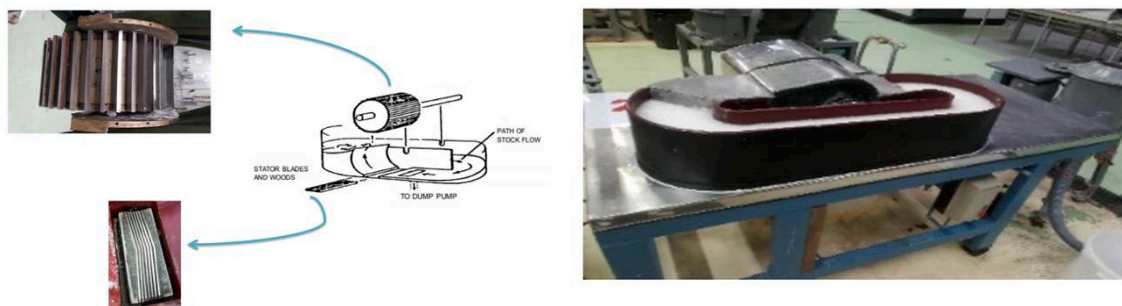


Figure 20. Valley beater.

1.6.5.5. Pulp modification by PFI refining

The PFI mill is a laboratory refiner often described as low intensity-high energy refiner (Kerekes, 2005). It is operated at a high pulp consistency of 10% and a small sample size, usually between 24 and 30 g per batch. The refining action occurs between the bar roll (rotor) and the smooth surface of the housing or refining chamber (Figure 21). The refining degree is described most times by the number of revolutions applied. The predominant refining effect attributed to the PFI mill is internal fibrillation/swelling, and the fiber shortening is minimal. Fiber swelling is due to the ease of water penetration into the delaminated fiber wall, which is facilitated by the presence of hydrophilic groups. According to (Abitz, P., & Luner, 1989), internal fibrillation is the most crucial refining effect in papermaking. It allows for increased fiber flexibility associated with superior strength properties and paper quality.

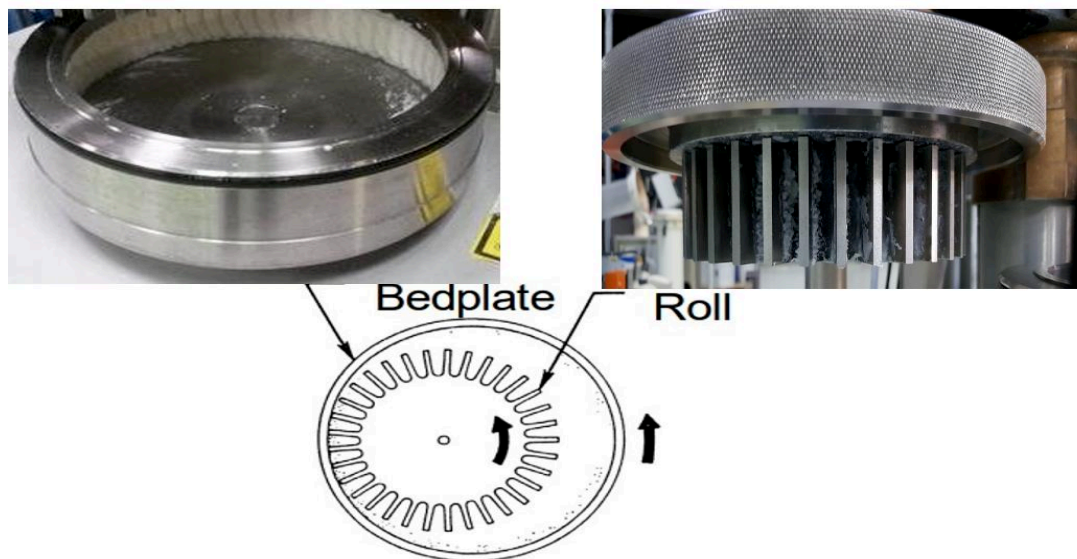


Figure 21. PFI refiner

1.6.5.6. Pulp modification by Disc refiner pilot

During refining, the bars of the rotor and stator of the disc refiner intersect so that the stock flows parallel to the bars. The plate pattern used for refining is selected according to the pulp type. For long fibers like softwood, plates with broad bar and groove width are suitable. However, for short fibers like the hardwood, plates used have narrow bars and grooves with a small width. According to (Lee et al., 2016), the broad bars and grooves of the plate used for softwood fibers promoted rapid fiber cutting while the narrow bars and grooves of the plate used for hardwood refining produced a mild cutting effect occurring over time. If the appropriate plate is not employed, pulp refining could be excessive (cutting) or inadequate. Poor fiber development, energy loss, and plate wear are some of the disadvantages of using the wrong plate (Hua et al., 2005; Kral et al., 2015). The pulp consistency is another important parameter to consider when using the disc refiner. For long fiber, severe fiber cutting occurs if the consistency is lower than it should be (less than 3%). On the other hand, for short fibers (hardwood), if the consistency is too low, the formation of the floc during the refining action is affected as the flocs are dispersed during refining. So, the fibers receive no refining action.

Other parameters of interest in the disc refiner pilot include (Figure 22); gap size and net power.



Figure 22. Disc refiner Pilot

1.7. Regenerated cellulose fibers

Regenerated cellulose fibers are man-made cellulose fibers derived from wood or other lignocellulosic biomass, dissolved in a suitable solvent, and regenerated through a spinning process in an anti-solvent ([J. Chen, 2015](#); [S. Wang et al., 2016](#)). The method of cellulose dissolution can occur by derivatization or direct dissolution. The two most important regenerated cellulose fibers are produced by the derivatization and dissolution (viscose) and direct dissolution (lyocell) processes. The viscose process produces regenerated cellulose via the derivatization by reaction with carbon disulfide that converts cellulose to cellulose xanthate, while the lyocell process uses a direct dissolution involving physical

interaction between the ionic bonds on the N-Methylmorpholine N-oxide (NMMO) and hydrogen bonds of cellulose (Figure 23). Other man-made cellulose fibers include cellulose acetate and cuprammonium rayon.

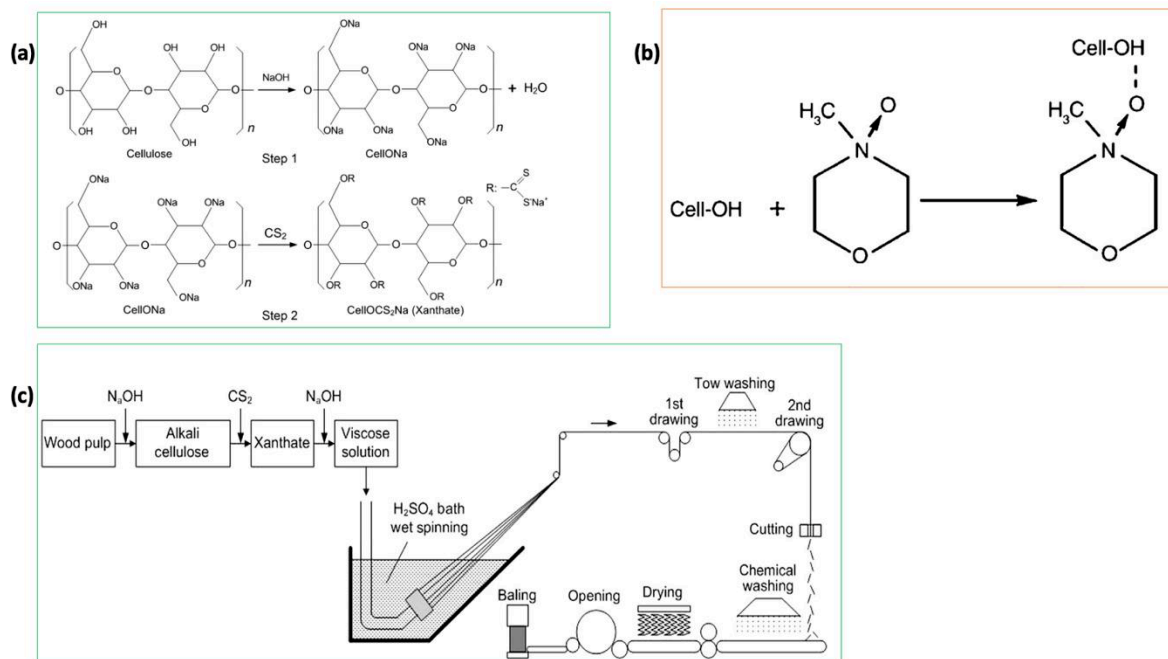


Figure 23. (a) Chemical reaction of carbon disulfide with cellulose in the viscose process; (b) mechanism of cellulose interaction with NMMO in the lyocell process; A scheme of the viscose fiber production (J. Chen, 2015; S. Wang et al., 2016).

Regardless of the environmental concerns, the viscose process covers the global market for regenerated cellulose fibers with a share of over 93% (J. Chen, 2015; Shen et al., 2010). For this reason, most manufacturing processes for dissolving pulp are designed to meet the dissolving pulp properties (reactivity to xanthation, molecular weight distribution, and degree of polymerization) tailored to the viscose process (Duan et al., 2016b; Gehmayr et al., 2011; Gondhalekar et al., 2019; Miao et al., 2014, 2015; Schild & Sixta, 2011).

1.7.1. Cellulose reactivity

Due to its natural structure and the presence of a multitude of intermolecular hydrogen bonds, the cellulosic fiber has a very low reactivity. This explains why very few systems have been shown to be able to solubilize cellulose molecules. In both viscose and Lyocell processes, special attention is paid to the

parameters which control the chemical reaction with Carbon disulfide (CS₂) or the solubilization in N-Methylmorpholine N-oxide (NMMO). For this reason, so-called fiber reactivity measurements have been developed.

The reactivity of dissolving pulp is the ease with which the hydroxyl groups on cellulose chains react with the reagent in the derivatization process or the solvent during the dissolution process. Factors such as the chemical composition of the dissolving pulp, the structure, and the morphology of the fibers significantly impact the reactivity (Tian et al., 2014). Generally, dissolving pulp properties are influenced by the source of the raw material (cotton, wood, or bamboo), the pulping process (acid sulfite or pre-hydrolysis kraft), and bleaching conditions. Compared to the sulfite process, the kraft pulping system has been reported to yield cellulose with low reactivity (to xanthation). This has been attributed to the hemicellulose removal mechanism. Hemicellulose extraction in alkaline medium proceeds via a swelling mechanism where the cellulose fibrils expand, leaving room for the solubilization of the hemicellulose fraction entrapped within the cellulose matrix. After the removal of the hemicellulose, there is a kind of collapse of the fibrils closing up spaces freed by the hemicelluloses leading to a reinforcement of the hydrogen bond network (Figure 24).

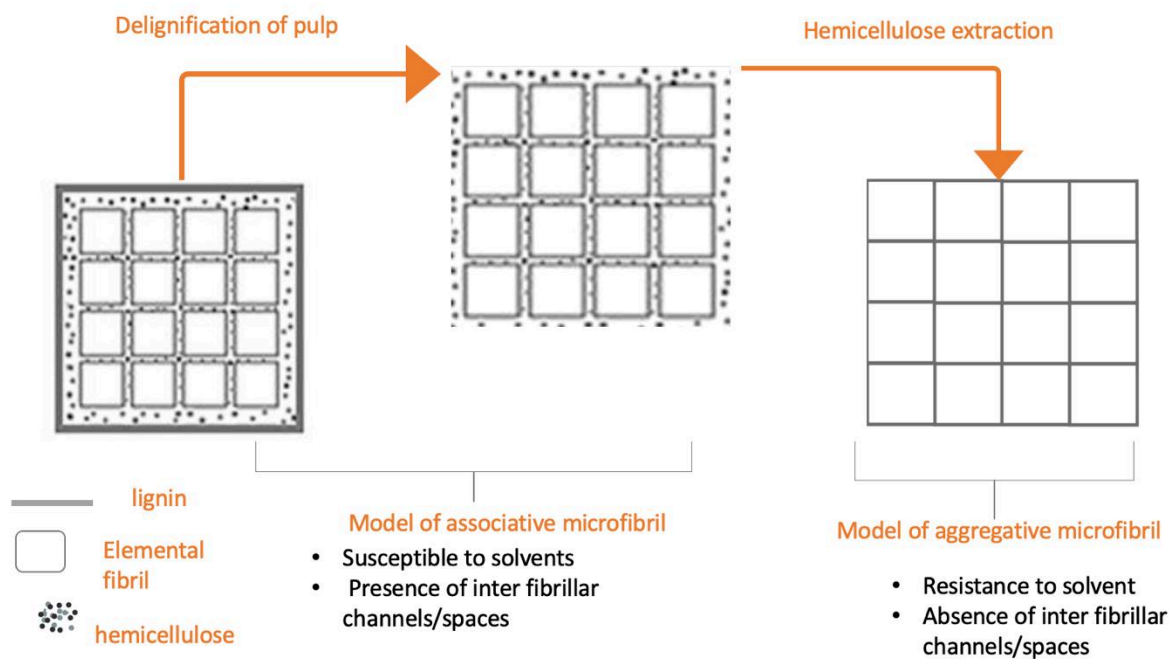


Figure 24. models of the cellulose microfibrils before and after purification adopted from (M. Y. loelovich, 2016).

Among the methods proposed in the literature to determine the reactivity of dissolving pulp in the viscose process, the Fock test/reactivity (Tian et al., 2013) is the most popular. The other methods are the Chinese filterability test (Duan, Li, et al., 2015) and viscose dope Filter Value (Gehmayer et al., 2011). The Fock test determines the reactivity of dissolving pulp by quantifying the percent regenerated/reacted cellulose in the viscose process. It follows a similar principle as the viscose process, which involves (i) the swelling of pulp in strong NaOH solution (mercerization), (ii) the derivatization to cellulose xanthate (xanthation: the reaction of the hydroxyl groups on cellulose with carbon disulfide) (iii) the dissolution of cellulose xanthate (iv) the regeneration of the dissolved cellulose (v) the oxidation and quantification of the regenerated/reacted cellulose.

Several approaches have been proposed to improve the reactivity of dissolving pulp, enzymatic and mechanical treatments being the most common. (Tian et al., 2014) explored the effect of mechanical treatment by PFI (refining) and coffee grinder on the reactivity of PHK dissolving pulp. They found an increase in Fock reactivity from 49% to 72% after grinding for 6 minutes. Refining the pulp

with the PFI at 25000 revolutions increased the Fock reactivity from 49% to 58%. The less impressive result obtained with the PFI was attributed to the inter-intra fibril/fiber hydrogen bonding enhanced by fibrillation during the PFI refining, which limits chemical accessibility. Also, the application of endoglucanase to 9% CCE extracted pulp increased the Fock reactivity from 23 to 62% (Duan et al., 2016a). Likewise, a study by (Miao et al., 2014) showed that PFI refining treatment alone at 5000 revolutions had no significant effect on Fock reactivity (and DP of cellulose), but the enzymatic treatment (cellulase) increased the Fock reactivity from 50 to 76%.

Actually, mechanical and enzymatic treatment (cellulases) of dissolving pulp may modify the morphology of the fibers as well as the DP of cellulose. Several reports on enzymatic modification of cellulose reactivity have attributed the increase in Fock reactivity due to the DP adjustment brought about by the enzymatic degradation of cellulose chains, but according to (Ferreira et al., 2020) the influence of the supramolecular structure of cellulose on reactivity (fibril aggregates dimension) outweighs the effect of the degree of polymerization. The authors reported that even with low DP (intrinsic viscosity $< 500 \text{ cm}^3/\text{g}$) and low crystallinity index ($< 50\%$), the Fock reactivity was influenced more by the lateral fibril aggregation.

To conclude, Figure 25 summarizes the factors influencing pulp reactivity according to the studies mentioned above.

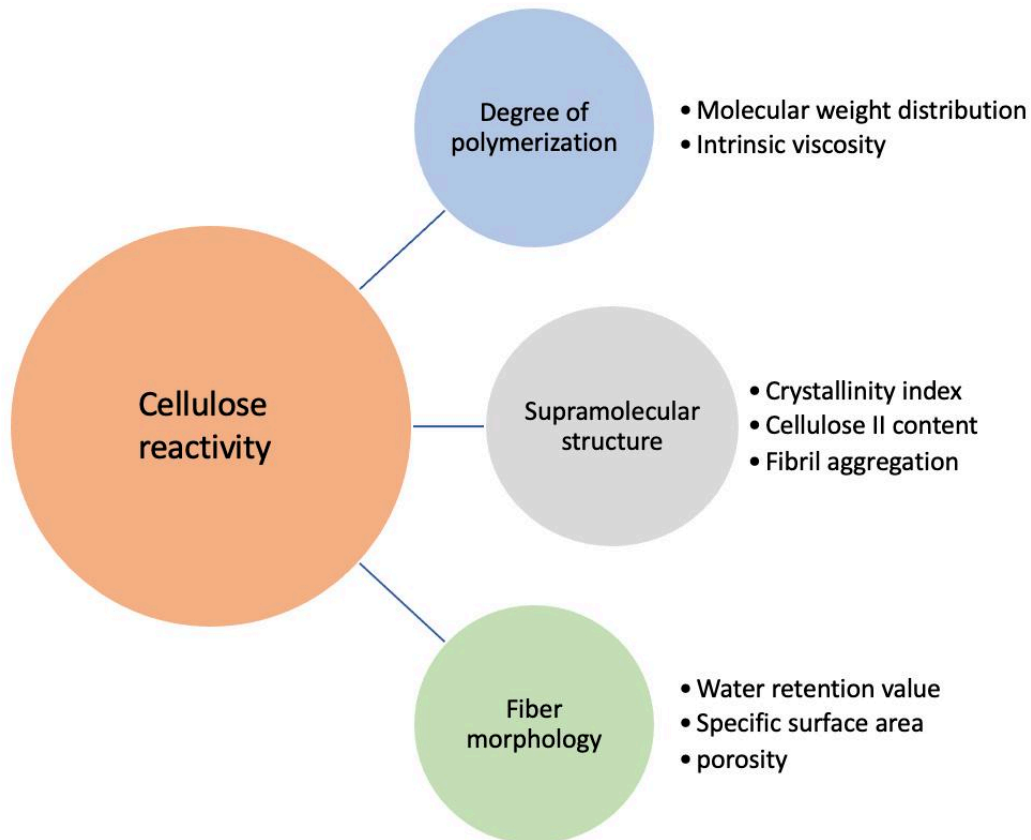


Figure 25. Factors that affect cellulose reactivity.

1.7.2. Fiber morphology

The fiber morphology is characterized by fiber length, fine fraction, water retention value, specific surface, and porosity. If the length of the fibers decreases and the fines content increases, the water retention value and the specific surface area are positively influenced and thus the accessibility of the pulp to the solvent. Mechanical refining can be adapted to produce structural changes that increase accessibility (Dou & Tang, 2017; Grönqvist et al., 2014; Jones et al., 2017; Miao et al., 2015; Tian et al., 2014; Zhou et al., 2018).

1.7.3. Degree of polymerization

The degree of polymerization (DP) indicates the number of monomer units that make up the polymer chain. The cellulose polymer is linear, which facilitates the aligned stacking of the fibrils that enables the dense network of hydrogen bonds.

Therefore, a decrease in the degree of polymerization, which implies a cut in the chain length, increases accessibility. The degree of polymerization/ molecular weight and intrinsic viscosity are positively correlated. Several studies report an increase in cellulose reactivity to xanthation with a decrease in the degree of polymerization (Duan et al., 2016b; Gehmayr et al., 2011; Grönqvist et al., 2014; Köpeke et al., 2008; Liu et al., 2019; Miao et al., 2014, 2015)

1.7.4. Supramolecular structure

The arrangement of cellulose chains in the supramolecular structure influences its response to chemical and enzymatic treatments. The dense network of hydrogen bonds (intra and inter) holding the chains together in the supramolecular structure can be strengthened or weakened by the processing history of the pulp. The degree of crystallinity and the lateral fibril aggregation can be increased or decreased by chemical treatments. Native cellulose has a parallel alignment of the cellulose chains, while cellulose II an antiparallel alignment of the chains in the crystal lattice. Cellulose II is a more stable structure than cellulose I, with an even denser network of hydrogen bonds after dewatering which impairs reactivity. The transformation of the crystal lattice structure of native cellulose to cellulose II occurs in strong alkaline solutions. During harsh alkaline treatment of pulp, native cellulose swells and then shrinks (hornification) after washing to a modified form of cellulose called cellulose II. The process is called mercerization. The change takes place in two steps; firstly, the conversion to Na-cellulose I and secondly, the progression of the change to cellulose II. Conditions that favor cellulose swelling increase the probability of cellulose II formation, while conditions that do not encourage swelling inhibit the formation of cellulose II. The two most important conditions for cellulose II formation are soda concentration and treatment temperature (Arnoul-Jarriault et al., 2015). More so, the NaOH concentration required to induce mercerization vary depending on the pulping process history; 9%w/v NaOH for sulfite pulp and 10%w/v NaOH for kraft/soda pulp (Dinand et al., 2002).

Conflicting reports exist on the influence of crystallinity index and lateral fibril aggregation on cellulose response to treatments (Dou & Tang, 2017; Ferreira et al.,

2020; Peciulyte et al., 2015). It appears that there isn't a precise mechanism or comprehension of how these properties (crystallinity index and lateral fibril aggregation) affect cellulose accessibility to chemicals and enzymes. However, there is some agreement on the negative influence of cellulose II on accessibility after dewatering of the pulp (Arnoul-Jarriault et al., 2015; Dou & Tang, 2017; Fernandes Diniz et al., 2004; Ferreira et al., 2020).

Conclusions on chapter 1

Forest resources, particularly woody biomass, can be sustainably exploited to meet the growing demand for dissolving pulp production driven by environmental concerns like climate change, fossil-based plastic pollution, and overpopulation. Paper pulp upgrade to dissolving pulp provides a potential alternative route for manufacturing dissolving pulp. The advantage of this approach over conventional methods of dissolving paste production has been discussed. Figure 26 shows the essential elements.

Acid sulfite pulping	Prehydrolysis kraft pulping	Paper pulp upgrade
<p>Pros</p> <ul style="list-style-type: none"> • higher reactivity • Isolation of lignosulfonates • Monomeric form of hemicelluloses recovered 	<p>Pros</p> <ul style="list-style-type: none"> • Uniform MWD • Higher α-cellulose (94%-96%) • Isolation of lignin precipitates • Oligomeric form of hemicelluloses recovered • Effective for hemicellulose removal (60%) 	<p>Pros</p> <ul style="list-style-type: none"> • Uniform MWD • Higher α-cellulose (95%-97%) • Isolation of lignin precipitate • Polymeric form of hemicellulose (xylan) recovered • Effective for hemicellulose removal (> 60%)
<p>cons</p> <ul style="list-style-type: none"> • Broad MWD • Lower α-cellulose (92%-94%) • Degradation of cellulose and hemicellulose 	<p>cons</p> <ul style="list-style-type: none"> • Low reactivity compared to the acid sulfite pulp 	<p>cons</p> <ul style="list-style-type: none"> • Fibril aggregation and formation of cellulose II which leads to poor cellulose reactivity with dewatering

Figure 26. Merits and demerits of dissolving pulp production methods.

Although the CCE is an efficient method for hemicellulose extraction from paper pulp, it does not quite achieve complete removal of the hemicellulose fraction due to the structural modification of the hemicelluloses during the pulping and bleaching process. The presence of hemicellulose in the downstream dissolving pulp processing compromises regenerated cellulose quality, increase chemical consumption, and other processing nightmares like clogging of the spinnerets. Moreover, harsh CCE conditions favor the formation of cellulose II, which may have a negative impact on cellulose reactivity if dewatering and drying are performed after CCE. Pretreatments such as acidic hydrolysis, enzymatic hydrolysis, and mechanical treatment are expected to facilitate the alkaline extraction process by improving accessibility. Mechanical refining of pulp, a process already existing in

the pulp and paper industry, can be maneuvered to achieve favorable pulp properties that can enhance the performance of the CCE. Refining effects like fiber shortening, fines generation, swelling, and external fibrillation modify fiber morphology to respond positively to hemicellulose extraction and cellulose dissolution chemicals.

This chapter provided a background of the proceeding study with details of the problem associated with hemicellulose extraction and methods that have been proposed to remedy it. The next two chapters (chapters 2 and 3) explores mechanical refining with different technologies and how the mechanism of refining influences the CCE process, while the last two chapters present the effect of refining on the solubility of cellulose and xylan recovery and characterization. Finally, the methodology is presented in the final chapter.

Chapter 2: Study of mechanical refining as pretreatment for hemicellulose extraction from hardwood paper pulp by cold caustic extraction and xylanase treatment.

Overview of chapter

This chapter has five sections. The first three examines the influence of Valley beater, PFI, and disc refining on fiber development and the refining-induced change in morphology on xylan extraction by cold caustic extraction (CCE) and xylanase treatment. The fourth section compares the refining effect of the laboratory refiners (Valley beater, PFI) to the industrial-like refiner (disc pilot) to determine if there is a substantial difference in the results obtained for xylan extraction on pulp refined at lab and pilot scale. The last section explores the potential of mild cellulase treatment as an alternative to mechanical refining. Conclusions on each section are presented at the end of the section. The chapter begins with a brief background to the study, with some relevant literature. The study starts with the effect of Valley beater refining pretreatment on xylan extraction as few studies exist on the subject, with most of the reports in the literature focused on the PFI mill. Finally, a general conclusion on the findings of the chapter was presented at the end.

Background of study

The main question in upgrading paper pulp to dissolving pulp is how the high hemicellulose content (18 – 29 % depending on the wood type) in the paper pulp can be sufficiently reduced (Arnoul-Jarriault et al., 2015; Dou & Tang, 2017; Gehmayr et al., 2012; Kim et al., 2019). Some studies available in the literature suggested applying a mechanical pretreatment prior to CCE (Duan, Verma, et al., 2015; Zhao et al., 2017). For instance, (J. Li, Liu, et al., 2015) studied the effect of PFI refining (10,000 revolutions) on the alkaline extraction of softwood sulfite pulp carried out at (10% pulp consistency, 25 °C, 30 minutes reaction time). The authors found that coupling the refining with CCE (4% NaOH) reduced hemicellulose from 9.5% to 5%, while CCE implemented alone led to a decrease of 9.5% to 7.8%.

These studies highlight the benefit of refining prior to the cold caustic extraction process, which is plausibly due to better accessibility. However, the full potential of refining is not known, considering that there exist different technologies to refine pulp and that several intensities may be applied. For example, the refining mechanisms of the PFI and Valley beater are quite different. The prominent effect of refining with the PFI is fibrillation, and that of the valley beater is cutting and fines generation (Gharehkhani et al., 2015; Motamedian et al., 2019), the likelihood exists that pulps treated by the PFI refiner and Valley beater might respond differently to chemical and enzymatic hemicellulose extraction.

2.1. Effect of Valley beater refining as pretreatment for hemicellulose extraction from hardwood paper pulp by alkaline and xylanase treatment

The study aimed to provide information on the effect of pulp modification via the Valley beater at different refining loads and the impact of such morphological changes on the removal of hemicellulose from regular hardwood kraft pulp containing around 20% xylan. The approach considered in this study to achieve quantitative removal of hemicellulose from the pulp is the sequential refining pretreatment followed by CCE.

2.1.1. Fiber modification with Valley beater refining

The modification of the fiber morphology during refining is achieved by controlled exposure to shear and compression forces, which results in fiber cutting, internal and external fibrillation, fiber delamination, and generation of fines (Gharehkhani et al., 2015; Li et al., 2015; Motamedian et al., 2019; Roux et al., 2017). These modifications ultimately lead to increased specific surface area (SSA), increased water retention value (WRV), increased pore size and volume, and decreased crystallinity index, all of which improve the reactivity of the pulp towards hemicellulose removal or dissolution of cellulose (Duan et al., 2016a; Grönqvist et al., 2014; J. Li, Liu, et al., 2015; Tian et al., 2014; Zhou et al., 2018).

The Valley beater is operated with a low consistency of $\leq 2\%$ and energy that is supplied to the pulp suspension can be adjusted through the loading level and the beating time. Refining action takes place between the bedplate and the rotor. The bed plate is fixed and has slightly inclined bars and grooves. Also, the Valley beater's refining mechanism make it easier to cut fibers.

The parameter used to evaluate the extent of refining or degree of refining in this study was the Schopper-Riegler ($^{\circ}$ SR). From the result presented in Figure 27, the evolution of pulp drainage resistance represented by the SR value at the different loading levels 3 kg, 4.5 kg, and 5.5 kg followed a similar trend, but the time it took to reach the target SR value (85) was different. The refining energy applied at the various loading conditions varied. The estimated refining energy was 344 kWh/t, 400 kWh/t, and 480 kWh/t for 3 kg, 4.5, and 5.5 kg. Therefore, the order of refining intensity for the loading levels was 5.5 kg > 4.5 kg > 3 kg. As the refining mechanism is influenced by the refining intensity, among other factors, we imagine that the mechanism of refining at the different loading conditions varies. For instance, lower intensity refining is characterized by a more gentle impact or refining action, unlike high-intensity refining (Abitz, P., & Luner, 1989).

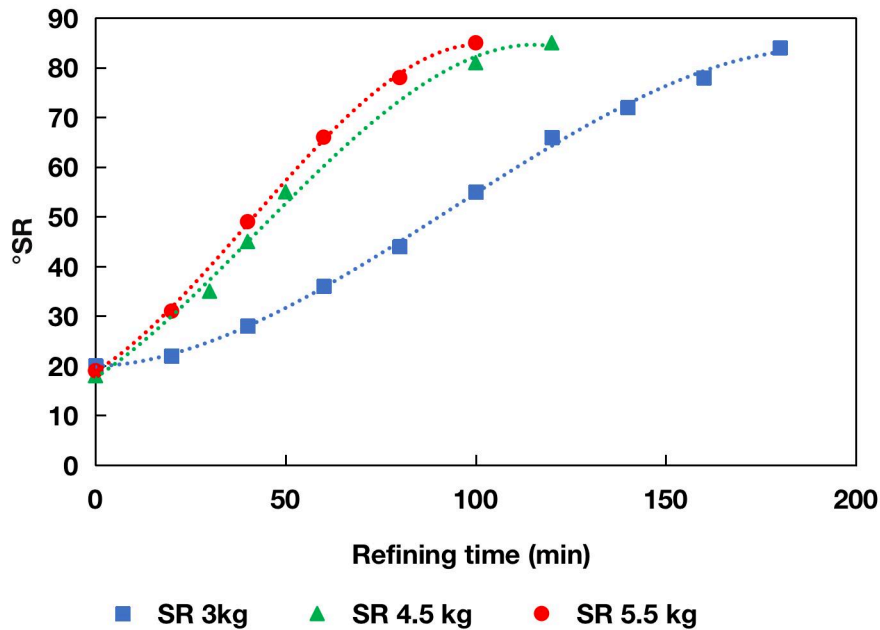


Figure 27. Evolution of (Schopper-Riegler) °SR with refining time and refining load.

Table 3 shows a significant reduction in fiber length and increases in fines content with refining. This indicates that Valley beater refining promotes fiber cutting, especially at a 4.5 kg load. Similarly, the WRV increased more than twofold with refining, and the highest increase was recorded at 4.5 kg load. Also, the fibrillation index, specific surface area (SSA), and pore volume dramatically increased with refining. The high loads gave, in general, the most increase in SSA.

Table 3. Effect of Valley beater refining on pulp characteristics at different refining loads (3kg, 4.5kg, and 5.5 kg).

Samples	Unrefined	3 kg	4.5 kg	5.5 kg
Fiber length (mm)	0.68	0.52	0.43	0.45
Fiber width (μm)	22	24	26	25
Fines % in length	41	63	71	70
WRV (g/g)	103	243	268	257
Macro-fibrillation index (%)	1.8	2.4	3.1	3.0
SSA (m^2/g)	0.4	1.8	2.8	3.4
Pore volume (cm^3/g)	1.16×10^{-03}	6.45×10^{-03}	7.99×10^{-03}	9.22×10^{-03}

The scanning electron microscopy (SEM) images were used to highlight the structural modification of fibers with refining. As shown in Figure 28, the effect of refining is evident when the unrefined fibers are compared to the refined fibers. Although a clear difference is not always visible between the morphology at the different loadings, the fibers refined with the 4.5 kg and 5.5 kg load show more external fibrillation, fragmentation of the fibers, and the presence of fibrillated fines surrounding the fibers. All these structural changes constitute favorable conditions that enhance the accessibility of chemicals and enzymes to active sites.

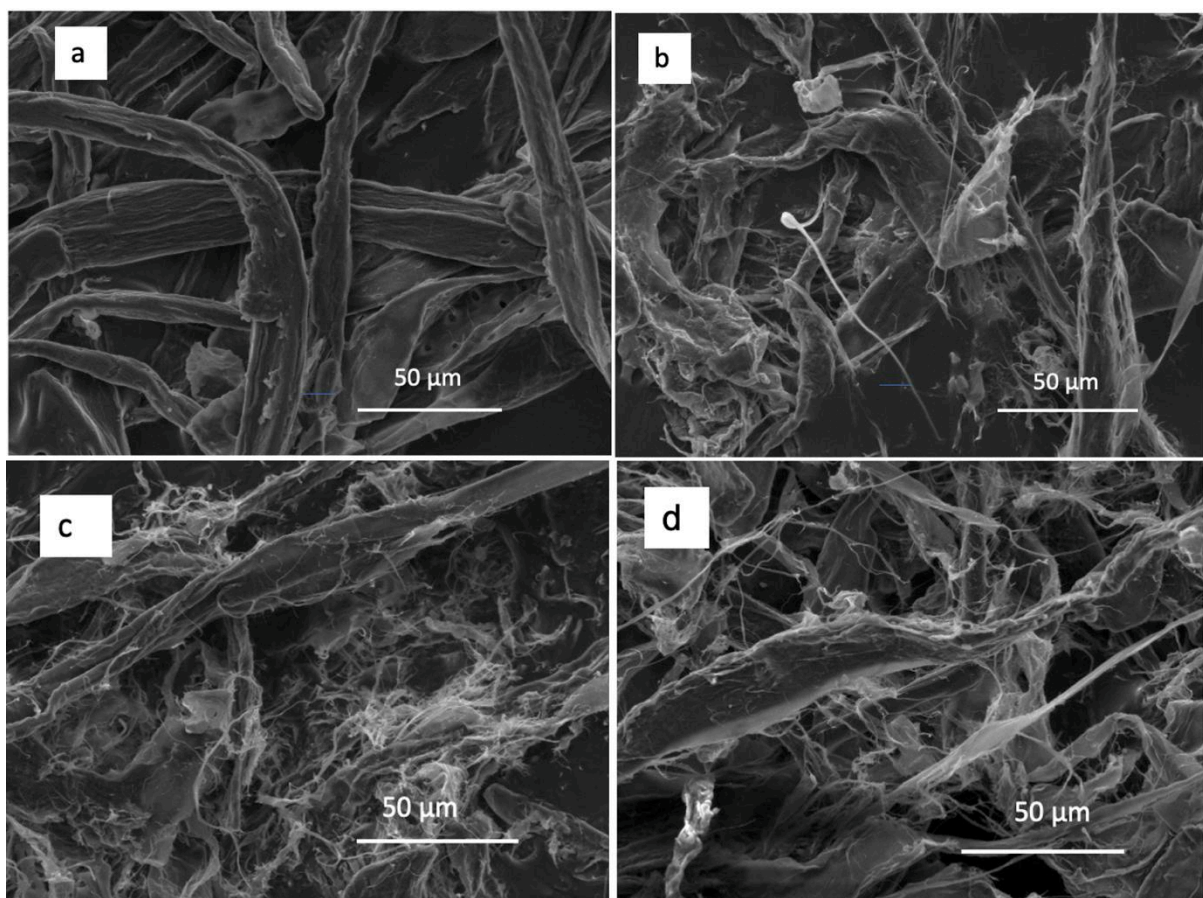


Figure 28. SEM images of pulp showing the modifications due to Valley beater refining: (a) unrefined pulp, (b) 3 kg load, (c) 4.5 kg load, and (d) 5.5 kg load.

2.1.2. Performance of cold caustic extraction with Valley beater refining

In the context of paper pulp upgrade to dissolving pulp, the cold caustic extraction method shows promise (Friebel et al., 2019; Hutterer et al., 2016; J. Li et

al., 2016; Sixta, 2008b). Several factors affect hemicellulose solubilization in alkali including, extraction temperature, residence time, pulp consistency, and alkali concentration (Hutterer et al., 2016; Sixta, 2008b). To better monitor the effect of the alkali charge on the extraction process, other parameters apart from the ion concentration were kept constant. The temperature was 25 °C, the residence time was 30 min, and the pulp consistency was 5%. The choice of a short residence time of 30 min was made because longer treatment time resulted in yield losses (J. Li et al., 2017) and 5% consistency was to ensure uniformity in mixing and the practicality for industrial application (Sixta, 2008b). Biphasic hemicellulose extraction from the pulp during the cold caustic extraction process has been reported (Hutterer et al., 2016; J. Li et al., 2017). The first phase occurs at the onset of the extraction process at a lower alkaline charge within the first few minutes. It involves the rapid extraction of the easily accessible xylan with low molecular weight while the second phase occurs at a lower rate and extracts the inaccessible high molecular weight hemicelluloses. More so, the latter phase requires a high alkaline charge (100 g/L) to obtain a sufficient swelling for good extraction.

Figure 29 shows the Xylan extraction performance of the cold caustic extraction treatment at various soda concentrations on unrefined and refined pulp. A 20 g/L NaOH concentration showed no significant xylan extraction even when refining is applied before the alkaline treatment. This means that the concentration is too low to allow the swelling process that initiates the first phase of xylan solubilization. As expected, a substantial hemicellulose solubilization occurred between 40 g/L and 60 g/L NaOH concentrations for both unrefined and refined pulps. The influence of refining, although noticeable, is not particularly relevant in the first phase of the xylan dissolution process as evidenced by the degree of xylan removal at both concentrations (40 g/L and 60 g/L NaOH) being respectively 34% and 58% for unrefined pulp and 39% and 68% for refined pulp (4.5 kg load). However, at higher alkali charge a considerable difference in the performance of the CCE is observed for refined pulp compared to the unrefined pulp. The results show that a soda concentration of 100 g/L removes 50% more xylan compared to the unrefined pulp, indicating a greater synergy between the high alkali charge and fiber wall modifications due to refining.

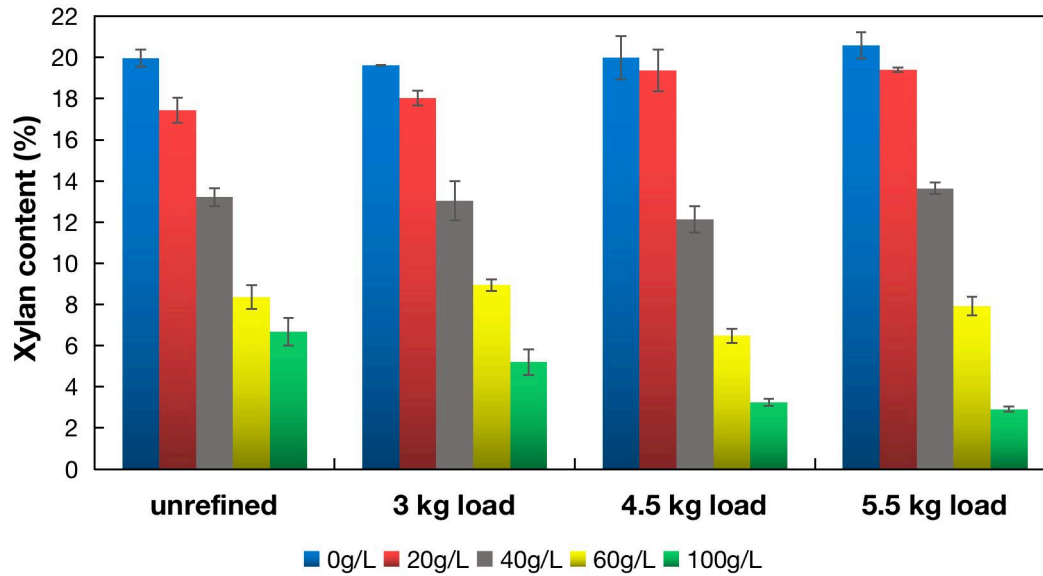


Figure 29. Xylan extraction performance of the cold caustic extraction treatment at various soda concentrations on unrefined and Valley beater refined pulp at (3 kg, 4.5 kg, and 5.5 kg loads) evaluated by the residual xylan content after treatment.

The refining energy and corresponding residual xylan content in the pulp after coupling refining at 3 kg, 4.5 kg and 5.5 kg with CCE (100 g/L) is shown in Figure 30. The linear curves obtained, suggests a correlation between the refining energy and the refining load. A similar observation can be seen between the residual xylan content in the refined pulp after CCE treatment and the refining energy applied. Therefore, an increase the refining load increases the energy consumption with improvement in xylan extraction evidenced by the lower xylan content. However, since a substantial difference in the energy consumed for 4.5 and 5.5 kg was observed (400 kWh/t and 480 kWh/t, respectively), with similar xylan extraction performance (3.25% and 2.9 %, respectively), the 4.5 kg refining load was preferred for further investigation.

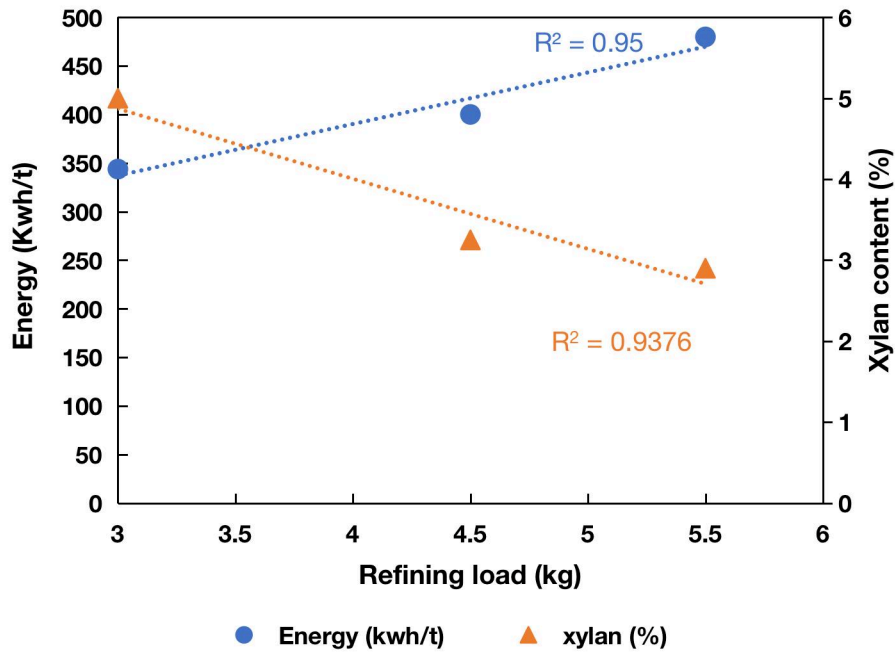


Figure 30. Evolution of the refining energy with refining load and residual xylan in the extracted pulp at 100 g/L NaOH.

2.1.3. Molecular weight distribution and degree of polymerization

The degree of polymerization (DP_v) of the pulp (Figure 31), which is determined by the viscosity of the pulp in cupriethylenediamine (CED), indicated that a slight degradation of the cellulose chain occurred during refining which was in agreement with other studies (Zicheng Chen et al., 2019; Duan et al., 2016a; Kim et al., 2019; Tian et al., 2014).

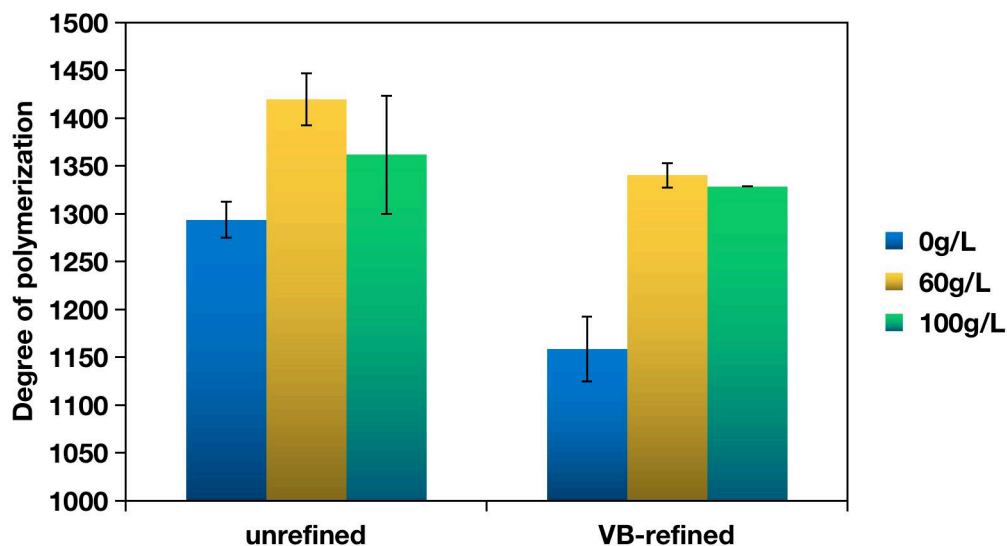


Figure 31. Evolution of the degree of polymerization (DP_v) with CCE at soda concentration (0 g/L, 60 g/L, and 100 g/L) of unrefined and Valley beater refined (VB refined).

Although the removal of residual xylan during the alkaline treatment results in an overall gain in degree of polymerization (since the xylan molecules are short-chain), the effect of the slight degradation of cellulose chains remains evident when comparing the DP_v values of the alkaline extracted unrefined and refined pulps. As shown in Figure 32, the molecular weight distribution (MWD) profile for the starting pulp is remarkably different from pulps treated by refining and CCE. The disappearance of the small peak (which signals hemicellulose loss) to form a unimodal distribution was observed. The numerical evaluation of the molecular weight and the polydispersity index (PDI) of the treated and untreated samples are shown in Table 4. A slightly higher PDI value was obtained for the extracted Valley beater refined pulp (R-10CCE) compared to the extracted unrefined pulp (UR-10CCE), which could be explained by the effect of slight cellulose chain degradation during refining.

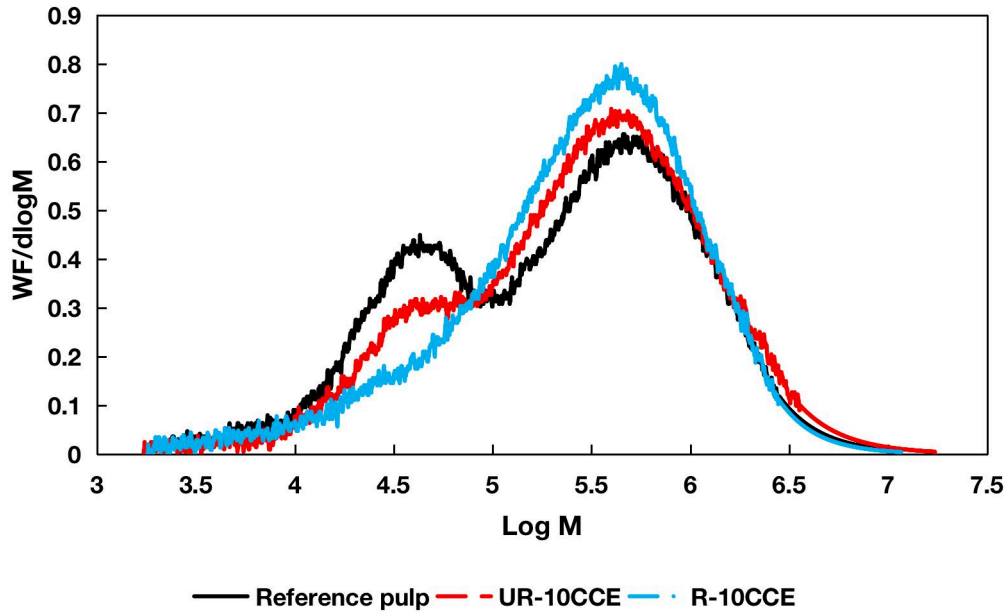


Figure 32. Molecular weight distribution profile of starting pulp without any treatment (reference pulp), unrefined pulp with 10 CCE (UR-10CCE), and refined pulp with 10CCE (R-10CCE).

Table 4 Numerical value of molecular weight with treatment.

Samples	DPw	DPn	PDI
Reference	3900	442	8.8
UR-10-CCE	4194	873	4.8
R-10-CCE	3983	742	5.4

2.1.4. Conclusions

The importance of mechanical refining with the Valley beater in producing high purity pulp from paper grade mixed hardwood kraft pulp was illustrated in this study. The study showed that fiber morphology could be influenced by controlling the refining load, which has a corresponding effect on the xylan extraction performance. Structural modifications associated with mechanical refining with the Valley beater, especially at a loading of 4.5 kg, were shown to facilitate the extraction of about 84 % of the residual xylan from kraft pulp by CCE. The next step will consist of scaling up this process with the disc refiner.

2.2. Influence of PFI milling on the fiber morphology and xylan extraction from paper pulp.

2.2.1. Pulp modification by PFI refining

In this part of the study, the PFI mill was used to modify the structural properties of the pulp prior to the removal of hemicellulose by cold caustic extraction (CCE). Since fiber development depended on refining conditions, the refining mechanism associated with PFI refining concerning hemicellulose extraction was investigated on hardwood kraft pulp.

To assess the fiber response to the refining action, the drainage resistance ($^{\circ}\text{SR}$), water retention value (WRV), fiber quality (fiber length, fines content) of the pulp was measured at various refining degree (PFI revolutions). Figure 33 presents the evolution of the WRV and drainage resistance with refining. The result showed that the WRV increased rapidly between 0 and 7000 revolutions, after which a gradually increase was observed as refining progressed.

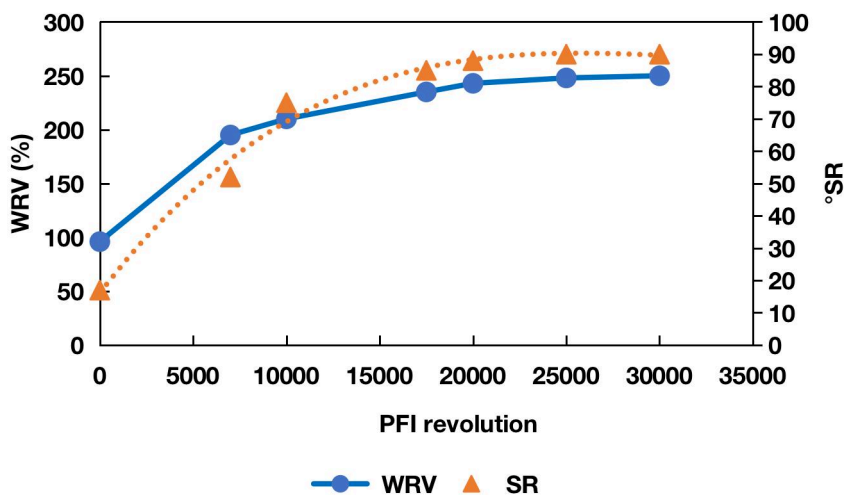


Figure 33. Evolution of WRV and $^{\circ}\text{SR}$ with refining.

A similar trend was observed for the fines generated with refining, except that, unlike the WRV, the gains in fines with refining plateaued at a higher refining

revolution of 17500 (Figure 34). Also, the shortening of the fiber with refining progressed rapidly until 17500 revolutions, after which it stabilized. (Abitz, P., & Luner, 1989) proposed two mechanisms of WRV rise, one due to fiber wall delamination and fibrillation and the other brought about predominantly by the effect of fiber cutting and fines generation. These mechanisms could be used to interpret the evolution of fiber quality with refining on the PFI mill. The rapid changes in WRV, between 0 and 7000 revolutions, could be attributed to fiber cutting and fines generation, while the gradual gain in WRV after stabilization could be consequent to fiber delamination and fibrillation.

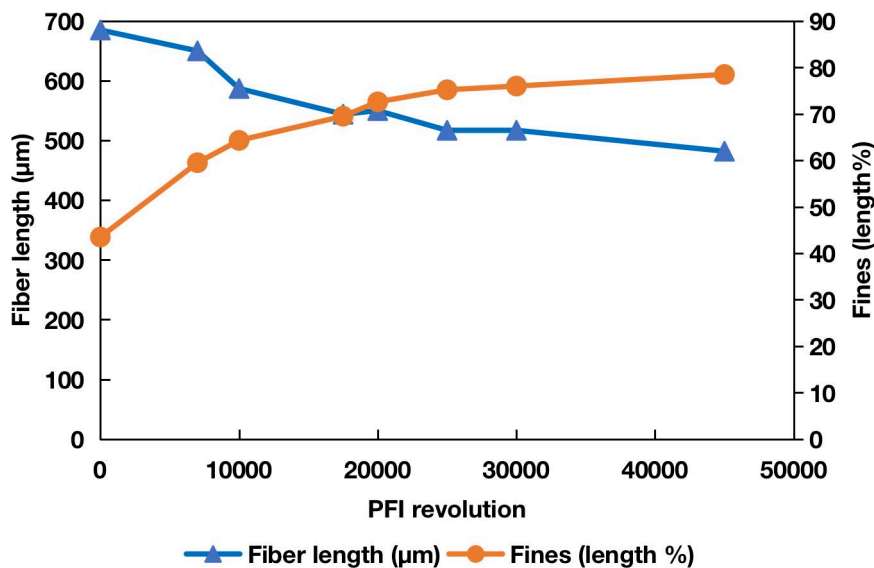


Figure 34. Evolution of fiber length and fines content with refining.

2.2.2. Influence of PFI refining on xylan extraction

The influence of refining at various revolutions on xylan extraction by the cold caustic extraction was examined (Figure 35). Two soda concentrations were used for this study, 60 g/L, and 100 g/L. For both soda concentrations, increasing the refining action resulted in a decrease in the initial xylan content in the pulp. This trend can be attributed to the exposure to new surfaces by refining and the penetration of chemical agents to initially inaccessible fiber regions. (Tian et al., 2014) reported that the PFI mill effectively altered the fiber structure, evidenced by the increase in specific surface area, fines content, and a decrease in the crystalline

ratio. They observed that the Fock reactivity increased with refining action from 50 % at a revolution of 5000 to 58 % at a revolution of 25000. The effect of applying refining prior to CCE was reported by (Duan et al., 2016a). They showed that at a PFI revolution of 3000 and soda concentration of 5.5 %, a hemicellulose removal of about 75% was obtained compared to 41 % for unrefined pulp. In a similar study, (J. Li, Liu, et al., 2015) obtained a hemicellulose removal of 47%, at a refining revolution of 10000, and soda concentration of 4%. Interestingly in the present study, no significant extraction was obtained at 7000 revolutions compared to the unrefined pulp. The result in Figure 35 shows that the xylan removal obtained at a soda concentration of 60 g/L was 57%, 64%, and 68%, with refining at 7000, 10000, and 17500 revolutions, respectively. Notably, the influence of refining became important at 10000 revolutions. The best extraction result was obtained at a soda concentration of 100 g/L for refining at 10000 and 17500 revolutions, with xylan removal of about 78% and 82%, respectively. Perhaps these variations in performance of PFI refined pulps concerning the effect of refining severity could be attributed to (i) bar sharpening and calibration of the refining equipment (Yasumura, 2012), and (ii) pulp history (fiber morphology and initial hemicellulose content).

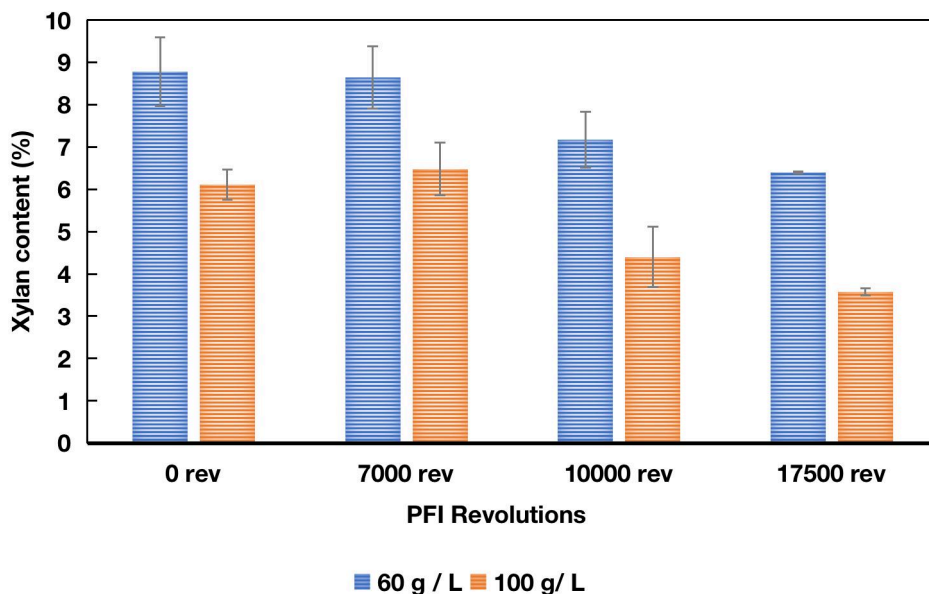


Figure 35. Performance of cold caustic extraction at different soda concentration and refining levels.

2.2.3. Impact of PFI refining on pulp viscosity and molecular weight distribution

The degree of polymerization (DP_v) was affected by refining and suggests a slight degradation of the cellulose chains, perhaps in the amorphous region (Figure 36). A gain in DP_v was also observed with soda treatment, which indicated the removal of the short-chained molecules.

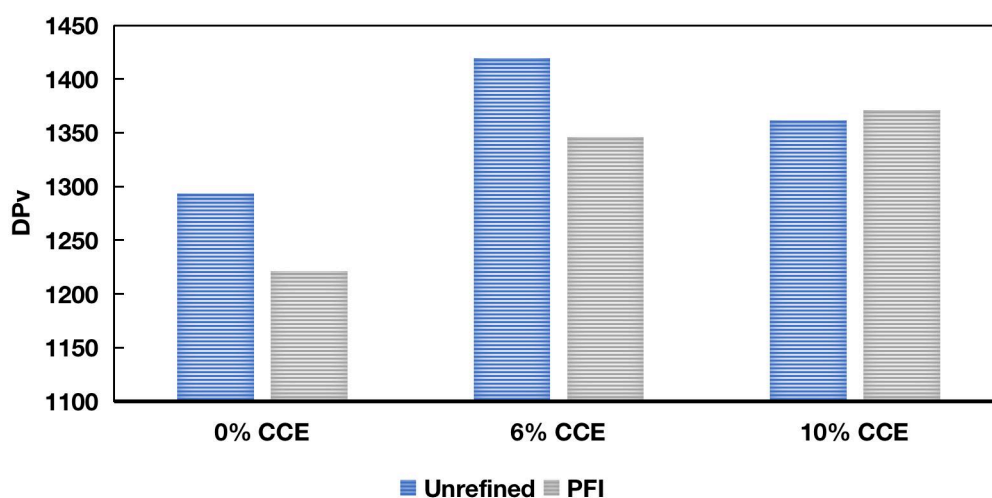


Figure 36. Effect of refining on the degree of polymerization (DP_v) at various soda concentrations of (PFI-CCE)

The molecular weight distribution profile of the PFI refined pulp coupled with cold caustic extraction was narrow for both soda concentrations, especially at 100 g/L (Figure 37). A decrease in dispersity index from 9 to 4.5 was obtained for the unextracted refined pulp and extracted refined pulp at 10% soda. (Table 5). The Unextracted pulp exhibited a bimodal molecular weight distribution, indicating low and high molecular weight polymers that make up the pulp. Usually, the short-chained polymers represent the hemicellulose fraction, but depending on the severity of treatment applied, be it chemical, enzymatic or mechanical, the low molecular weight fraction might include degraded cellulose chains. Thus, the variation in DP_w (Table 5) between the reference pulp (unrefined) 3900 and the refined pulp (PFI 0%) 3271 suggested degradation of the pulp with refining, which agrees with the DP_v values.

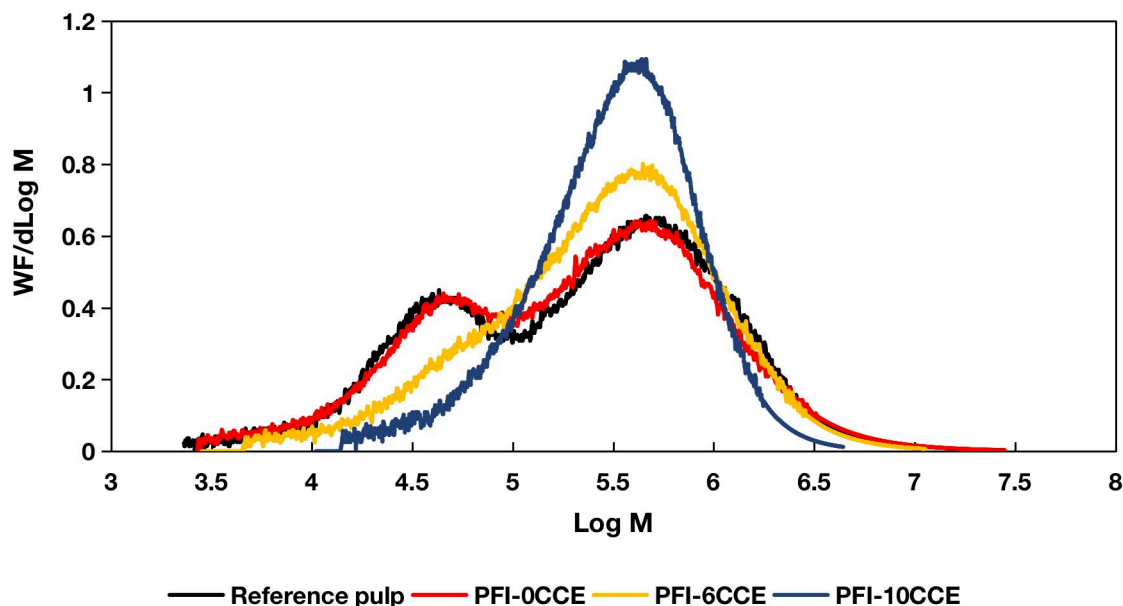


Figure 37. Molecular weight distribution profile of the reference pulp and PFI refined pulp extracted at various NaOH concentration (0 g/L, 60 g/L, and 100 g/L).

Table 5. Statistical representation of molecular weight and uniformity of pulp.

samples	DPw	DPn	PDI
Reference	3900	442	8.8
PFI-0CCE	3271	363	9.0
PFI- 6CCE	3474	641	5.4
PFI- 10CCE	3422	723	4.7

2.2.4. Conclusions

This study demonstrated the importance of refining by the PFI mill for fiber development at various revolutions and the subsequent effect of such pretreatment on xylan extraction via cold caustic extraction. The results show that increasing the refining action increased pulp accessibility to the alkaline solution, which improved the extraction of residual xylan. A Significant removal was not observed for low refining revolution (7000) with either of the investigated soda concentrations (60 g/L and 100 g/L), but increased refining (17500 revolutions) led to a xylan removal rate

of 68% and 82%, respectively. Finally, the xylan content and the MWD meet the requirements for dissolving pulp quality.

2.3. Effect of disc (pilot) refining pretreatment on Alkaline hemicellulose removal

2.3.1. Fiber modification by Disc refiner pilot

The disc refiner pilot is a small-scale industrial refiner designed and operated at similar conditions as mill refiners. Applying refining on the pilot allows for easy upscaling in the industries as the results obtained could be replicated in the mills (Jones et al., 2017). The refining parameters like specific energy consumption, rotational speed, refining time, temperature, flow rate, pressure is programmed to control the refining outcome.

In the present study, which involves refining hardwood pulp, the appropriate plate pattern was used (narrow bars and grooves). The varied parameter was the net power, while other parameters were not manipulated (keep constant as much as possible). The evolution of the fiber quality development at different net powers was done to determine the optimum net power that gave fiber properties best suited for improved pulp accessibility to chemical and enzymatic agents.

2.3.2. Evolution of fiber properties with disc refining at various net power

The fiber quality development of pulp refined on the disc refiner pilot was studied at net powers (P_{net}) of 4.4kW, 7.9 kW, and 11kW. The pulp was refined to an °SR value of 85, with samples collected at intervals during the refining process. The evolution of the SR value with specific energy consumption was similar for the net powers investigated (Figure 38).

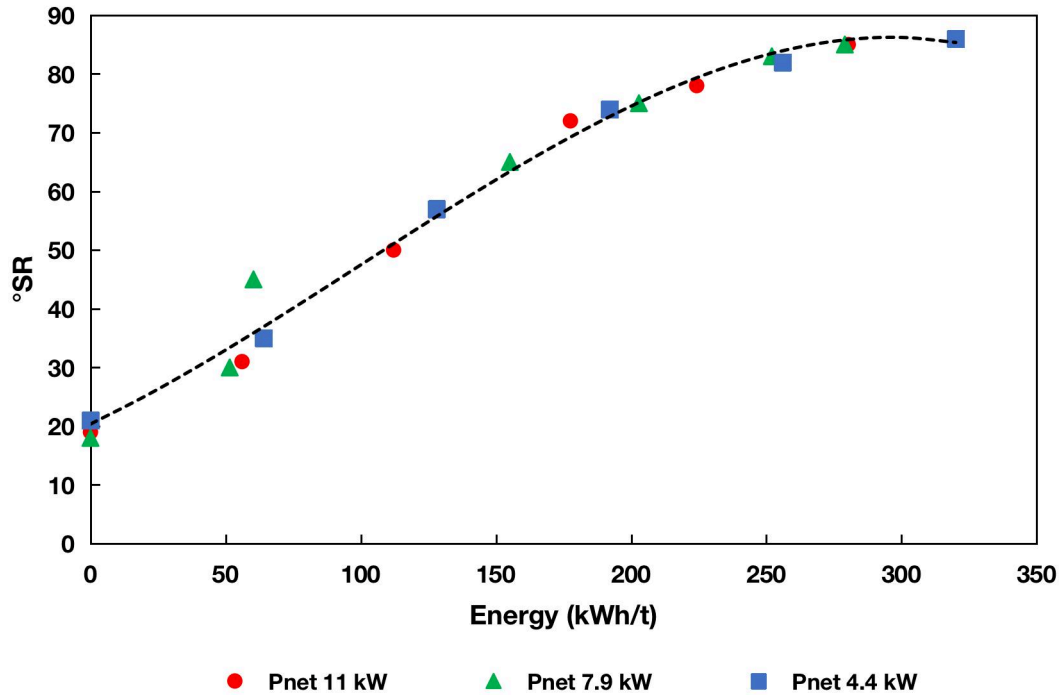


Figure 38. Evolution of °SR with energy at various values of net power (Pnet).

contrary to the evolution of °SR with energy which was similar for all the net powers investigated, the evolution of fiber length with energy was slightly different for each net power. All three pulp samples exhibited decreased fiber length with increasing energy, but more fiber cutting was observed for the pulp refined at Pnet 7.9 and 11 kW compared to 4.4kW, as illustrated by the steep slope obtained for 7.9 and 11 kW (Figure 39).

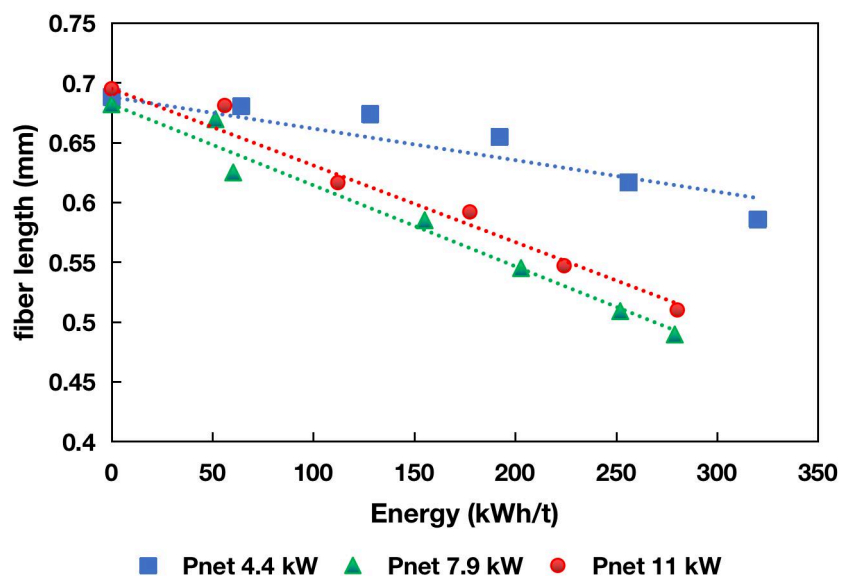


Figure 39. Evolution of fiber length with energy at various values of net power.

A similar trend was observed for the evolution of WRV with the specific energy consumption (Figure 40). The WRV increased with refining energy and was slightly higher at 7.9 and 11 kW compared to 4.4 kW. The somewhat lower WRV values and the mild cutting effects observed at 4.4 kW could be explained by inadequate refining action at that net power.

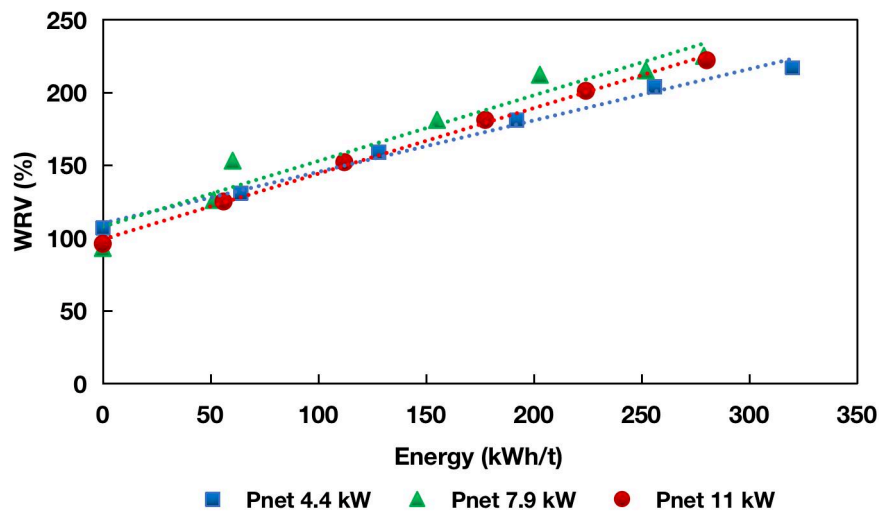


Figure 40. Evolution of WRV with energy at various values of net power.

2.3.3. Evolution of xylan content in pulp with disk refining

Based on the investigation of the morphological properties of the fibers with refining at various net power described in the previous section, the pulp refined at 7.9 kW was selected for further studies. The decision was due to the beneficial fiber length and WRV changes obtained at the moderate net power. Cold caustic extraction was performed at soda concentrations of 60 g/L and 100 g/L on the disc refined pulp obtained at a regular interval during the refining process. The result obtained is shown in Figure 41. At both soda concentrations studied, the residual xylan content in the extracted refined pulp decreased with increasing refining energy. It was apparent that at the same refining energy, alkaline extraction at 100 g/L soda produced pulp with less xylan than extraction at 60 g/L.

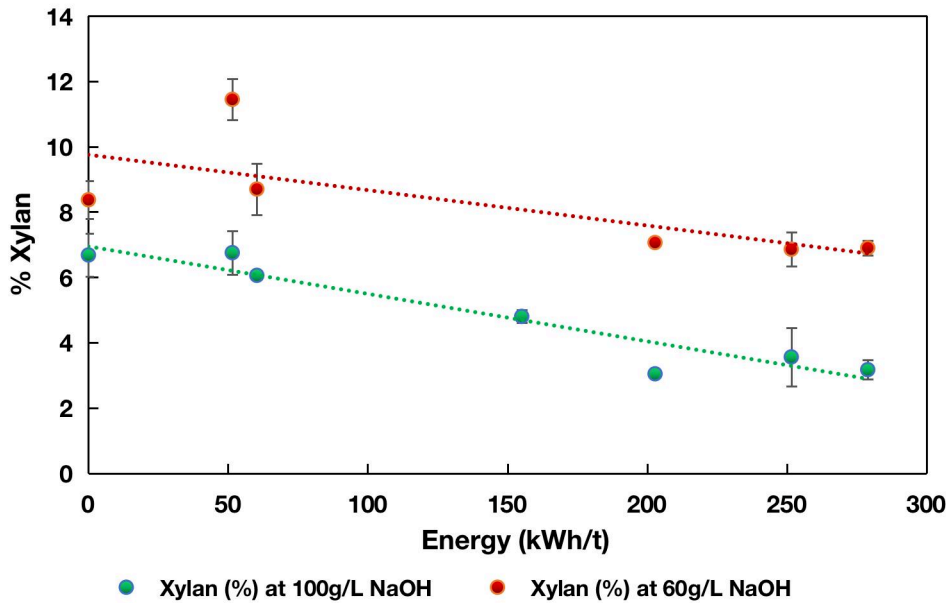


Figure 41. Evolution of % xylan content in pulp with energy at soda concentrations of 60 and 100 g/L.

The relationship between WRV and residual xylan content in the extracted refined pulp with increasing energy is illustrated in Figure 42. The increase in refining energy resulted in an increase in WRV, which improved the CCE process, as evidenced by the reduction in xylan content. It is logical to expect that, further increase in the refining energy/WRV beyond what is presented in Figure 42 would lead to more decrease in the xylan content as factors that create or enhance accessibility would invariably result in better xylan removal.

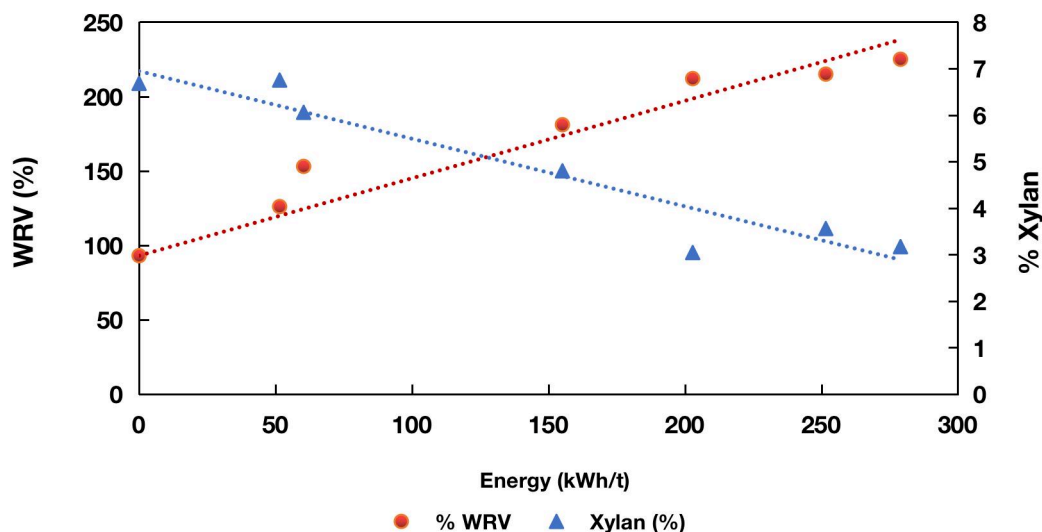


Figure 42. Evolution of % xylan and WRV % with energy at 100g/L NaOH.

Several studies have shown that increasing the specific surface area and WRV was a strong indication of improved accessibility (Grönqvist et al., 2014; J. Li, Liu, et al., 2015; Zhu et al., 2009) which resulted in better reagent penetration and, in the case of cellulose purification, enhance solubilization and diffusion of the hemicellulose component. The residual xylan content in the pulp after CCE at 100 g/L correlated with the water retention value (WRV%), as shown in Figure 43. From this result, it can be said that the WRV could be used as an indication of CCE efficiency or performance. Similar results were obtained for cellulose total sugar conversion experiments, where the WRV was shown to correlate positively with the enzymatic hydrolysis of cellulose determined by the 48 hour total sugar conversion (Jones et al., 2017). The authors discovered that performing refining on a pilot-scale disc refiner at 5% consistency and gap width of 0,03 mm resulted in a 36% increase in cellulose conversion to sugar when the WRV increased from 111 to 269%.

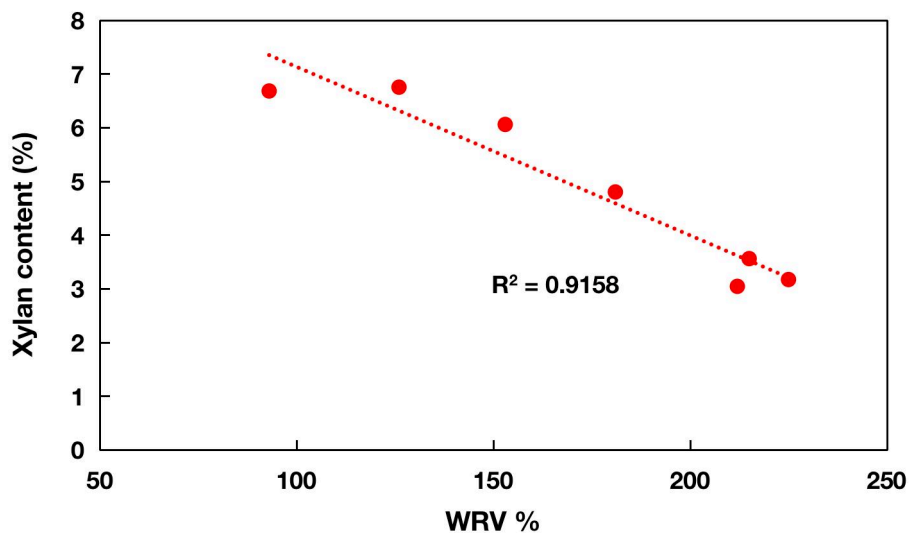


Figure 43. Xylan content in pulp after CCE at 100g/L NaOH as a function of WRV %.

As to the question of the optimum water retention value required to achieve the best results regarding xylan removal, it would depend on:

- (i) The intended application of the purified cellulose: Applications involving dissolving cellulose range from the production of viscose rayon staple fibers (requiring a maximum xylan content of 5%) to cellulose derivatives where higher purity is required. From the result in Figure 43, at a WRV of 181%, the residual xylan content obtained was 4.8% which is suitable for the viscose rayon, but a further increase in the WRV to 225% resulted in an even lower xylan content of 3.17%. Looking at the energy implication, a xylan reduction of about 34% (4.8 to 3.17%) led to energy consumption of about 44% (124kWh/ton). Therefore, to ensure the feasibility of the process, some compromises might be made between energy and purity.
- (ii) The initial WRV of the pulp, which is dependent on biomass type and the process history: For instance, the WRV of a sample of unrefined bleached hardwood kraft and unrefined cotton linter pulp were determined as 103% and 60%, respectively. After being subjected to the same refining treatment, the WRV increased to 237% for hardwood and 181% for cotton linter. Therefore, the optimum WRV might not be the same for all substrates.

2.3.4. Conclusions

Refining was performed on the disc refiner pilot at three different net power (4.4 kW, 7.9 kW, and 11 kW). The fiber quality development varied slightly depending on the net power applied, mainly in the evolution of the fiber length and WRV. The WRV proved to be a suitable indicator for the xylan removal performance by CCE at 100 g/L NaOH as a correlation was obtained between the residual xylan content in alkaline extracted pulp and the WRV.

2.4. Comparing the influence of refining technology on fiber morphology and xylan removal performance

The influence of refining as a mechanical pretreatment to improve the removal of residual xylan from paper pulp in its transformation to dissolving pulp was investigated. The mechanical refining pretreatment was carried out on

laboratory refiners (Valley beater and PFI mill) and then upscaled to a disc pilot refiner. Through refining, the study aimed to obtain structural modifications that would enhance xylan removal via the cold caustic extraction and enzymatic hydrolysis of hemicelluloses. The objective was to investigate the impact of the refining technology on the process. Several studies have been conducted on the effects of various refining technologies, particularly Valley beater, PFI, and disc refiners, on fiber development with regard to paper quality. Still, to the best of our knowledge, there is no study comparing the effect of the refining technology on hemicellulose removal. According to (Abitz, P., & Luner, 1989) the refining mechanism at work in the PFI mill was quite different from the mechanism operating in the Valley beater, partly due to the difference in refining condition (pulp consistency) and refiner design. Likewise, (Somboon, 2011) studied the evolution of fiber structure and properties with refining on the Valley beater, PFI mill, and an industrial pilot disc refiner. Pulps treated with the laboratory refiners showed superior strength properties, while the pulp treated with the industrial pilot had low density and higher light scattering. In another study by (Lee et al., 2016), the refining effects of the Valley beater and disc refiner on hardwood fiber were investigated.

Their investigation showed a significant difference in fiber development between the two refining technologies, with more cutting of the hardwood fibers recorded for the Valley beater than the disc refiner. In addition, the investigations of (Van Hai et al., 2013) on the effect of the refining technology of the PFI and Valley beater refiners on the alpha-cellulose content, crystallinity index, and degree of polymerization of cotton linter, hardwood, and softwood revealed a more drastic fiber shortening with the Valley beater compared to the PFI especially for the cotton linter, which was also reflected in a lower degree of polymerization. However, the alpha-cellulose content and crystallinity index were reported to have changed only slightly. Notably, the effect of various mechanical refining technology on the enzymatic digestibility of whole corn stover was carried out by (X. Chen et al., 2013). The refining technologies investigated included a twin-screw extruder, PFI mill, and disc refiner. The authors reported a higher glucose yield for the PFI mill than the disc refiner and that upscaling on a pilot-scale Szego mill produced similar results as the laboratory refiners. These studies report on the effect of different refining

technologies on fiber development and how they affect not only pulp and paper quality but also other critical parameters for assessing dissolving pulp quality like degree of polymerization, alpha-cellulose, and crystallinity index. Mechanical refining technology also plays a vital role as pretreatment in enzymatic hydrolysis of lignocellulosic biomass. So, it is crucial to provide some data and explanation on the impact of refining technology and upscaling (on the disc refiner pilot) on the efficiency of residual hemicellulose removal from paper pulp. That is what we aim to do in this study.

2.4.1. Effect of refining technology on the evolution of fiber properties

It has been reported that laboratory refiners like the Valley beater and PFI produce pulp modifications that are quite different from industrial refiners. This has been attributed to the impact of scale on the process. Regarding papermaking applications, some reports show a significant difference between the paper quality obtained from laboratory and industrial refiners ([Somboon, 2011](#)). As for biorefinery applications involving enzymatic carbohydrate hydrolysis, similar results were obtained for treatments on both scales ([X. Chen et al., 2013](#); [Jones et al., 2017](#)).

To monitor the refining effects imposed by the Valley beater, PFI, and disc Pilot refiners on bleached hardwood kraft pulp, the WRV and SR were measured at intervals as the refining progressed. These two parameters (WRV, SR) are commonly employed in assessing the extent of mechanical refining in both laboratory trials and paper mills. The evolution of WRV and SR on the Valley beater, PFI, and disc pilot was monitored as a function of refining time, revolutions, and refining energy, respectively. As shown in Figure 44, the fiber development on the laboratory and industrial-like refiner followed a similar trend. The SR value increased with refining in a nonlinear fashion, while the increase in the WRV followed a linear progression. The three technologies could not be plotted on a common scale because the metrics used for measuring the refining progression were different (refining time for Valley beater, revolutions for PFI, and energy for the disc pilot). The Valley beater produced pulp with the highest WRV, followed by the PFI and the disc pilot. According to ([Abitz, P., & Luner, 1989](#)) the rise in WRV could be fines driven or fibrillation driven. We suspect that in the case of the Valley beater, the

increase in WRV was primarily due to a rise in fines with some contributions from fibrillation and vice versa for PFI and disc refined pulp.

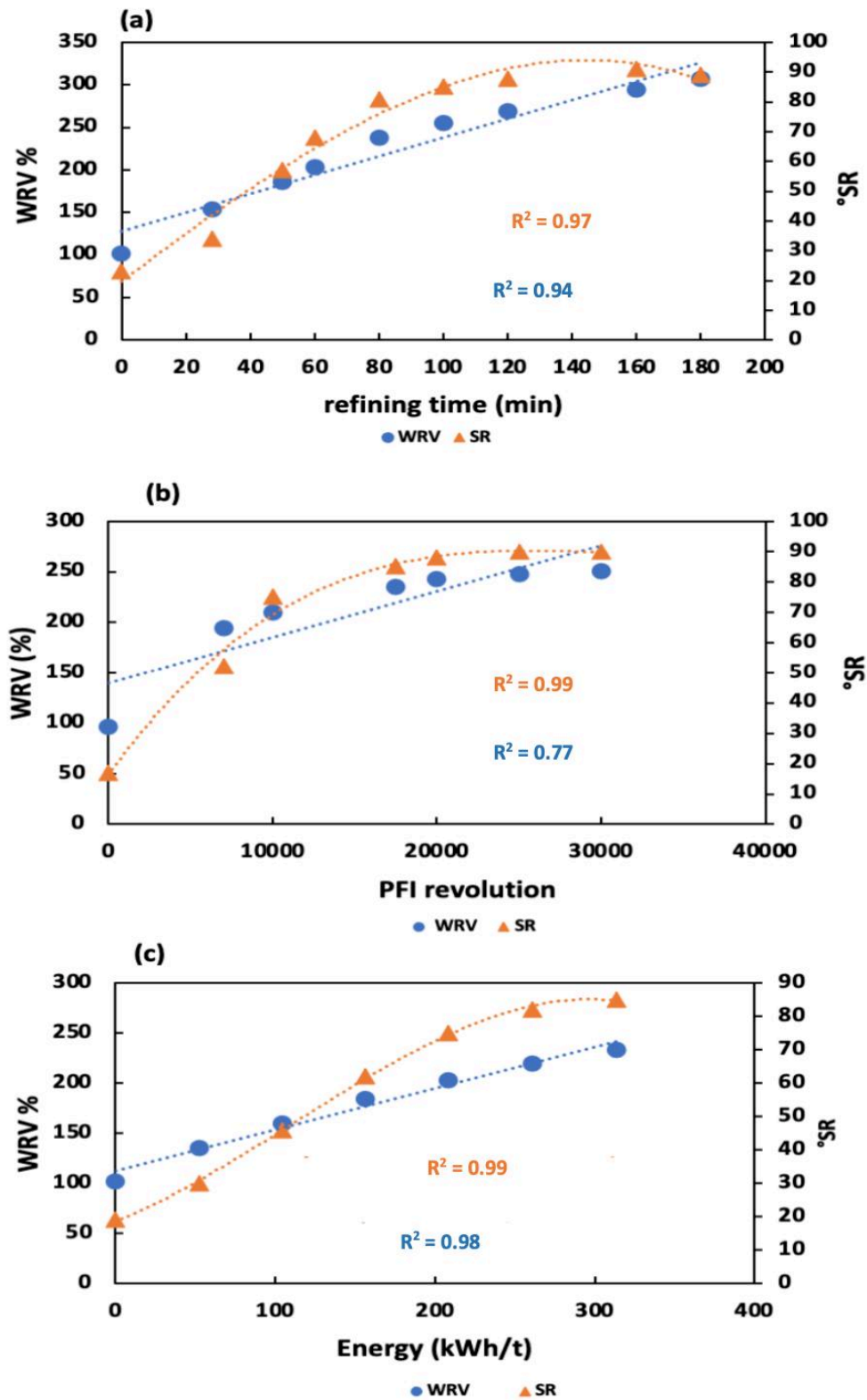


Figure 44. Evolution of WRV and SR with refining on the (a) Valley beater, (b) PFI, and (c) Disc refiner pilot.

The effect of the different refining mechanisms operating in the Valley beater, PFI, and disc pilot refiners was again assessed by the changes in fiber length and fines content of the treated pulp. A milder fiber cutting effect was observed for the PFI and disc refiners, as seen in Figure 45 compared to the Valley beater. The severity of the refining mechanism in the Valley beater was also apparent in the evolution of the fines generated with refining, as evidenced by the steeper slope compared to that of the PFI and disc refiners. Although the refining mechanism of the disc and Valley beater are relatively similar, with refining action occurring at bar edges, unlike the PFI where the refining action occurs between the rotor bar and the smooth surface of the housing chamber, we observed more similarity in fiber development between the PFI and disc refiner instead. This could be attributed to the refiner design and refining conditions, particularly the refining consistency. The pulp consistency in the Valley beater, disc refiner, and PFI were 2%, 3%, and 10%, respectively.

The effect of the refining mechanism on the WR and fiber length of the pulp refined with the Valley beater, PFI, and disc pilot was further illustrated by plotting the WRV and fiber length against the drainage resistance ($^{\circ}$ SR) (Figure 46). The fiber shortening effect of the Valley beater and the corresponding gain in WRV was visualized. Suffice to say that the PFI and disc refiner produced a gentle treatment of the fibers, while the Valley beater imposed a harsh treatment on the fibers.

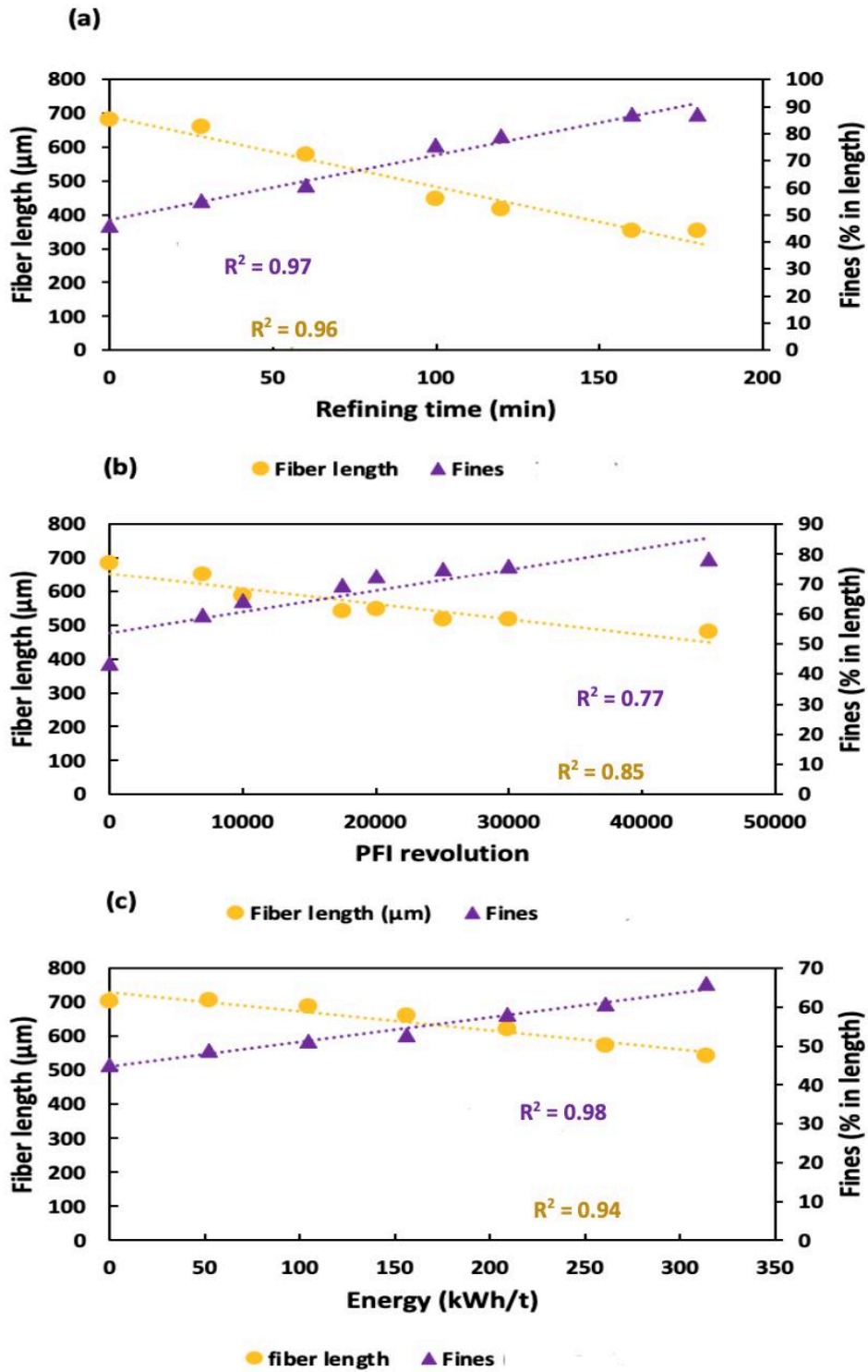


Figure 45. Evolution of fiber length and fines content (% in length) with refining on the (a) Valley beater, (b) PFI, and (c) disc refiner pilot.

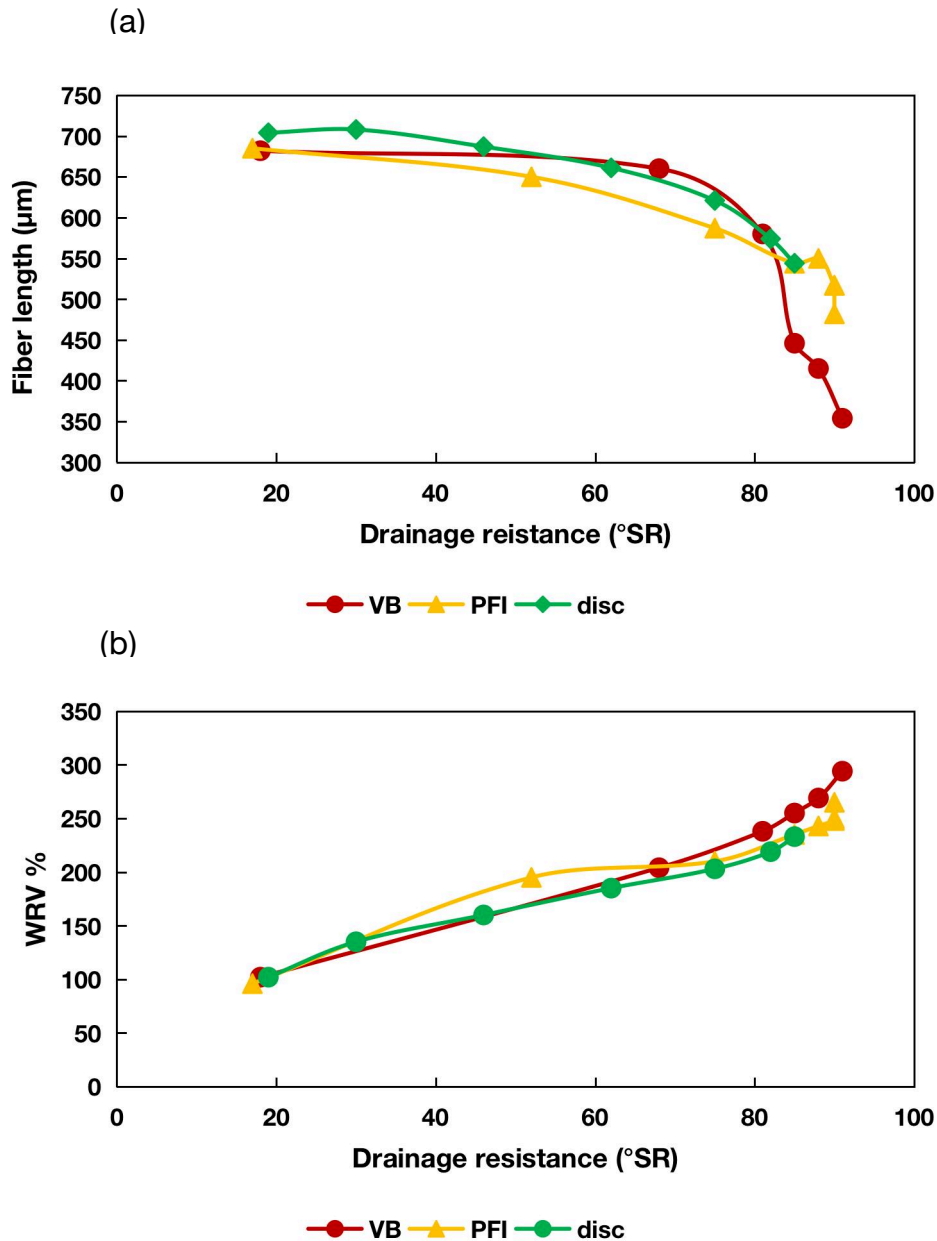


Figure 46. Evolution of fiber length (a) and WRV (b) as a function of drainage resistance ($^{\circ}\text{SR}$) on the Valley beater (VB), PFI, and disc refiner pilot.

The SEM images of the unrefined pulp, Valley beater, PFI, and disc pilot are shown in Figure 47. Comparing the images of the unrefined pulp with the refined pulp, a remarkable difference in the fiber morphology can be visualized. These images validate the data obtained in Figures 44 - 46. External fibrillation of the refined pulp was apparent for all three technologies, but it was more pronounced in the Valley beater and PFI refiners. The Valley beater refined fibers looked like the fibrillated fibers were surrounded by fibrillated fines (aggregated by drying). In

contrast, the fibrillated fibers seen in the PFI and disc refined pulp possessed less fibrillated fines.

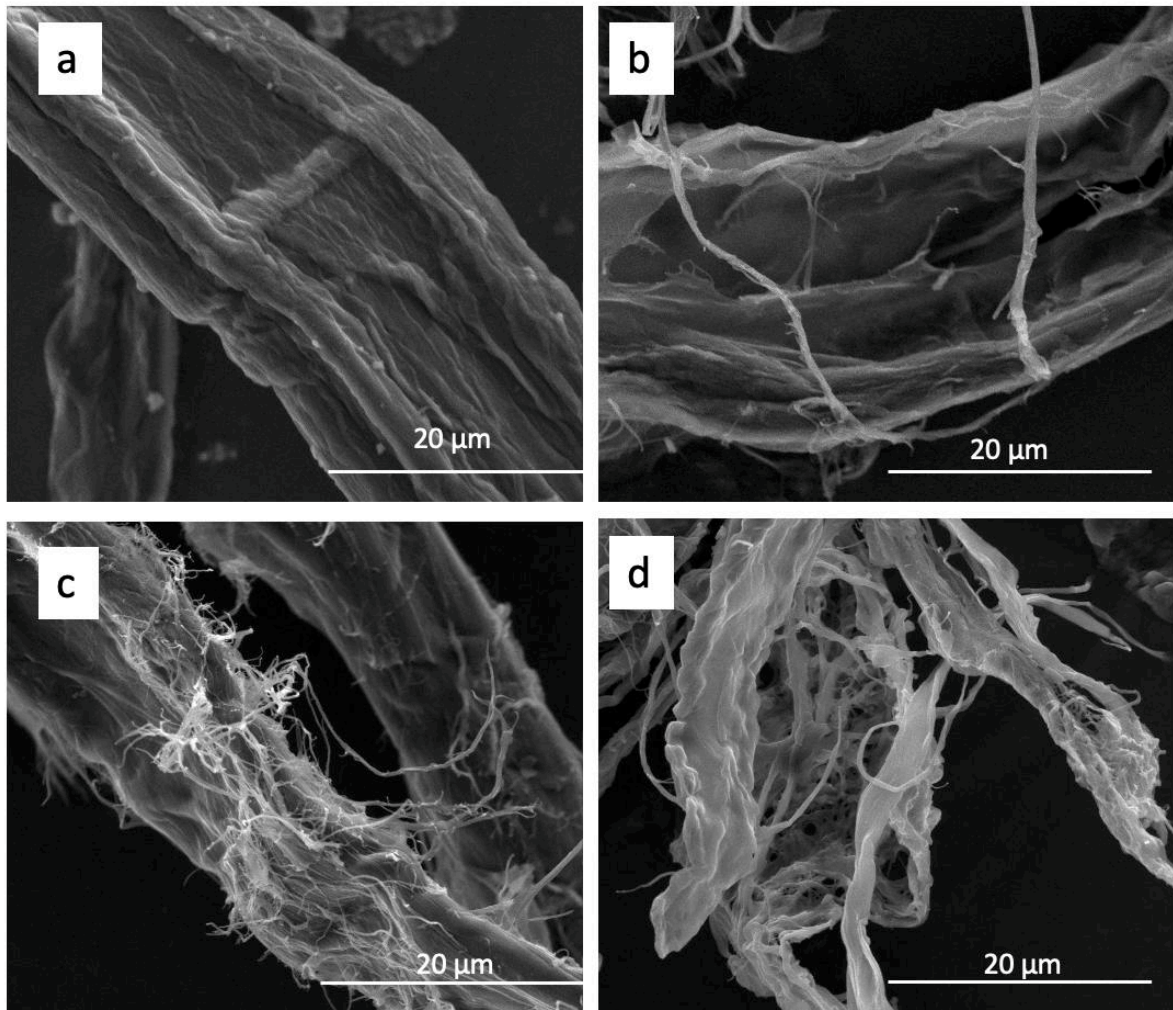


Figure 47. SEM images of pulp samples depending on refining technology. (a) Unrefined pulp (b) disc refined pulp (c) PFI refined pulp (d) Valley beater refined pulp (the pulps were refined to SR° 85).

A summary of the fiber properties of the unrefined pulp, PFI, Valley beater, and disc refined pulp at a given °SR value (85) is shown in Table 6. The variation in fiber length, WRV, and SSA with refining technology was evident. The following section will be assessing how the different changes in fiber morphology imposed by the refining technology influence xylan extraction performance.

Table 6. Structural properties of unrefined and refined pulps at 85°SR.

Refining technology	Valley beater	PFI	Disc pilot	Unrefined pulp
Fiber length (µm)	430	544	544	685
WRV %	268	237	233	103
SSA (m ² /g)	1.3	1.0	0.6	0.3

2.4.2. Comparing the influence of refining technology on xylan extraction performance by CCE

Studies of the cold caustic extraction carried out on the unrefined pulp, and refined pulp are presented in Figure 48. A correspondence between the fiber morphology induced by the different refining technologies is evident in their response to the alkaline extraction treatment. The best results were obtained at a soda concentration of 100 g/L for all pulps, with the Valley beater ahead with a xylan removal degree of 84%, followed by the PFI and disk pilot at 82% and 79%, respectively. However, the difference in performance between laboratory and pilot refiners was not significant enough to pose a challenge to upscaling. Interestingly, close to 50% residual xylan were removed when the soda concentration was increased from 60 to 100 g/L in refined pulp against only 20% for unrefined pulp.

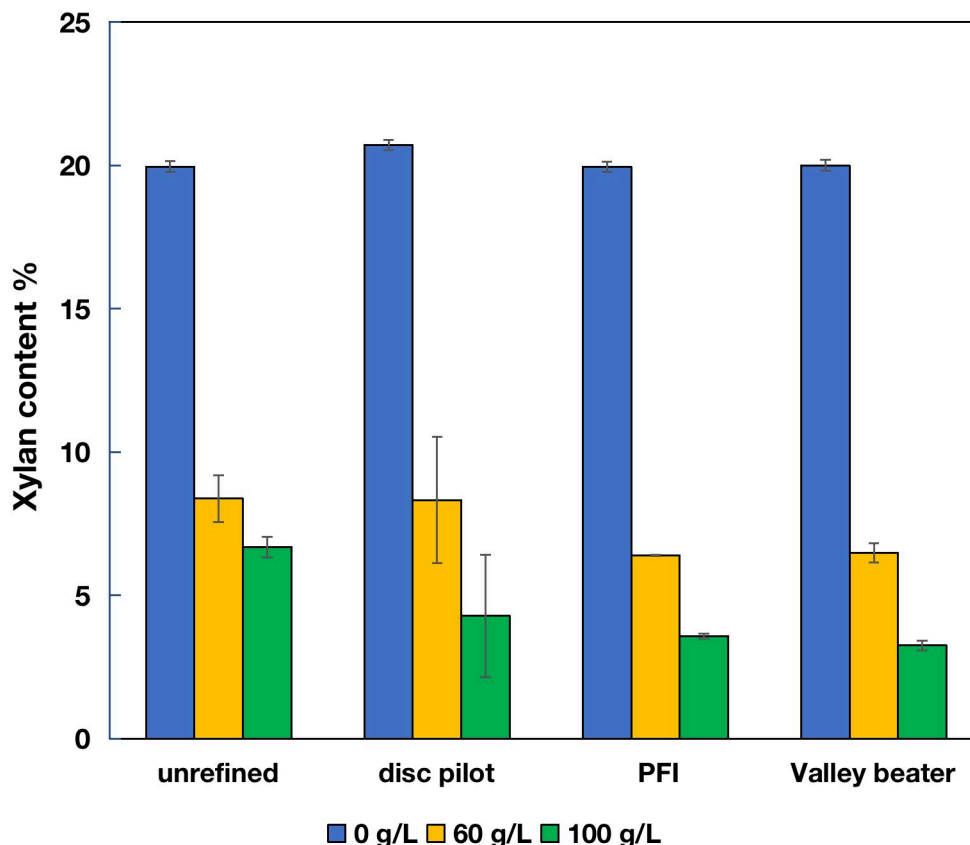


Figure 48. Performance of CCE at various soda concentrations on refined with different technology.

2.4.3. Influence of treatment on molecular weight

The molecular weight distribution profile of unrefined and refined pulps extracted at 100 g/L NaOH is shown in Figure 49. Evidence of xylan removal is seen in the substantial decrease of the low molecular weight peak from the reference pulp (without refining or extraction) to the extracted unrefined and refined pulps. The result shows that coupling refining with soda extraction at 10% produces pulp with narrow molecular distribution irrespective of the technology applied. Looking at the statistical values of the molecular weight distribution of the extracted pulps (Table 7), it can be seen that the PDI of the Valley beater refined pulp was higher than the other technologies. Considering that the PDI should be as low as possible in dissolving pulp, it appears that based on the PDI values, the conditions used on the Valley beater refined pulp extracted with 10% NaOH were not the best. However, comparing the PDI for Valley Beater (VB-10CCE) and some

values in the literature (Sixta, 2008b) obtained for Harwood sulfite-CCE (PDI; 6.5), VB-10CCE appeared to be better.

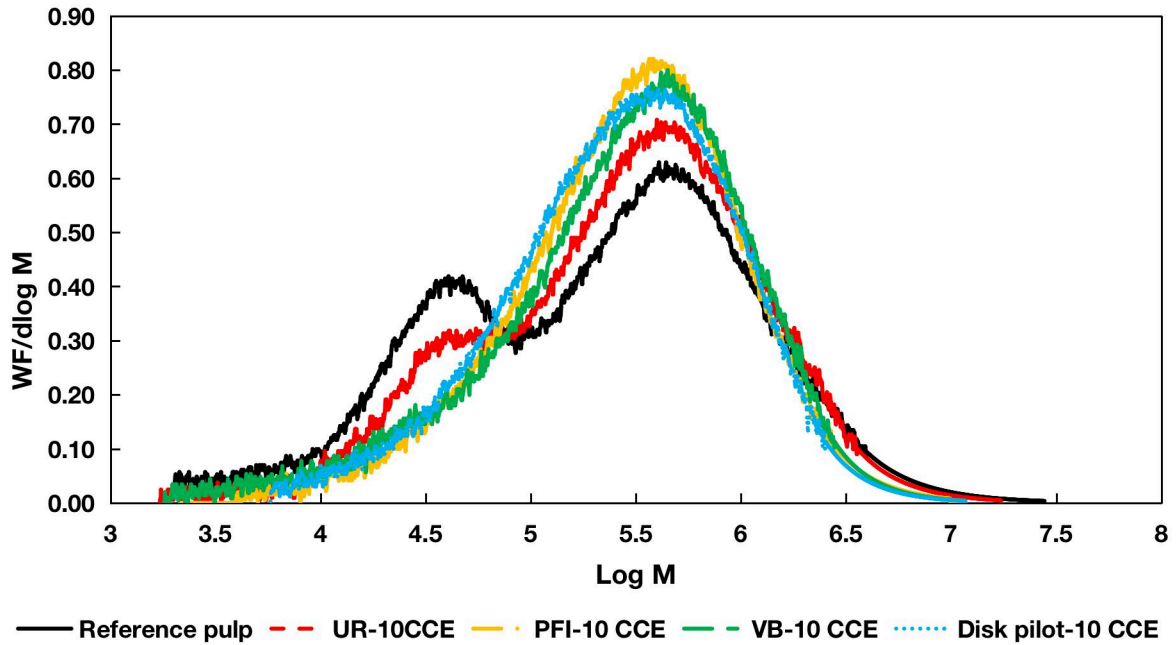


Figure 49. Molecular weight distribution of reference pulp, unrefined pulp extracted at 10% soda (UR-10CCE), PFI refined pulp extracted at 10% soda (PFI-10CCE), Valley beater refined pulp extracted at 10% soda (VB-10CCE), disk pilot refined pulp extracted at 10% soda (Disk pilot-10CCE).

Table 7. Statistical representation of the molecular weight of extracted unrefined and refined pulps.

Samples	DPw	DPn	PDI	xylan content
UR-10 CCE	4194	873	4,8	6.7
PFI-10 CCE	3422	723	4,7	3.6
VB-10 CCE	3983	742	5,4	3.3
Disk 10CCE	3255	709	4,6	4.3

2.4.4. Comparing the influence of refining technology on xylan extraction performance by xylanase treatment

Enzymatic extraction of hemicellulose has been reported and favored because of the reaction specificity and benign environmental impact. It is known that residual xylan in hardwood pulp after bleaching becomes less accessible to enzymatic hydrolysis compared to xylan in the unbleached pulp. This was attributed to the chemical modification of the xylan backbone (cleavage of the methylglucouronic acid) and the perhaps lack of easily accessible xylan on the fiber surfaces (Gübitz et al., 1997; Schild & Sixta, 2011). In Figure 50, the unrefined pulp was treated at various xylanase dosages ranging from 0 U/g to 500 U/g to determine the optimum enzyme concentration required to hydrolyze the residual xylan in the pulp. A reduction in the initial xylan content of the pulp was observed with xylanase treatment (especially at a dosage of 50 U/g), and further increase in the enzyme dosage slightly improved the xylan removal. The best result was obtained at a xylan dosage of 500 U/g with about 25% of the initial xylan content release. Surprisingly, the performance of the xylanase treatment alone in unrefined pulp was lower than values reported in the literature (Hutterer et al., 2017; Köpcke, 2008; Zhao et al., 2017). The plausible explanation for the poor performance of the xylanase treatment might be the hornification effects associated with the process history (the pulp was supplied as dried sheets).

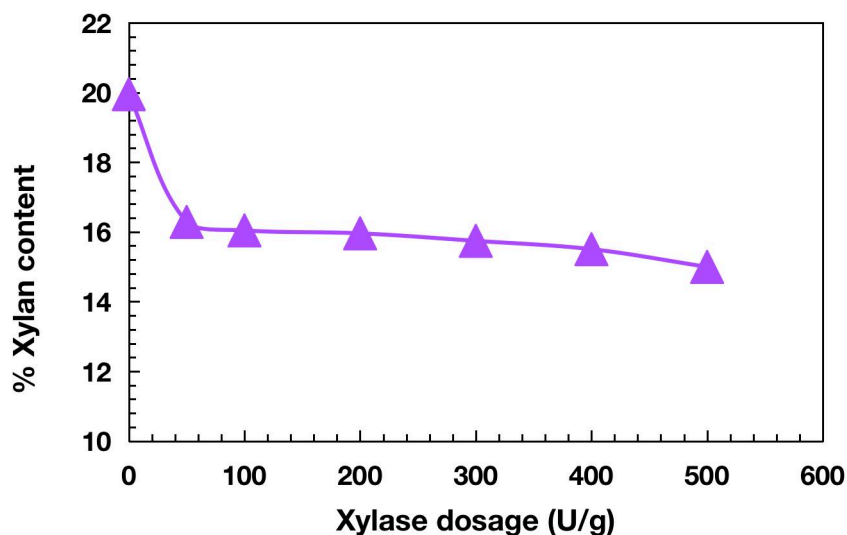


Figure 50. Xylan content of unrefined pulp after xylanase treatment at various dosage 50, 100, 200, 300, 400 and 500 U/g performed at 50 °C, pH 6.

According to the literature, pulp accessibility to xylanase can be improved by (i) the treatment with endoglucanase, which induced random chain scission prior to xylanase treatment (Hutterer et al., 2017) or simultaneously with the xylanase (Gübitz et al., 1997) (ii) applying mechanical refining before xylanase treatment (Zhao et al., 2017). In the present study, mechanical refining was explored as a means of increasing the accessibility of the pulp to xylanase, and the performance of the xylanase treatment on unrefined pulp and refined pulp is shown in Figure 51. The pulp was treated with xylanase at various concentrations ranging from 0 U/g to 500 U/g dry pulp. The effect of the refining technology was considered, and the results showed that refined pulp responded better to xylanase treatment than unrefined pulp, especially when the pulp was refined by the Valley beater. The maximum xylan removal degree (38%) achieved by the xylanase treatment was obtained with the valley beater at 500 U/g. The improvement in xylan removal with refining is indicative of the structural changes associated with refining that ultimately increase accessibility, as shown in Table 7. Even with mechanical refining, xylan hydrolysis by xylanase was generally much lower than that brought about by alkaline treatment. The probable cause of the poor performance of the xylanase treatment are (i) insufficient enzymes to pulp ratio, which might be overcome by increasing the enzyme dosage. (ii) insufficient enzyme activity to the substrate (wood pulp) relating to the xylanase type or source (Christov et al., 1996; Gübitz et al., 1997) and (iii) still insufficient accessibility because of the much larger size of enzyme molecules compared to NaOH. (iv) the saturation of the hydrolysis products in the reaction medium (Dhiman et al., 2008; Hutterer et al., 2017). Besides, (X. Chen et al., 2013) studied the effect of PFI milling on the enzymatic digestibility of corn stover. The authors reported that although a modification of the fiber morphology occurred with increasing refining action, the enzymatic hydrolysis decreased from 77% to 70% when the refining revolution was increased from 8000 to 10000. They attributed the loss of enzymatic activity to the collapse of macropores with increased refining. In summary, unlike the alkaline extraction, several factors could interfere with the performance of hemicellulose degrading enzymes and so we must take this into account.

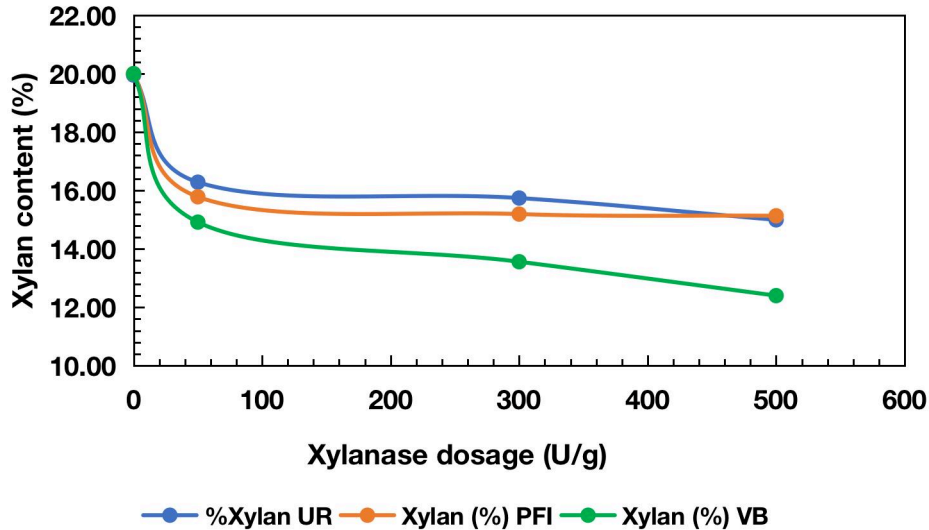


Figure 51. Performance of xylan removal with xylanase treatment for unrefined pulp, valley beater, and PFI refined pulp.

2.4.5. Conclusions

Upgrading paper pulp to dissolving pulp grade was performed by coupling refining with cold caustic extraction, and mechanical refining with xylanase treatment. Mechanical refining, a crucial pretreatment step that produces fibers with structural changes beneficial for the penetration and accessibility of chemical or enzymatic agents, was carried out on both laboratory refiners (Valley beater, PFI mill) and an industrial-like refiner (disc pilot). The effect of refining technology on the xylan extraction process was studied. The Valley beater refining mechanism was found to produce structural changes that increased WRV, external fibrillation, and increased surface area, leading to better xylan removal than PFI and disc refiner.

The best condition for xylan removal for all the refining technologies (Valley beater, PFI and disc-pilot refiners) investigated was achieved when the refined pulp was extracted with 10% NaOH resulting in 84%, 82% and 79% xylan removal respectively. This corresponds to 3.3%, 3.6% and 4.3% residual xylan in the extracted pulp from 20% in the reference pulp. In terms of upscaling, it was determined that though the laboratory refiners performed better than the industrial-like refiner, the difference was marginal. Therefore, the risks associated with upscaling would be minimal in this process.

2.5. Comparing refining and cellulase pretreatment for the removal of hemicellulose by cold caustic extraction

The complex structural organization of the cellulose chains, limits the accessibility of the chemical agents or enzymes to the reaction sites and hinders the diffusion of solubilized hemicellulose molecules from the interior to the exterior regions of the fiber wall. To mitigate the problems associated with poor accessibility of pulp, a modification of the fiber morphology was proposed. Refining was investigated in the previous sections. The observed improvement was linked to strong modifications of the properties of the fibers like length, width, specific surface area, pore volume and diameter, water retention value, fines content, and fibrillation. On the other hand, cellulase pretreatment of pulp affects the cellulose chains (visualized by the decrease in DP) which allows the cellulosic network to relax and thus improve the accessibility of hemicelluloses. Few studies have focused on this subject ([Hutterer et al., 2017](#); [J. Li et al., 2018](#)). On the other hand, it has been established that treatment with cellulases promotes the functionalization of cellulose such as the formation of xanthate, the first step of the viscose process and dissolution in NaOH/ ZnO ([Duan et al., 2017](#); [Gehmayr et al., 2011](#); [Grönqvist et al., 2014](#); [Ibarra et al., 2010](#); [Köpcke, 2010](#); [Köpeke et al., 2008](#); [H. Li et al., 2018](#); [Miao et al., 2014](#)). This is attributed to the generation of pores within the fiber walls brought about by the random enzymatic hydrolysis process.-

This study investigates the effect of cellulase treatment on fiber and cellulose properties. Also, the hemicellulose extraction performance of cellulase treated pulp was assessed and compared to that of the mechanical treated pulp.

2.5.1. Fiber properties modification by cellulase treatment

In the present study, endoglucanase (cellulase from Megazyme), which enables random cleavage of cellulose chains generating new reducing ends, was employed. Investigations into the presence of exoglucanase and glucosidases activities were not carried out. To determine the appropriate enzyme dosage to apply, the effect of various dosages on the pulp characteristics was studied.

Table 8 presents the fiber characteristic of pulp treated with cellulase at various dosages. The data shows that, at the different cellulase dosages studied from 10 U/g to 250 U/g, no change in fiber length, fiber width, or WRV occurred. This observation does not necessarily mean that enzymatic hydrolysis did not take place, but it showed that the physical, structural modification, or changes occurring during the hydrolysis were probably marginal and outside the range of the measurement employed. Indeed, there are some contradictory reports on the effect of cellulase treatment on fiber morphology. Some studies report the appearance of a smoother surface after enzymatic hydrolysis with cellulase, along with an increase in the crystallinity index. In contrast, others report the presence of external fibrillation with cellulase treatment (Hutterer et al., 2017). A similar study (Grönqvist et al., 2014) reported a significant increase in total pore volume and accessible surface area of cellulase treated sulfite dissolving pulp. Likewise, in their study on bleached acid sulfite pulp, the authors observed an increase in WRV and specific surface area of the cellulase-treated pulp (J. Li et al., 2018). The variations in these reports regarding the effect of cellulase treatment on fiber morphology can be explained by the difference in the enzyme type, source, concentration, and most importantly, the pulp type (sulfite versus kraft) and process history.

Table 8. Fiber characteristic of cellulase treated pulp.

SAMPLES	Fiber length (mm)	fiber width (μm)	finer %	WRV %
Blank	0.71	19.4	39.8	105
10 U	0.70	19.4	39.3	104
25 U	0.70	19.5	38.6	104
50 U	0.68	19.2	41.4	106
100 U	0.70	19.6	40.7	102
150 U	0.71	19.8	38.7	104
250 U	0.70	19.4	39.8	105

2.5.2. Influence of cellulase treatment on degree of polymerization (DP_v)

Figure 52 shows the evolution of the pulps viscometric degree of polymerization (DP_v) with cellulase dosage. An increase in the enzyme dosage resulted in a decrease in the pulp viscosity, which is indicative of cellulase chain scission. This is true until a dosage of 50 U/g, after which further increase in

cellulase dosage results in a marginal decrease in DPv. This trend is common in most enzymatic treatments of pulp. It has been attributed to a saturation of the accessible active sites or the concentration of the hydrolysis product in the reaction medium. (Duan, Long, et al., 2015) reported that the adsorption of cellulase on the cellulose fiber was the limiting factor for enzymatic hydrolysis of cellulose since enzymes activity is linked to the available surface area.

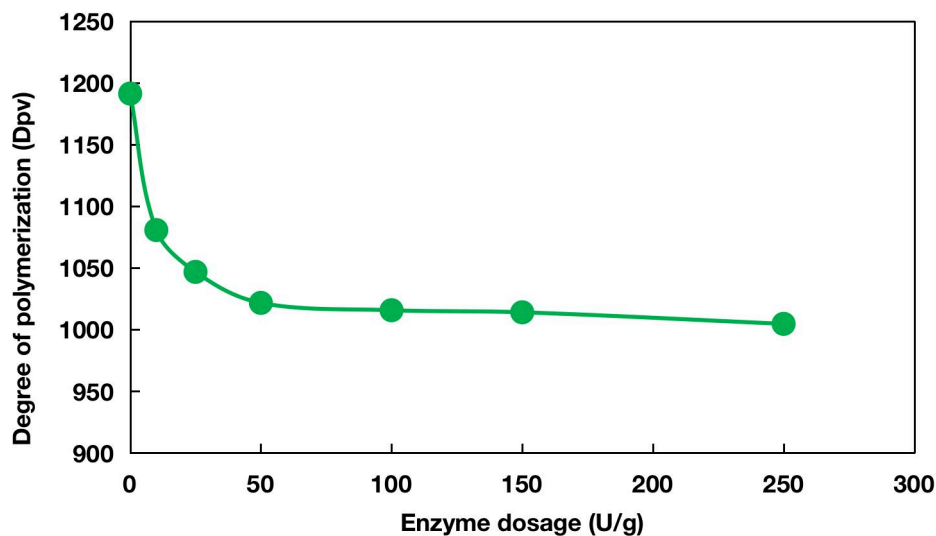


Figure 52. Evolution of DPv with cellulase dosage.

To compare the effect of enzymatic hydrolysis and mechanical refining on fiber morphology, cellulose hydrolysis performed at an enzyme dosage of 50 U/g was used. Figure 53 presents the impact of the pretreatment method on the DPv of bleached hardwood kraft pulp. As expected, the cellulase treated pulp experienced the most loss in DPv, followed by the Valley beater refined pulp and then the PFI refined pulp. The loss in viscosity is typical of cellulase treatment which occurred by the random cleavage of accessible glycosidic linkages within the cellulose chain. In the case of the mechanical treatment, there isn't a targeted attack of the glycosidic bonds; although fiber lengths are shortened, it does not necessarily reflect molecular chain scission. The latter can be seen only after extensive shortening of the fibers (Tian et al., 2014).

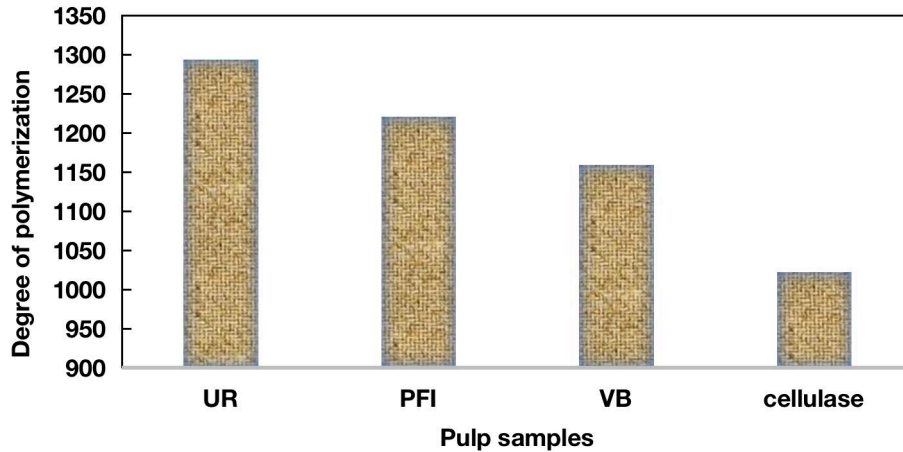


Figure 53. Influence of pretreatment method on degree of polymerization (DPv) (UR: Unrefined pulp, PFI: PFI refined (SR° 85), VB: Valley beater refined (SR° 85), cellulase: cellulase treated pulp (50 U/g pulp)).

The SEM images shows a clear distinction between the mechanical treated pulp and the cellulase treated pulp. Effects of refining, mainly external fibrillation, are apparent in the mechanically treated fibers compared to the unrefined and cellulase treated fibers. The image of cellulase-treated pulp (50 U/g) displayed in Figure 54(b) showed no external fibrillation on the fibers, and they appeared unchanged by the enzymatic treatment, unlike mechanical refined pulp. This observation does not explain the difference in DPv values of the pulp but correlates strongly to the fiber properties like WRV, fiber length, fines content, and SSA shown in Table 8.

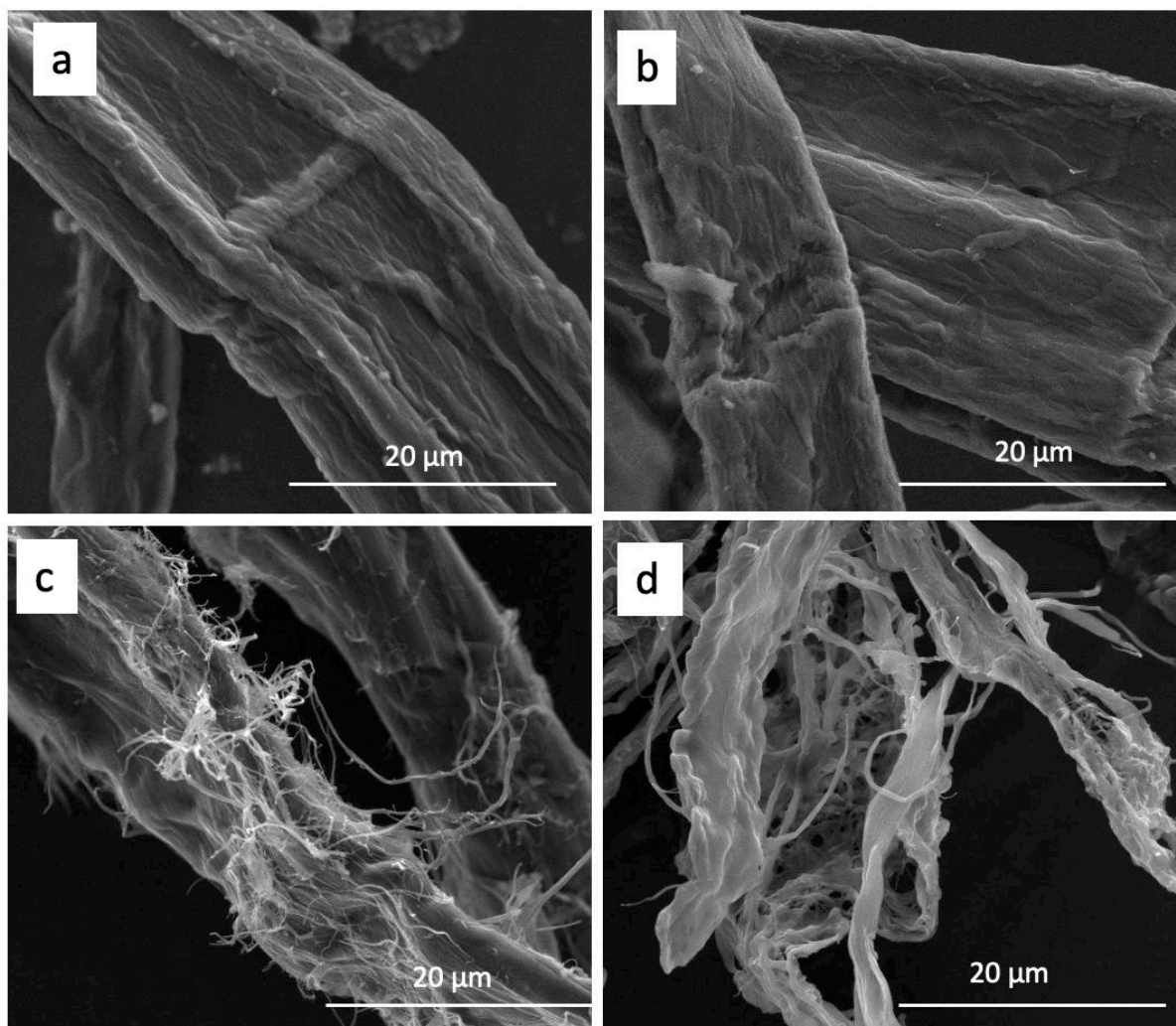


Figure 54. SEM images of pretreated pulp samples (a) Unrefined pulp (b) Cellulase treated pulp (50 U/g) (c) PFI refined pulp (d) Valley beater refined pulp.

2.5.3. Effect of pretreatment on residual xylan extraction from pulp

The result presented in Figure 55 shows the performance of alkaline xylan extraction on unrefined pulp, cellulase pretreated pulp, and mechanically pretreated pulp (with an initial xylan content of 20%) at soda concentrations of 60 g/L and 100 g/L. Even though pulp pretreated with cellulase improves alkaline xylan extraction compared to the untreated pulp, it was not as efficient as the mechanical pretreatment. This can be explained by the limited accessible surface area for the penetration of the alkali solution. Unlike the cellulase treatment, in mechanical refining of pulp, compression and shear forces disrupt the organization of the fiber wall by enlarging pores, delaminating the layers of fiber wall, creating new fiber ends (reaction site), and reducing the particle size, which enhances solvent

penetration that results to the solubilization of the residual xylan and its diffusion from the interior of the fiber wall to the exterior. However, the beneficial effect of cellulase, although modest, is interesting since it is obtained by a different mechanism based on the sole reduction of the DP of cellulose, causing the loosening of the cellulosic network and thus promoting the accessibility of the xylan. This effect should be amplified with a cocktail cellulases leading to greater drops in DP.

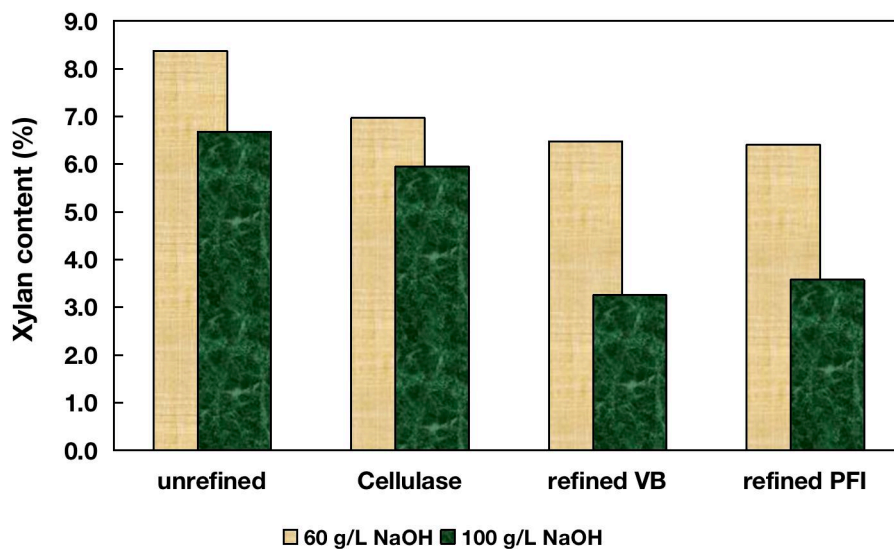


Figure 55. Xylan extraction performance of pretreated pulps.

2.5.4. Effect of pretreatment on the molecular weight of the extracted pulp

The pulp molecular weight distribution (MWD) profile before and after alkaline extraction is presented in Figure 56. When comparing the MWD of the reference pulp and the cellulase treated pulp before soda treatment, we first observe a shift towards the center from the higher molecular weight region; secondly, the hemicellulose (low weight fraction) remains unchanged, indicating the absence of any hemicellulase activity. Looking at the extracted pulp at a soda concentration of 100 g/L, a narrower MWD was obtained for the PFI and VB refined pulps with the elimination of the hemicellulose peak. In contrast, although narrow, the MWD obtained for the extracted cellulase treated pulp showed a significant portion of the low molecular weight fraction. This can be explained by the random chain scission/

hydrolysis of the high molecular weight fraction, resulting in shorter cellulose chains and the presence of a significant hemicellulose content compared to the PFI and VB treated pulps. Furthermore, a considerable decrease in DPw was recorded for the cellulase-treated pulp with a very low polydispersity index (Table 9) which is an advantage in the perspective of viscose production.

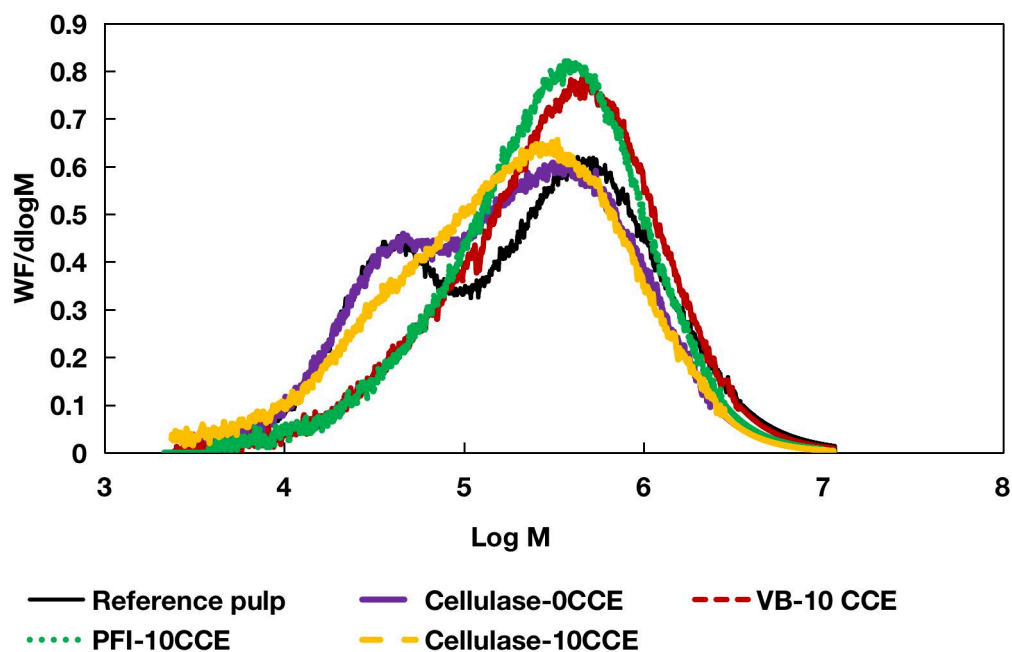


Figure 56. Molecular weight distribution profile of the reference pulp without alkaline extraction; cellulase treated pulp (50 U/g) without alkaline extraction (Cellulase-0CCE); Valley beater refined pulp followed by 10% alkaline extraction (VB-10CCE), PFI refined pulp followed by alkaline extraction at 10% (PFI-10CCE).

Table 9. statistical representation of molecular weight.

Samples	DPw	DPn	PDI
Reference	3900	442	8.8
Cellulase-0 CCE	2643	385	6.9
Cellulase-10 CCE	1635	1197	1.4
VB-10 CCE	3983	742	5.4
PFI-10 CCE	3422	723	4.7

2.5.5. Conclusions

The pretreatment of bleached hardwood kraft pulp by endoglucanase (cellulase from Megazyme) was conducted to assess its influence on alkaline xylan extraction. It was observed that there was no notable modification of the fiber morphology, especially the fiber length, WRV, fines content, but a significant decrease in DP_v was observed. On extraction of the cellulase pretreated pulp with soda concentrations of 6% and 10%, there was some improvement of the xylan removal performance. This better performance must be linked to the loosening of the cellulosic network due to the cleavage of cellulose chains, thus improving accessibility. This mechanism, although different from that observed with mechanical refining of the pulp, could complement each other when combined leading to improved accessibility. An additional advantage would be the drastic decrease in the polydispersity of the mass distribution of the cellulose molecules, which is said to be an important parameter in the viscose process.

Although the improvement in the extraction observed here with the cellulase pretreatment was relatively modest, we cannot exclude the fact that the use of cellulase cocktails which are more effective on the reduction of the DP might further improve the removal of the xylans.

Conclusions on chapter 2

This chapter explored the potential of mechanical refining as a vital pretreatment stage in upgrading paper pulp to dissolving pulp. The effect of refining technology (laboratory and industrial-like refiners) was investigated. The results showed that mechanical refining effectively induced beneficial structural changes on pulp, making it more susceptible to chemical and enzymatic treatments. Also, the potential of mild cellulase hydrolysis treatment (for increased accessibility) as an alternative to mechanical refining was investigated.

Three refining loads were tested for the Valley beater (3kg, 4.5 kg, and 5.5 kg), and the best result was obtained with a 4.5 kg load (with a WRV of 268%). Subsequent treatments were performed with pulp refined with a 4.5 kg load. About 50% more xylan was removed from the Valley beater refined pulp than unrefined pulp extracted at 100 g/L NaOH.

Similar xylan removal was obtained for PFI and Valley beater refined pulp treated at 60 and 100 g/L soda. The laboratory refiner performance to xylan removal by CCE was better than the disc pilot, especially at low soda concentration. At a soda concentration of 100 g/L, the xylan removal for the Valley beater, PFI, and disc pilot refined pulp were 84 %, 82 %, and 79%, respectively. Therefore, there is no significant risk for upscaling as the xylan removal degree between both scales was not too far apart. A good correlation between the residual xylan content in extracted pulp and the WRV of the pulp before the CCE treatment was obtained for pulp refined by disc pilot at 7.9kW net power.

Also, starting from a paper pulp containing 20% hemicelluloses (essentially xylans) it is possible to go down to 3% xylan, which qualifies the pulp for dissolving pulp applications. Xylanase activity increased in Valley refined pulp compared to PFI refined pulp with a xylan removal degree of 38% against 24% obtained for the PFI refined pulp.

The pretreatment with an endoglucanase, which has no effect on the morphology of the fibers unlike the refining, also provides a slight improvement in the extraction of xylans from the pulp by CCE. This is due to the significant drop in the DP of cellulose. The performance could certainly be improved by choosing an appropriate cellulase cocktail. This treatment could advantageously complement the refining

treatment, which would give the additional benefit of reducing the polydispersity of the cellulose.

Chapter 3: Study of new xylan extraction approaches involving simultaneous mechanical refining and cold caustic extraction/xylanase treatment; Fractionation of the fines from the refined pulp prior the xylan extraction

Overview of chapter

In the previous chapter, we discussed the conventional processes for hemicellulose extraction in upgrading paper pulp to dissolving pulp in the context of “the modified kraft process” (Gehmayer et al., 2011). The usefulness of mechanical refining as pretreatment was confirmed using laboratory (Valley beater, PFI mill) and industrial-like (disc pilot) refiners. In this chapter, some strategies to improve the efficiency of hemicellulose removal were investigated. The first strategy explored was the simultaneous refining-cold caustic extraction process inspired by the study of (Ibarra et al., 2009). They reported a slight decrease in the xylan content with stirring during the cold caustic extraction process, attributed to the homogenous mixing. Since mechanical refining could be considered a kind of rigorous mixing process involving compression and shear forces acting on fiber floc between the edge of bars at neutral pH, resulting in disruption and modification of the structural properties of the pulp fibers. Increasing the pH during refining would allow for the usual fiber modifications occurring parallel to rapid chemical penetration, leading to increased accessibility of chemicals to hard-to-reach regions of the fiber wall, ultimately improving the efficiency of xylan solubilization and extraction. This hypothesis was tested for cold caustic extraction on Valley beater and PFI refiners, whereas the xylanase treatment was tested on the PFI mill alone.

The second strategy investigated was the influence of fines fractionation of refined pulp on alkaline and enzymatic hemicellulose removal efficiency. It was based on the assumption that the mechanical refining treatment led to some sort of peeling of the fiber surface, which has a high concentration of hemicellulose due to reprecipitation during the kraft process (Sixta, 2008a). The stripped surface which concentrates in the fines could be fractionated and isolated, resulting in a reduction in the hemicellulose content. Also, the fines fractionation serves as a means of homogenizing the fiber size so that the hemicellulose extraction process can occur more evenly.

Finally, the effect of severe refining on the performance of CCE was also discussed.

3.1. A new approach to xylan extraction from paper pulp by implementing simultaneous mechanical refining with chemical or enzymatic treatment

The simultaneous refining-CCE was conducted on the Valley beater and PFI refiner at a soda concentration of 60 g/L. A refining load of 4.5 kg was used for the Valley beater for about 60 min while the PFI was run at 8750 revolutions for about 6 min. At the end of the treatment, the resulting pulp was washed until neutral pH before analysis. The refining time (Valley beater) and revolution (PFI) adopted for this study were half of what we used for the sequential treatment (chapter 2).

3.1.1. Performance of simultaneous Valley beater refining-CCE on residual xylan extraction

The result presented in Figure 57 shows 79.2% xylan removal for the simultaneous treatment against 68% obtained for the sequential refining and CCE treatment performed at the same soda concentration of 60 g/L. The higher efficiency of the simultaneous refining-CCE treatment could be attributed to the rigorous mixing effect achieved in the process. Since pulp swelling occurs instantaneously in a soda solution (Sixta, 2008b), the action of the refining actually takes place on a swollen substrate, which certainly amplifies its effects. It can therefore be assumed that more surfaces become accessible and that therefore the solubilization of the xylans from the pulp is increased.

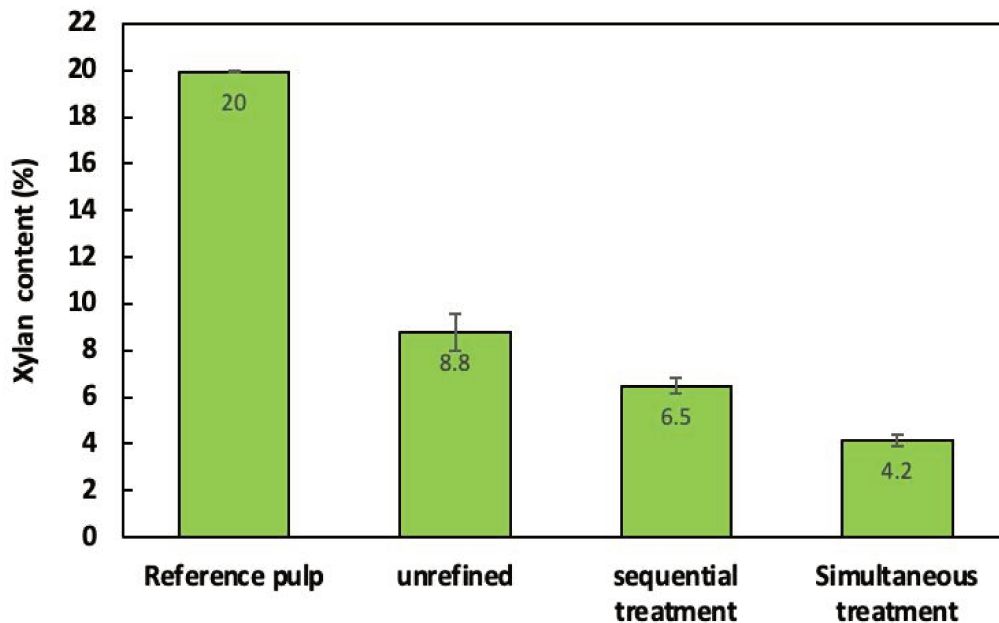


Figure 57. Performance of xylan removal with CCE at 60 g/L for unrefined pulp, sequential treatment (refining prior to CCE at 60 g/L), and simultaneous treatment (refining-CCE at 60 g/L), Reference pulp represents the starting pulp without any treatment (refining was carried out on the Valley beater at a pulp consistency of 2%).

In a study conducted by [\(Dinand et al., 2002\)](#), they reported that the impact of mercerization was more intense for individual fibrils than bundles which means that less xylan solubilization is expected from bundles. It is likely that less bundles survive during simultaneous treatment, which may be another way to explain the observed improvement.

Notably, the xylan removal degree achieved by the simultaneous treatment with 60 g/L NaOH was similar to results obtained for sequential treatment at a higher soda concentration (100 g/L), making it a more attractive process. The simultaneous treatment was carried out at low pulp consistency of 2% and refining time of 60 min unlike the sequential treatment where the CCE was done at 5% with a refining time of 120 min. Resulting in a lower refining energy consumption in the simultaneous treatment (273 kWh/t) compared to the sequential treatment (400 kWh/t). Besides, the spent lye can be recycled and reused for subsequent extractions [\(Gong et al., 2017\)](#).

When the study was carried out with the PFI mill, the performance of the simultaneous treatment was slightly lower than the sequential treatment as shown

in Figure 58. If we consider the influence of the pulp consistency and refining revolution used for the sequential and simultaneous treatments, (5%, 17500 rev) and (10%, 8750 rev) respectively, then we might most likely conclude that the simultaneous treatment was comparable if not better than the sequential CCE treatment. In order to reach an even lower xylan content in the simultaneous treatment, refining time and soda concentration might be increased to aid the process.

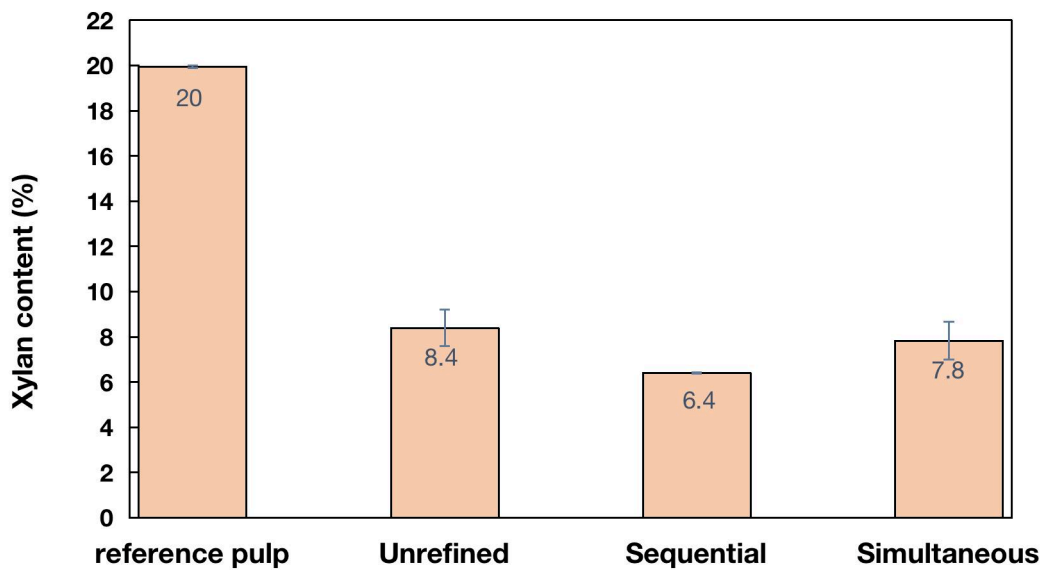


Figure 58. Performance of xylan removal with CCE at 60 g/L for unrefined pulp, sequential treatment (refining prior to CCE at 60 g/L), and simultaneous treatment (refining/CCE at 60 g/L), Reference pulp represents the starting pulp without any treatment (refining was carried out on the PFI mill at a pulp consistency of 10%).

Figure 59 compares the simultaneous treatment performances for the refining equipment used. The treatment in the Valley Beater fared better than the PFI mill. This was reasonable as the operating conditions in the Valley beater allowed for a more rigorous mixing. Apart from the effect of the refining time which is usually longer in the Valley beater compared to the PFI mill, the influence of the pulp consistency during the treatment (2% and 10% respectively) was probably a major factor accounting for the result obtained.

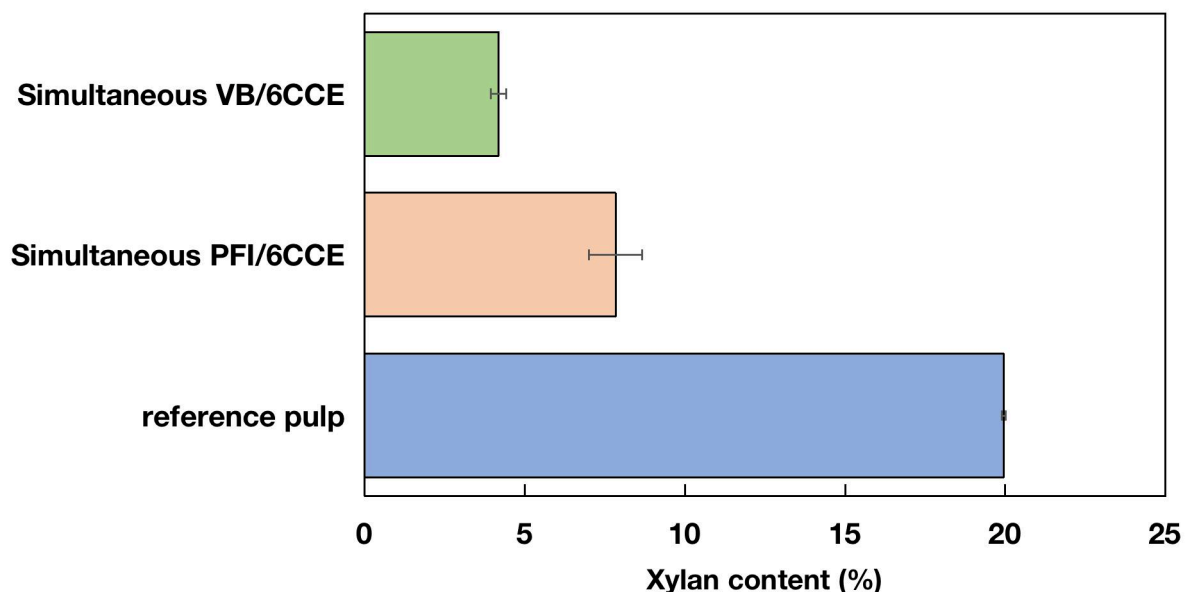


Figure 59. Comparison of Performance of xylan removal for simultaneous treatment (refining-CCE at 60 g/L), carried out on the Valley beater (VB) and PFI refiners (Reference pulp represents the starting pulp without any treatment); 6CCE represents 60 g/L NaOH cold caustic extraction).

The effect of applying a xylanase step (500 U / g) on the pulp processed by simultaneous refining/CCE and by sequential refining-CCE is shown in Figure 60. The result showed that in both refining technologies (PFI and Valley beater), the xylanase treatment gave better results on the pulp treated simultaneously than on the pulp treated sequentially. From the data presented in Figure 60, the Valley beater treated pulp resulted in xylan removal of 72% for the sequential treatment and 84% for the simultaneous treatment. Whereas the PFI mill produced 73% xylan removal for sequential treatment and 79% for simultaneous treatment.

These results are easy to explain if, as already mentioned, the simultaneous treatment increases the refining effects such as delamination, fibrillation, etc. because of the swelling of the cellulose structure and thus leads to better accessibility of the hemicelluloses. The action of the enzymes being particularly dependent on the accessibility, the latter are found in a more favorable situation to hydrolyze the xylans which are still present in the fibers (because of their high molecular weight or low content in COOH groups).

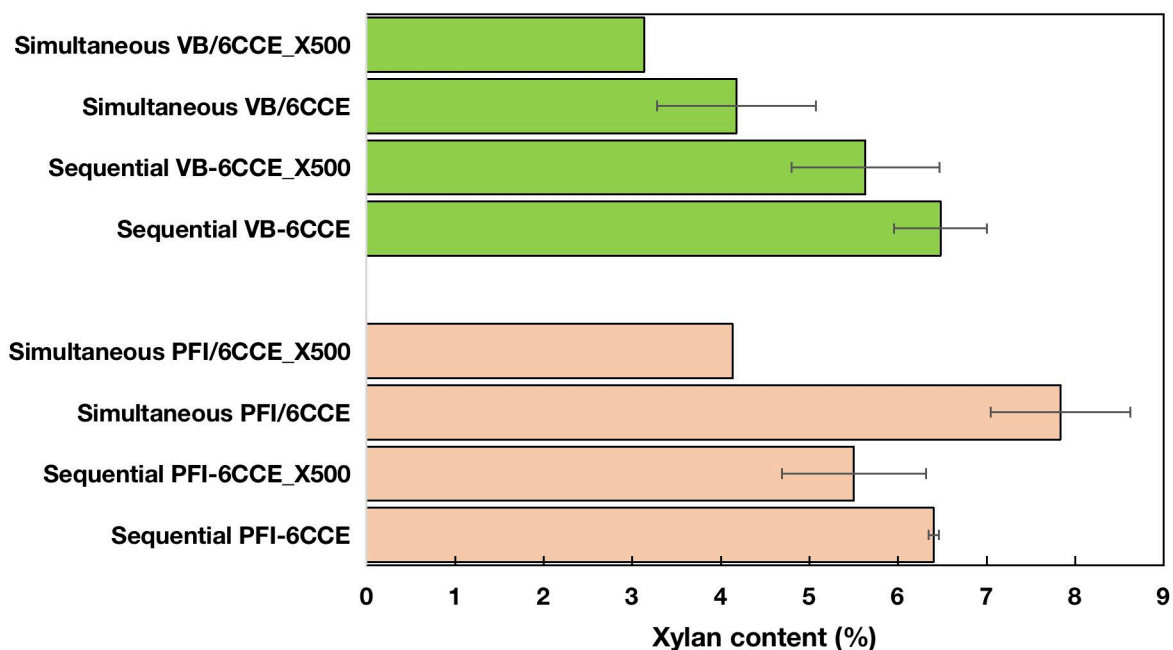


Figure 60. Comparison of Performance of xylan removal with CCE at 60 g/L for sequential treatment (refining prior to CCE at 60 g/L followed by a sequential xylanase treatment), and simultaneous treatment (refining/CCE at 60 g/L followed by a sequential xylanase treatment), carried out on the Valley beater and PFI refiners; (X500 represents xylanase dosage of 500 U/g odp, 6CCE represents 60 g/L NaOH cold caustic extraction).

3.1.2. Effect of simultaneous refining-xylanase treatment on subsequent alkaline extraction of residual xylan.

Based on the positive outcome of the simultaneous refining-CCE described in the previous section, a similar process was carried out for xylanase treatment. The refining process was performed in the presence of xylanase at a dosage of 50 U/g dry pulp at pH 6 on the PFI refiner. From the result presented in Figure 61, it can be seen that when refining was performed simultaneously with xylanase treatment, fewer xylan hydrolysis occurred than when the refining and xylanase treatment were carried out sequentially. The poor enzyme activity observed with the simultaneous treatment is rather intriguing. In fact, It was interesting to show that in itself a gentle mixing (250 rpm with a magnetic stirrer), unlike the vigorous mixing brought about by the refining action, had a positive effect on the xylanase treatment. This is shown in Figure 62. The xylanase activity, represented by the residual xylan content in the pulp after the xylanase hydrolysis, was measured for unrefined pulp,

PFI refined pulp, and Valley beater refined pulp at a dosage of 50 U/g. The treatment carried out with continuous agitation in a controlled temperature reactor performed always better than the same experiment conducted in a plastic bag with hand mixing, thus showing that the mixing action of a refiner should be positive, which was apparently not the case.

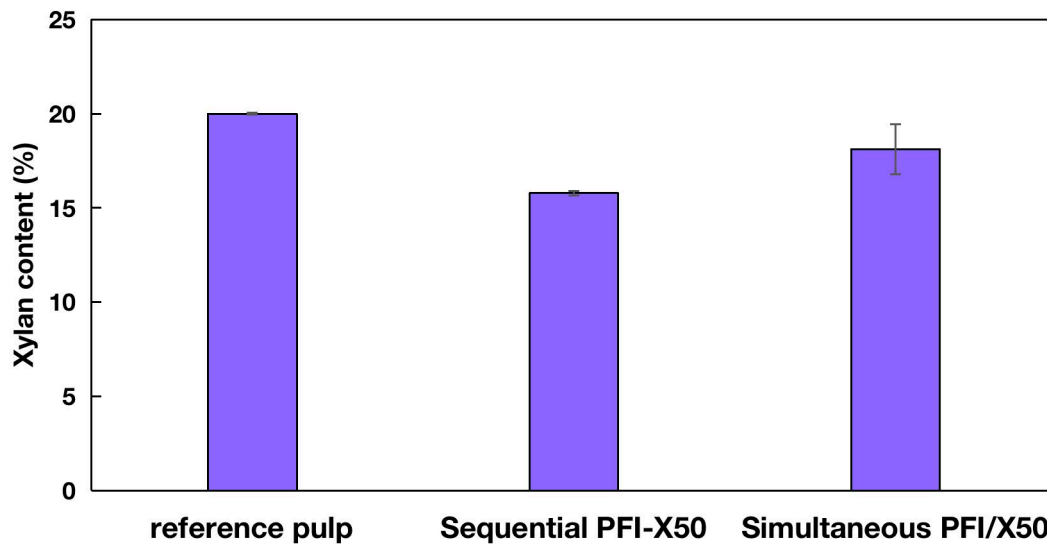


Figure 61. The effect of Sequential PFI refining-xylanase treatment and simultaneous PFI refining/xylanase treatment on the residual xylan removal performance (X50 represents xylanase dosage of 50 U/g).

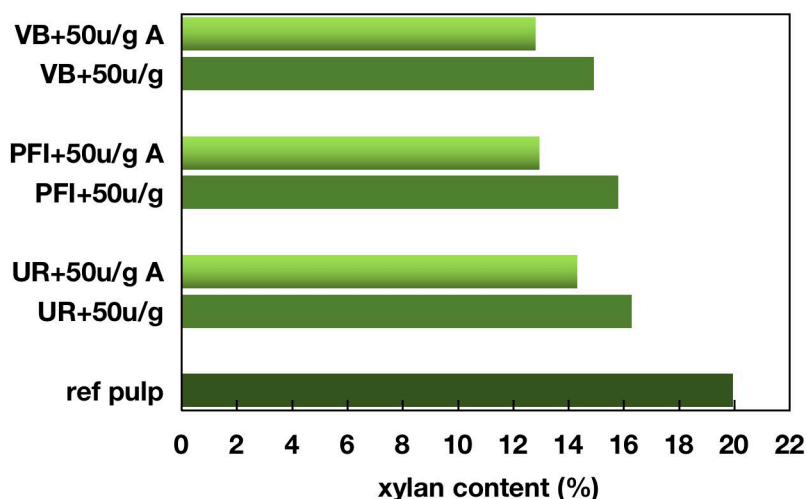


Figure 62. Effect of constant agitation on the performance of xylanase treatment of pulp. VB+50u/g: Valley beater refined pulp with xylanase dosage of 50 U/g of dry pulp; VB+50u/g A: Valley beater refined pulp with xylanase dosage of 50 U/g of dry pulp agitated at 250 rpm; PFI+50u/g: PFI refined pulp with xylanase dosage of 50 U/g of dry pulp; PFI+50u/g A: PFI refined pulp with xylanase dosage of 50 U/g of dry pulp agitated at 250 rpm; UR+50u/g: Unrefined pulp with xylanase dosage of 50 U/g of dry pulp; UR+50u/g: Unrefined pulp with xylanase dosage of 50 U/g of dry pulp agitated at 250 rpm.

The apparent negative effect of performing the xylanase treatment at the same time as the refining could be attributed to the fragile nature of enzymes. Most enzymes are known to be sensitive to their reaction conditions and environment. Several explanations may then be given: the vigorous mixing could (1) local increase in the temperature prevent enzymes from attaching to the active site (2) or harm done to the enzyme molecules under the effect of compression and shear forces (3). We cannot confirm that any of these effects does occur.

However, the removal of xylan might not be the right way to measure the activity of the enzyme. In fact, it is plausible that hydrolysis takes place but not sufficient to solubilize the residual xylan in the acidic environment of the treatment. More particularly, under refining conditions, more xylan chains become accessible and at the same time the homogeneity of the enzyme treatment is increased because of the vigorous agitation, thus reducing the number of hydrolysis sites per molecule of accessible xylan. This hypothesis would explain the very interesting results obtained when cold caustic extraction was performed after simultaneous refining/xylanase treatment (Figure 63). On performing the cold caustic extraction at

60 g/L on the xylanase treated pulp, it was observed that sequential and simultaneous treatments gave very close results, with 3.9% and 4.3% residual xylan left in the pulp after the CCE treatment respectively, difference which can easily be explained by the difference in enzyme charge. When the soda concentration of the CCE process was further increased to 100 g/L, more xylan molecules were solubilized in the case of simultaneous treatment giving rise to a higher purity pulp (less than 2% residual xylan) despite the lower enzyme charge. From the data obtained in this study, it is clear that coupling refining, enzymatic, and CCE either simultaneously or sequential yielded high purity pulp (less than 5%) at a lower than usual soda concentration of 6%, against the conventional extraction performed at 10%. We will see in a next chapter that this reduction in NaOH concentration will limit the formation of cellulose II.

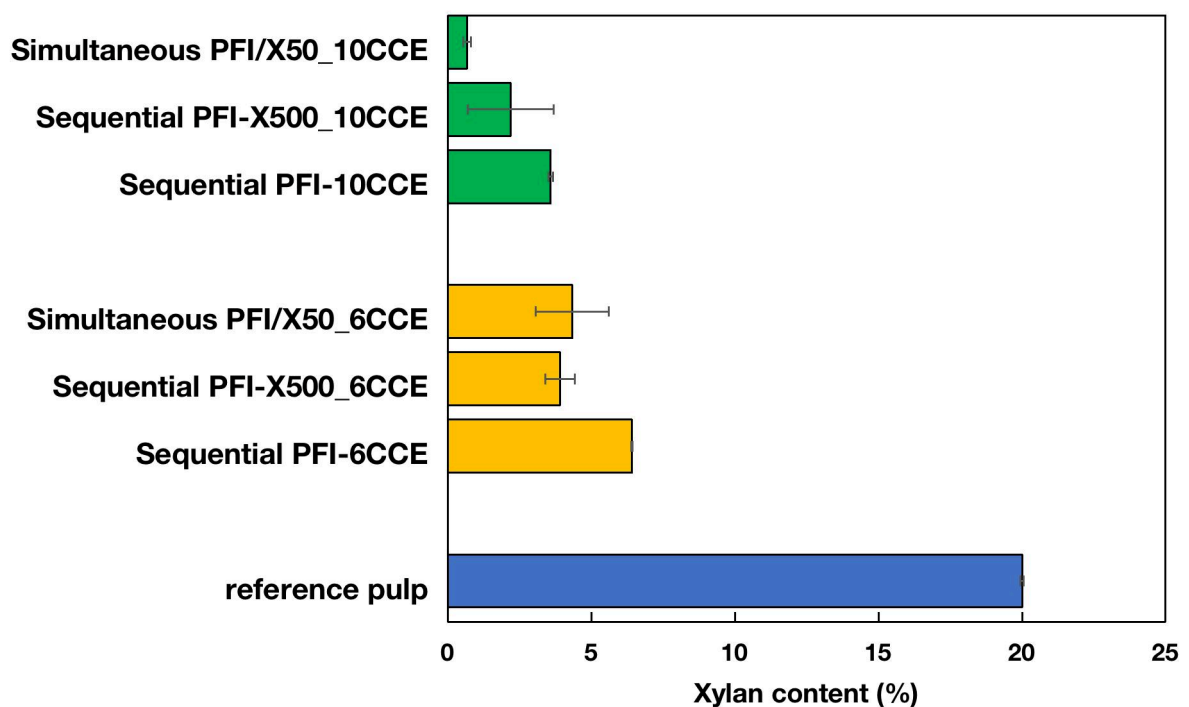


Figure 63. The effect of sequential PFI refining-xylanase treatment and simultaneous PFI refining/xylanase followed by a CCE treatment on the residual xylan removal performance (X500 represents xylanase dosage of 500 U/g odp, X50 represents xylanase dosage of 50 U/g odp, 6CCE represents 60 g/L NaOH cold caustic extraction, 10CCE represents 100 g/L NaOH cold caustic extraction).

3.1.3. Molar mass distribution of pulp samples

Changes in molecular weight distribution brought about by various pulp treatments and the corresponding polydispersity index (PDI) can be visualized in Figure 64 and Table 10. As seen previously, the bimodal distribution depicted by the reference pulp shows two peaks, the low peak representing the short-chain polymer (hemicellulose) while the high peak long-chain polymer (cellulose). All the treatments applied yielded pulp with a unimodal MWD, particularly for the simultaneous Valley beater refined/CCE pulp (Simultaneous VB/6CCE). The unimodal MWD indicated that a bulk of the short-chain polymers had been removed. Slightly more short-chain macromolecules can be seen in the low peak region for (Simultaneous PFI/6CCE) and (Simultaneous PFI/X-50_6CCE) samples compared to (Simultaneous VB/6CCE), which is in accordance with the measured residual xylan. In parallel, the PDI values decreased with the removal of xylans (Table 10). For the (Simultaneous VB/6CCE), a shift of the MWD toward the center was observed, which could be explained by a slight degradation of the fragile cellulose chains (shift from the high molecular weight to the center) and the removal of the short-chain component of the pulp (shift from the low molecular weight to the center), explaining the lower PDI. The MWD obtained for the (Simultaneous VB/6CCE) sample best satisfy the requirement for dissolving pulp grade.

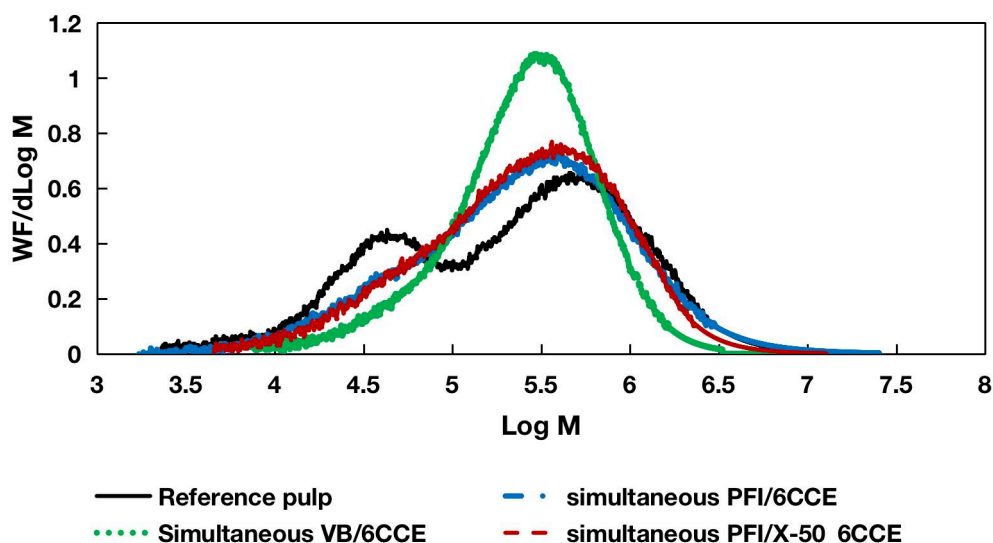


Figure 64. Molecular weight distribution profile of pulp (Simultaneous refining and CCE at 60 g/L on the PFI; Simultaneous PFI/6CCE); Simultaneous refining and CCE at 60 g/L on the Valley beater (Simultaneous VB/6CCE); simultaneous refining-xylanase treatment at a dosage of 50 U/g pulp followed by a CCE at 60 g/L (Simultaneous PFI/X50_6CCE).

Table 10. Statistical representation of the molecular weight of the pulp.

Samples	DP _w	DP _n	PDI
Reference	3900	442	8.8
Simultaneous VB/6CCE	2706	883	3.1
Simultaneous PFI/6CCE	2976	613	4.9
Simultaneous PFI/X50_6CCE	3618	555	6.5

3.1.4. The influence of severe refining to enhance the removal of residual xylan from paper pulp

In chapter 2 the effect of refining prior to Cold Caustic Extraction or xylanase treatment was investigated. The refining conditions were varied but stayed in an industrially realistic range of values. The beneficial effect of refining was attributed to the liberation of new cellulosic surfaces containing xylan molecules. Despite that there were still some unextractable xylans left after treatment. To clarify whether the fiber deconstruction potential of refining was fully met or whether some other reasons for the incomplete removal of xylans had to be invoked (like chemical bonding to some fiber components such as lignin fragments or even cellulose) the

effect of more severe refining (SR° higher than 85) on fiber morphology and the corresponding impact on the xylan extraction by the CCE was studied. To achieve this, refining was performed on both PFI and Valley beater at a higher refining degree than usual. In Table 11, the changes in fiber length, fines content, and WRV are presented. A substantial decrease in fiber length accompanied by an important rise in WRV was observed compared with the harshest conditions used in chapter 2. Valley beater produced a stronger deterioration of the fiber structure.

Table 11. Changes in the morphology of fiber with severe refining.

SAMPLES	Fiber length (µm)	Fines % (in length)	Crystallinity index (%)	WRV %
Reference pulp	068	46	75	103
VB-120	430	70	64	268
VB-180	351	87	62	307
PFI-17500	544	70	68	237
PFI-45000	482	79	75	265

Valley beater (4.5kg load) refined for 120 min (VB-120); Valley beater refined for 180 min (VB-180); PFI refined for 17500 revolutions (PFI-17500); PFI refined for 45000 revolutions (PFI-45000)

The impact of severe refining on the degree of polymerization of the pulp was also studied (Figure 65). For both technologies, evidence of cellulose chain scission was observed, as indicated by the decrease in viscosity (DP_v). This implied that more active sites for reaction and accessibility of chemical agents were created. The fiber cutting effect of the severe refining and chain scission was more pronounced for the Valley beater refined pulp.

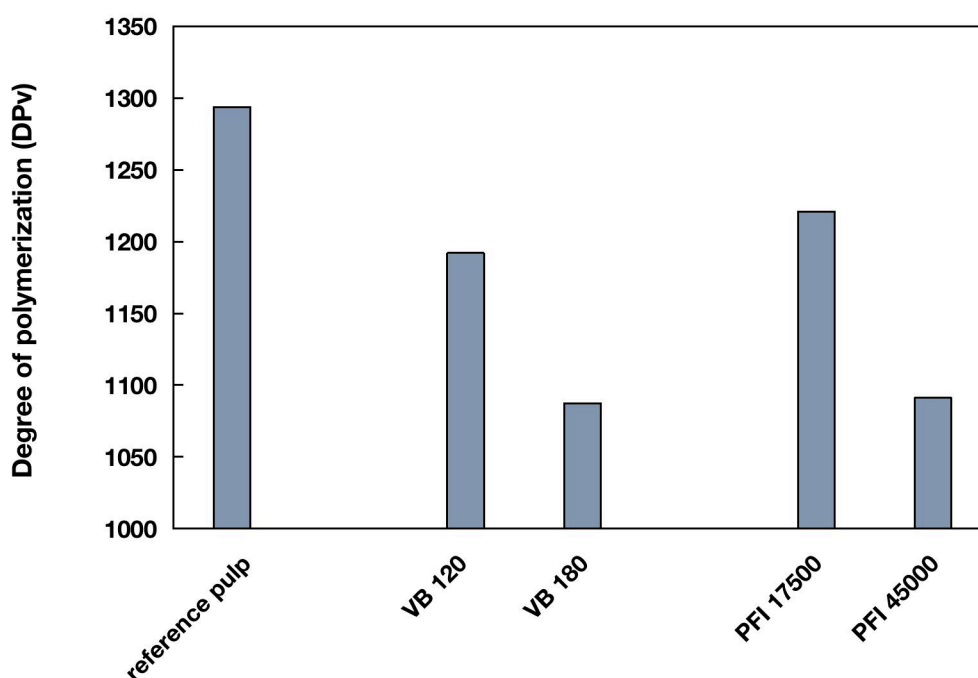


Figure 65. Effect of severe refining on DPv of pulp (VB-120: Valley beater refined for 120 min; VB-180: Valley beater refined for 180 min; PFI-17500: PFI refined for 17500 revolutions; PFI-45000: PFI refined for 45000 revolutions).

on evaluation of the xylan extraction performance (Figure 66), it was observed that Valley beater refining at 180 min (VB-180) and CCE at 6% resulted in a xylan removal of about 76% against 68% obtained for 120 (VB-120). When the soda concentration was increased to 10%, the VB-180 achieved a 94% removal against 84% obtained for (VB-120). The result showed that more severe refining improved xylan removal in such a way that around 1% residual xylan could be reached (against 20% in the paper pulp) which indicated that the main obstacle to the elimination of xylan was their accessibility and not for example resistant chemical bond to cellulose or lignin. Under these conditions (severe refining coupled with CCE at 10% alkali charge) no xylanase treatment would be needed for applications that require pristine cellulose. The difference in refining mechanism between the Valley beater and PFI mill was magnified when the refining severity was increased. Although the refining revolution was more than doubled for the PFI refiner, the impact on the fiber morphology was somewhat marginal, as evidenced by the performance of the CCE at both 6 and 10%. The residual xylan in the pulp after CCE at 6% was more or less the same for PFI refined pulp at 17500 and

45000 revolutions (around 6%). However, a significant decrease in residual xylan left in the pulp after CCE at 10% was observed for PFI refining at 45000 revolutions against PFI refining at 17500 revolutions (2.5% against 3.5%).

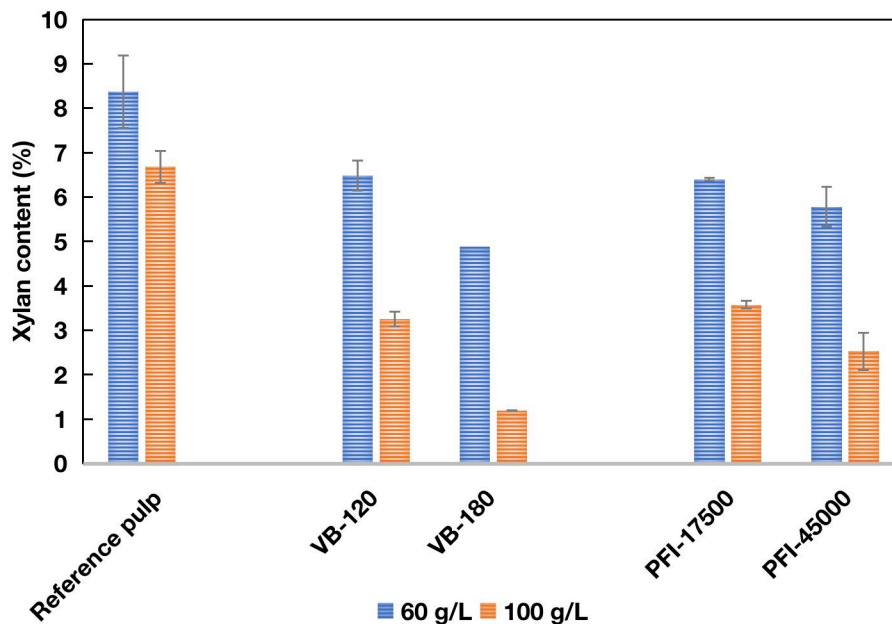


Figure 66. Effect of severe refining on xylan removal by CCE (VB-120: Valley beater refined for 120 min; VB-180: Valley beater refined for 180 min; PFI-17500: PFI refined for 17500 revolutions; PFI-45000: PFI refined for 45000 revolutions).

In summary, severe refining improved xylan removal for both technologies, but the severity of the refining was more pronounced in Valley beater refined pulp, as was the xylan removal performance. This confirms that accessibility problems are the main obstacle to xylan extraction. Severe refining with the PFI refining was less promising for improving xylan removal from pulp via the CCE. This is because the changes in fiber morphology and more particularly the production of fines, was not considerably different from what was observed with moderate refining (17500 revolutions).

3.1.5 Conclusions

Some strategies to improve the residual xylan removal from pulp were investigated. The simultaneous refining/CCE performed on the Valley beater and PFI showed promise. The performance of valley beater was found better, likely because of the lower consistency. The simultaneous refining/xylanase treatment was apparently inferior to the sequential treatment when the xylan removal was considered. However, when CCE was subsequently performed, xylan extraction was equal or even substantially better than for the sequential refining-xylanase-CCE treatment, thus indicating that xylanase hydrolysis occurred in the refiner in a different manner. Actually, the use of simultaneous refining/CCE followed by Xylanase treatment or simultaneous refining/Xylanase followed by CCE, were promising approach to produce dissolving grade pulp (less than 5% xylan) at relatively low NaOH charge in CCE (60g/L), which should limit the formation of cellulose II.

Severe refining under harsher conditions than those used industrially led to greater degradation of the fiber structure and the formation of a greater amounts of fines. At the same time, better extraction of the xylans was obtained (From a paper pulp containing 20% xylan, some of these treatments made it possible to obtain a pulp with a xylan content as low as 1%), thus indicating that the lack of accessibility of the xylans is the most likely reason for the difficulty in removing them.

3.2. Fines fractionation of refined pulp and the impact on hemicellulose removal

Mechanical refining involves a physical disruption or disturbance of the organization of the cellulose fiber structure, which leads to delamination of the layers of the fiber wall, a shortening the fiber length, an abrasion of the fiber surface, which could lead to tearing off of some parts of the loosely held fibers. Typically, a refined, bleached chemical pulp comprises fibrillated fibers of various lengths and structures (straightened, curled) and fines composed of fibrils, fiber wall materials, and broken fiber parts (Guo et al., 2009). Fibrillated fibers and fines are unlikely to respond the same way to chemical or enzymatic treatments, because of their different accessibility, surface area and composition. In that respect, fractionation may offer some advantages by offering a more appropriate substrate for the envisaged application. Interestingly, the research of (Zhu et al., 2009) mentions the importance of the fractionation of disc milled cellulosic substrate from spruce wood on the enzymatic conversion of cellulose to sugar (glucose). The authors found that the enzymatic digestion of cellulose to glucose could be characterized by the size of the fibers which is associated with the volumetric specific surface. However, the effect of increasing the specific surface on cellulose conversion was more evident in fractionated fibers compared to the unfractionated. Indicating that fractionation allowed for homogenous treatment of fibers and thus an increase in the yield of cellulose conversion unlike the unfractionated substrate.

However, few studies have been conducted regarding the influence of fiber fractionation to improve hemicellulose removal and cellulose reactivity. One study investigated the effect of fiber fractionation prior to cold caustic extraction of softwood sulfite pulp and reported that the longer fiber fractions performed better than the short fiber fractions. This was attributed to the low hemicellulose content recorded for the long fibers and the high pore volume compared to the short fiber fractions (J. Li, Zhang, et al., 2015). Another study (Duan et al., 2017) compared the viscosity adjustment of hardwood kraft dissolving pulp fractionated according to fiber size before cellulase treatment (and then recombined prior to the xanthation

process) to the conventional application of cellulase to the whole pulp (unfractionated). The authors reported a boost in reactivity to xanthation from 76 to 86% for the fractionated pulp compared to the whole pulp (without fractionation). In the present study, a sequential treatment involving mechanical refining followed by fines fractionation prior to cold caustic extraction (CCE) treatment was carried out. The CCE was performed on the fiber fraction of the pulp while the fines were collected as reject (which could be used as additives in the papermaking process or other applications (Micro-fibrillated cellulose)). The hypothesis adopted for this study was based on the assumption that hemicelluloses are unevenly distributed across the fiber wall layers, with slightly more concentration on the outer surface than on the inside (Hult et al., 2002). We propose that the refining action which causes external fibrillation and enable loosely held fibrils attached to the fiber surface to be torn off as fines would lead to the generation of hemicellulose-rich fines if isolated, leaving a highly fibrillated fiber with reduced hemicellulose content. Therefore, a separation of the fines from the fibers prior to the alkaline treatment would result in:

- (i) Fiber fraction with particles of more equal size
- (ii) and of more similar hemicellulose composition
- (iii) and globally of lower hemicellulose content, compared to the whole pulp (unfractionated),

All these conditions might improve the overall extraction process.

3.2.1. Pulp quality development with refining and the influence of fines fractionation

In this study, fines were described as fibers of length $\leq 200\mu\text{m}$ or particles that can pass through 150 mesh wire. The fractionation process was carried out using the Bauer McNett fiber classifier. Fiber fractions retained on mesh sizes 28, 48, 65, and 150 were collected as the fibers and used for further studies. The mechanical refining treatment was performed by the Valley beater and the PFI mill. Tables 12 and 13 show the fiber characteristics of the refined pulp before and after the fines were removed.

Table 12. Fiber characteristic of refined pulp before fines removal.

Samples	Fines content (% in length)	Fiber length (μm)	WRV (%)
Unrefined (SR° 17)	41	680	103
VB-3 kg load (165 min, SR° 85)	63	520	243
VB-4.5 kg load 120 min, SR° 85)	71	430	268
VB-5.5 kg load 100 min, SR° 85)	70	450	257
PFI-refined (17500 rev, SR° 85)	70	544	237

Secondary fines (generated from mechanical refining action) are usually fibrillated and have higher swelling capacity than fibers due to their high surface area, which explains the increased WRV of the refined pulp (Mayr et al., 2017; Olejnik et al., 2017). Besides, fibrillation of fibers occurs during refining, which also contributes to WRV. When the fines are separated from the fibers, an increase in fiber length and a loss in WRV were observed (Table 13). Interestingly, the contribution of fines to the WRV was more pronounced in the PFI refined pulp, with 62 points drop after fines removal. The drastic drop in WRV with fines removal for the PFI refined pulp compared to the Valley beater refined pulp could be due to the more fibrillated character of the PFI fines. The fines of the Valley beater, originating from more intensive fiber cutting were probably less fibrillated. After fines removal the WRV values are still relatively high reflecting the external and internal fibrillation of the fibers.

Table 13. Fiber characteristic of refined pulp after fines removal.

Samples	Fines content (% in length)	Fiber length (μm)	WRV (%)
Unrefined (SR° 17)	3	817	92
VB-3 kg load (165 min, SR° 85)	9	587	202
VB-4.5 kg load 120 min, SR° 85)	11	569	228
VB-5.5 kg load 100 min, SR° 85)	11	551	222
PFI-refined (17500 rev, SR° 85)	11	643	175

The evolution of drainage resistance represented by the Schopper-Riegler degree ($^{\circ}\text{SR}$) of Valley beater refined pulp (3 kg loading level) over time is shown in Figure 67 a and b. These figures illustrate the influence of fines on the $^{\circ}\text{SR}$ value. In Figure 65a, the presence of the fines led to a steep rise in the drainage resistance, which follows the typical trend (the sigmoid curve), but after the fines are removed, a substantial drop in SR was observed (Figure 65b). The $^{\circ}\text{SR}$ value after removing the fines increased with refining time because of the combined effect of fiber cutting (generation of new fiber ends) and external fibrillation.

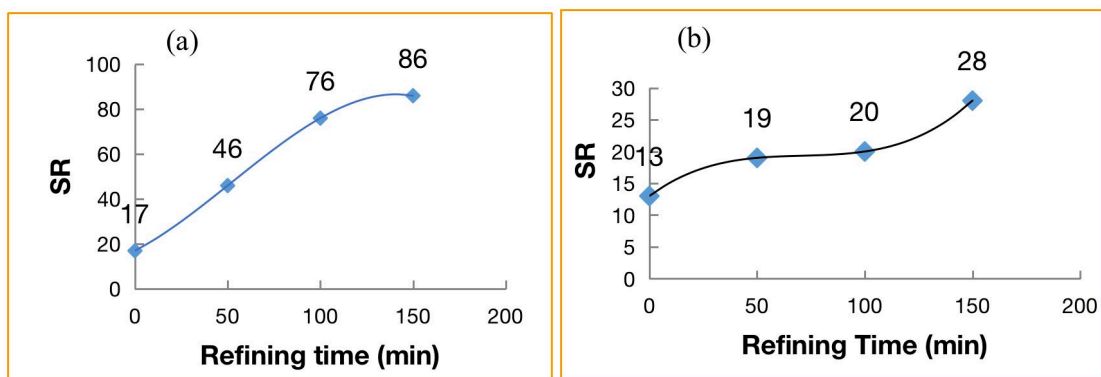


Figure 67. (a) Evolution of SR with refining time (3kg refining load). (b) Evolution of SR with refining time (3kg refining load) after fines removal.

At the SR° value of 85, the evolution of drainage resistance with refining time reaches a saturation point so that °SR measurement was no longer sensitive to the refining degree. The insensitivity of the °SR could be attributed to the excessive quantity of fines. Consequently, the water retention value, which is a more efficient parameter in measuring the swelling and extent of refining, was employed to characterize the refining effect further. Since the WRV was also reacting sensitively to the fines content, it was determined for the whole pulp (with fines) and after fines fractionation. Comparing the sensitivity of both WRV and °SR to fines content as shown in Figure 68 a and b, it was observed that the contribution of fines to WRV was considerably less compared to °SR. This explained why the WRV was a more reliable parameter for characterizing the refining degree.

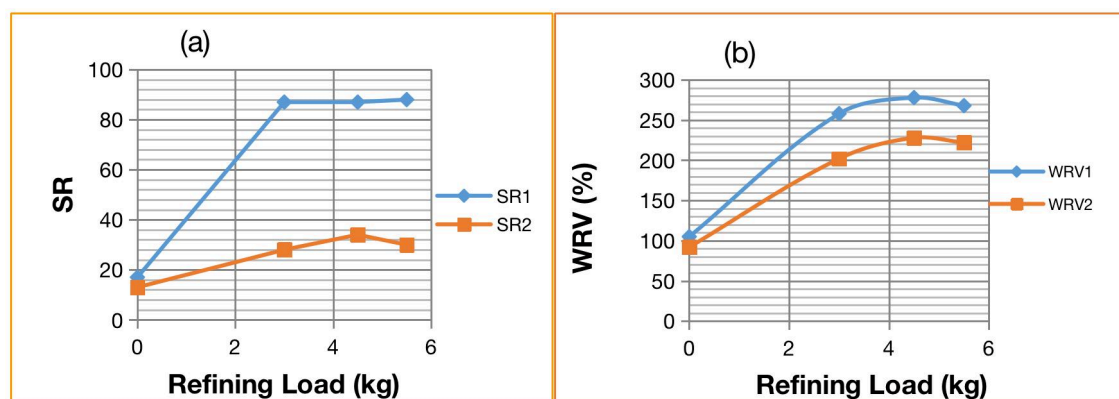


Figure 68. (a) Evolution of SR with refining load (b) Evolution of WRV with refining load (SR1= Schopper Riegler value with fines, SR2= Schopper Riegler value without fines, WRV1= Water Retention Value with fines, WRV2= Water Retention Value without fines).

3.2.2. Influence of fines fractionation on xylan removal

The impact of fines removal on the xylan extraction performance was studied. First of all, the initial xylan content of the reference pulp (unrefined) was determined and compared to that of the fractionated fibers and the fines. As shown in Figure 69, the xylan content of the fractionated fibers decreased by 26% when compared to the xylan content of the whole pulp (without fractionation). A similar result was

reported by (Bäckström et al., 2008) where the authors obtained a 15% reduction in the initial xylan content after the fractionation of the refined softwood pulp. Also, when the fines content (reject) was collected and analyzed, a slight increase in the xylan content compared to the whole pulp was recorded. We expected a higher value for xylan content in the fractionated fines but the result obtained could be explained by losses that might have occurred during the fractionation process (which in itself is a kind of a washing process). According to the (Page, 1989), the hemicellulose portion of the pulp undergoes a leaching process during mechanical refining, especially at high freeness (pores are opened and recrystallized carbohydrates, especially xylans, are solubilized and expelled from the fiber).

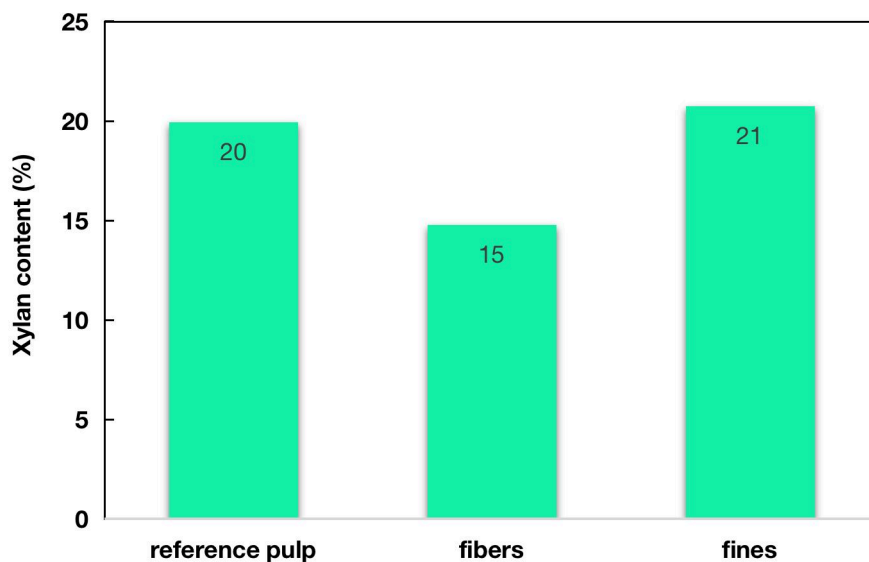


Figure 69. Xylan content of the reference pulp (whole, unrefined pulp), Valley beater refined fibers (4.5 kg load) after fines fractionation (fibers), and fines fraction.

The xylan content of unrefined pulp, Valley beater refined pulp, and PFI refined pulp after fines fractionation are shown in Figure 70. For refining with the Valley beater, a high reduction in the initial xylan content was recorded after the separation of fines.

Although similar values for the fines content (% in length) as determined by the Morfi apparatus (optical fiber analyzer) was obtained for both PFI and Valley beater refined pulps, the gravimetric measurement of the fines content (% in weight) was

quite different. The fines (% in weight) for the PFI and Valley beater refined pulp were 37% and 70%, respectively. The difference in fines content could account for the slightly lower xylan content obtained for the Valley beater refined fibers. Finally, one can conclude that the secondary fines have about the same xylan content as the fibers from which they come, while the primary fines are richer in xylan than the fibers in the pulp.

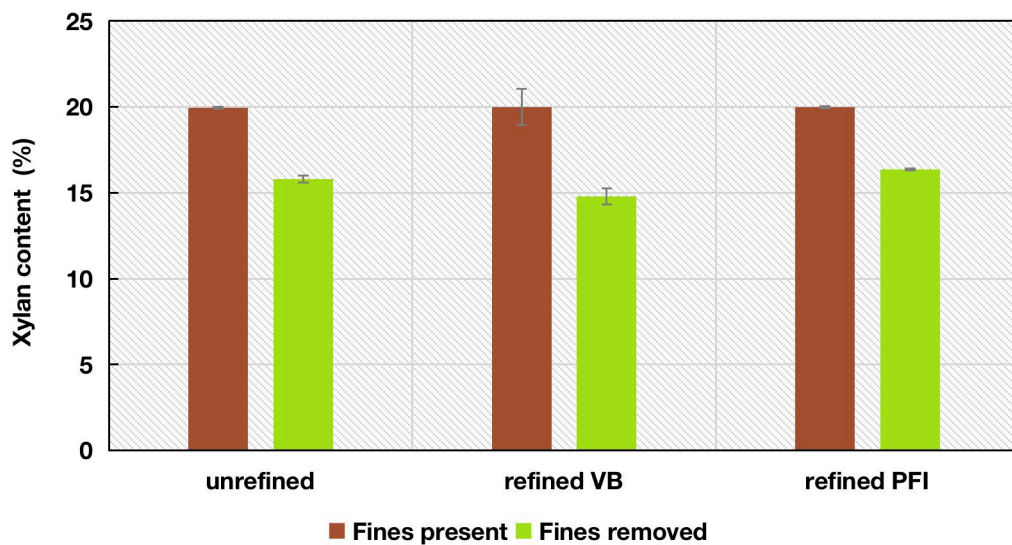


Figure 70. Effect of refining technology on xylan content after fines removal (VB: Valley beater, (4.5 kg load)).

The cold caustic extraction treatment at soda concentrations of 0 g/L, 60 g/L, and 100 g/L, was performed on the fiber fraction of the pulp refined in the Valley beater (4.5 kg load). The xylan content of the treated fibers was measured and compared to corresponding values obtained on refined pulp (including fines) (Figure 71). As seen before, fines fractionation reduces the initial xylan present in the refined pulp by about 26% before CCE. The residual xylan content in the fibers and pulp after the alkaline extraction treatment at 100 g/L was 2% and 3.3%, respectively, that is, about 1 point below the corresponding values without fractionation. Besides, extraction of the fibers at 6% soda concentration resulted in a residual xylan content of about 5%, which could pass for dissolving pulp grade.

The investigations of (Duan et al., 2017; J. Li, Zhang, et al., 2015) reported lower final hemicellulose content in the fractionated fibers and also better cellulose reactivity when a sequential fractionation of the pulp was carried out prior to cellulase treatments. Because of the homogeneity of the fractionated substrate the cellulase hydrolysis was more efficient so that on performing the Fock test, higher reactivity was obtained. A similar logic could be applied here to further explain result obtained in this study.

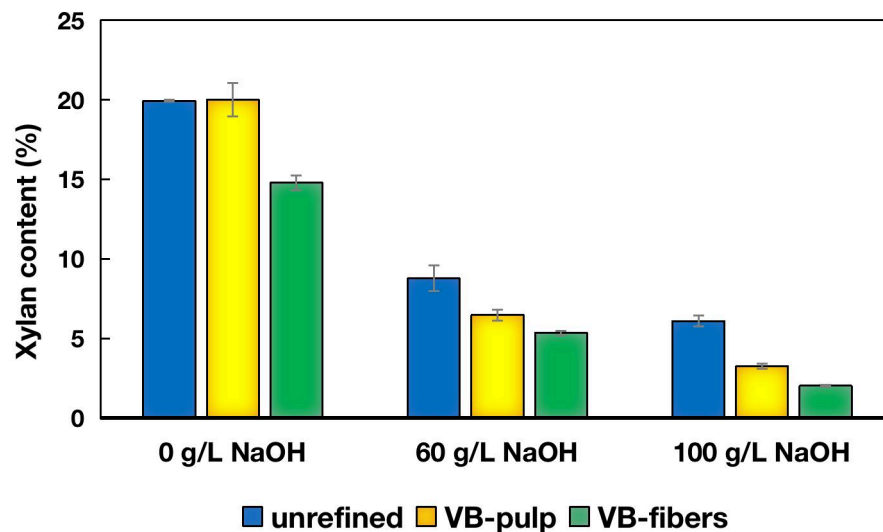


Figure 71. Performance of Valley beater refined pulp and fibers to alkaline extraction at soda concentrations of 0 g/L, 60 g/L, and 100 g/L.

Similarly, the fibers separated from refined pulp with Valley beater (4.5 kg load) and PFI (17500 rev) were subjected to xylanase treatment (50 U/g dry pulp) to investigate the influence of fines removal on xylan extraction. In Figure 72, the residual xylan is given after xylanase treatment of reference pulp (20% xylan), VB refined pulp, PFI refined pulp, fibers from VB refined pulp (without fines) (15% xylan), fibers from PFI refined pulp (16% xylan). Removing fines after refining allowed for a lower xylan content after xylanase treatment (around 14% and 13% in the case of PFI and Valley beater, respectively). However, since the untreated fibers were respectively at 16% and 15% xylan content, there is nothing unexpected. The only conclusion here is that the strategy consisting in fines removal after refining is an interesting way to obtain fibers with lower xylan content after extraction treatments.

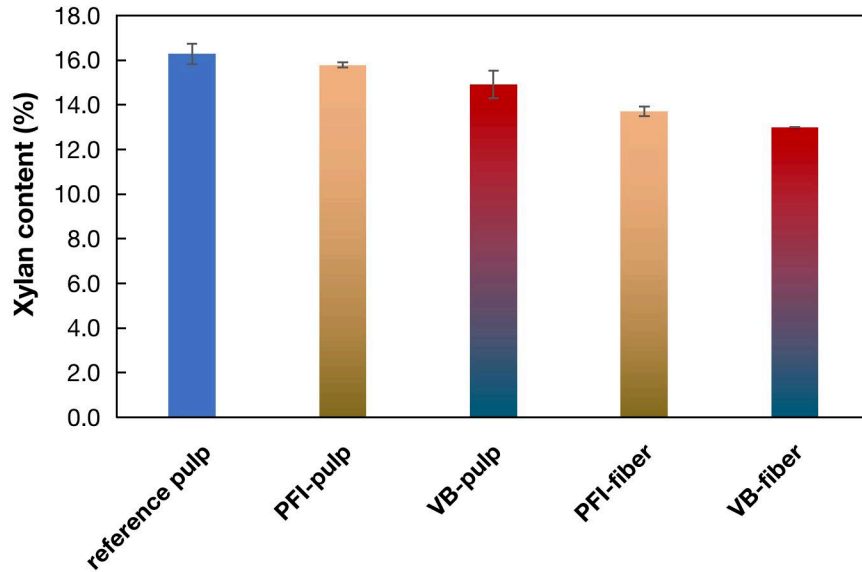


Figure 72. Effect of xylanase treatment on Valley beater and PFI refined pulp and fiber samples <xylanase dosage: 50 U/g (oven-dried pulp/fiber), performed at pH 6, for 2 hours at 50°C>.

3.2.3. Effect of fines fractionation on the degree of polymerization and MWD

The evolution of DP_v of the pulp samples with respect to refining technology and fines fractionation is shown in Figure 73. The DP_v decreased with refining treatment, especially with the Valley beater, which was expected. A slight gain in DP_v was recorded for the fibers compared to the refined pulp (containing fines). The DP_v of the fines was remarkably lower than the other samples, indicating that the fines had more short-chain polymers than the fibers. These changes in DP_v with refining and fines fractionation confirm that cellulose chain degradation occurred with mechanical treatment.

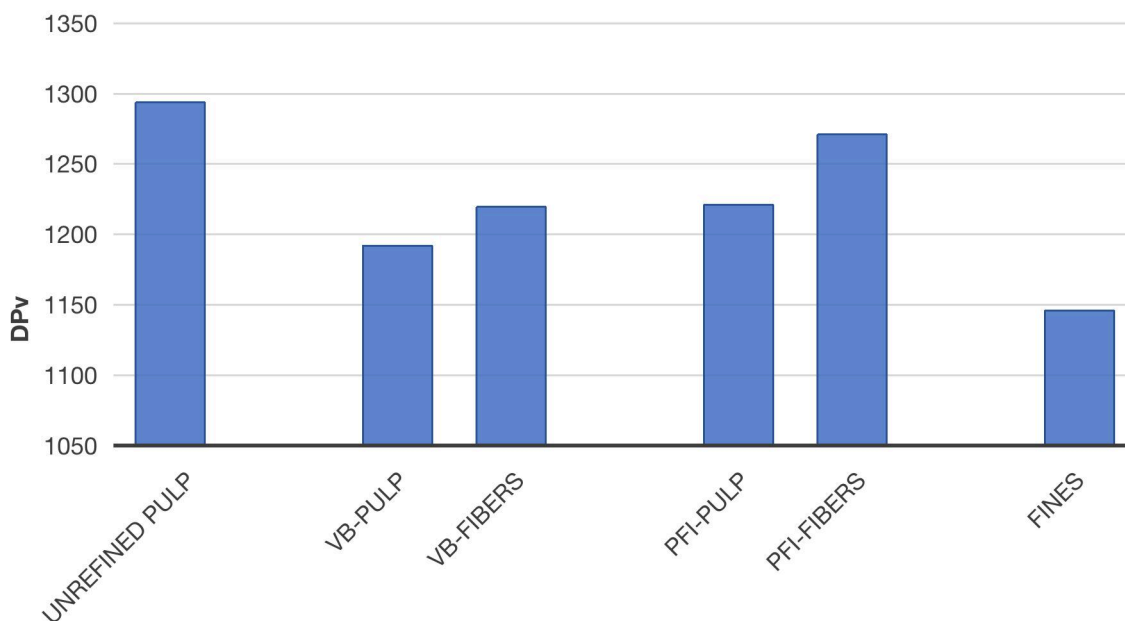


Figure 73. Evolution of the degree of polymerization (DPv) of the pulp as a response to morphology (fibers and fines were collected from Valley beater (4.5 kg load) refined pulp).

The molecular weight distribution profile of pulp and fiber samples was determined and shown in Figure 74. Sequential treatment by Valley beater refining followed by fines fractionation and then alkaline extraction produced a narrow distribution centered at the middle with fewer short-chain polymers than for the other samples. The PDI obtained for the refined fiber was 3.8, while that of the refined pulp was 5.4. These results are consistent with the numerical molecular weight values represented by the DPw and DPn are shown in Table 14.

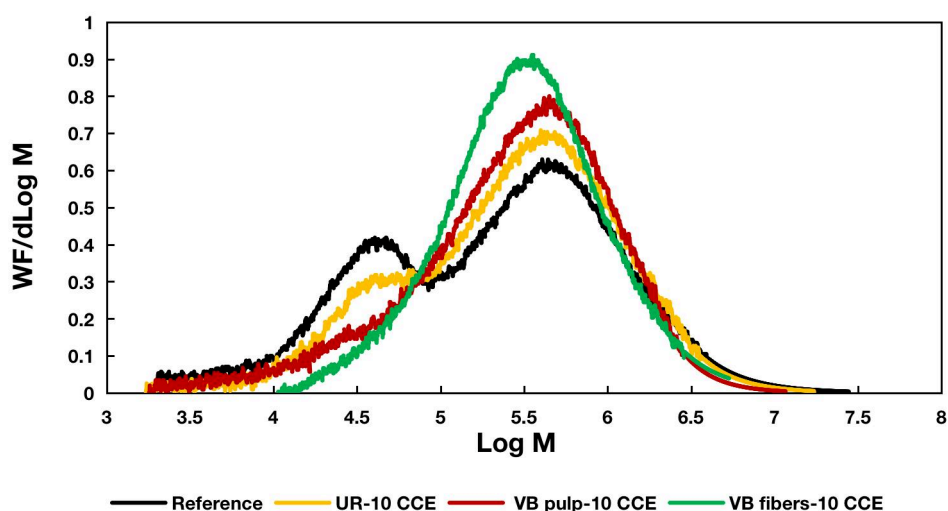


Figure 74. Molecular weight distribution profile of untreated pulp (reference), unrefined pulp extracted with at 10% NaOH, Valley beater refined pulp extracted at 10% NaOH, and Valley beater refined fibers (after fines removal) extracted at 10% NaOH.

Table 14. Numerical values for the molecular weight distribution of various pulp and fiber samples

Sample	DPw	DPn	PDI
Reference	3900	442	8.8
UR-10 CCE	4194	873	4.8
VB pulp-10 CCE	3983	742	5.4
VB fibers-10 CCE	3233	853	3.8

3.2.4. Conclusions

The influence of separating fines from fibers of refined pulp was investigated. Fines removal decreased the WRV, and initial xylan content prior to alkaline or xylanase extraction. The performance of CCE treatment and xylanase hydrolysis on the fiber fraction was similar to what was obtained on the whole pulp but lower xylan level was reached after treatment of the fibers. The extracted fibers at 60 g/L and 100 g/L caustic soda produced pulp of a purity suitable for dissolving applications, with residual xylan content of 5 and 2%, respectively. However, the drawback of this approach is the tedious process of fines fractionation and the

large portion of fines removed. Still, the separated fines could be used as additives in papermaking processes, enzymatic sugar conversion processes or microfibrillated cellulose production.

Conclusions of chapter 3

This chapter explored two new strategies for efficient residual xylan removal from bleached hardwood kraft paper pulp. The simultaneous refining/xylan extraction approach covered in the first section of the chapter was conducted on the PFI and Valley beater refiners. The response of the residual xylan in the pulp to the simultaneous refining/CCE was high with a xylan reduction of 79% and 61% at a soda concentration of 60 g/L for Valley beater and PFI, respectively. A subsequent xylanase treatment applied on the pulp brought about further xylan removal with an overall xylan reduction of 84% and 79% for Valley and PFI, respectively, which represents a residual xylan content of 3.1% and 4.3% respectively. Implementing the simultaneous refining/xylanase led to an apparent loss of xylanase activity.

Among the possible explanations are the harsh refining condition which, one way or another, would damage the enzymes and a more homogeneous hydrolysis which would reduce the average number of cuts per xylan chain. The number of cuts per chain is obviously a parameter governing xylan solubility at acidic pH. The latter hypothesis seems confirmed by the fact that after complementary CCE (100 g/L) performed on the simultaneous Valley beater refining/xylanase treatment gave better results than the sequential Valley beater refining-xylanase treatment.

Severe refining as pretreatment for alkaline xylan extraction was also tested to see whether total removal of the xylans was possible. About 94% xylan reduction was obtained with the Valley beater (against 89% for the PFI mill) at soda concentrations 100g/L. Indicating that the difficulty in removing xylans from paper pulp by alkaline extraction is mostly caused by accessibility problem.

The second section of the chapter investigated the impact of fines fractionation on xylan extraction, and some promising results were also obtained. One benefit of fines fractionation of refined pulp is the reduction of the initial hemicellulose content of the pulp before chemical or enzymatic treatment. As a result, the fractionation of refined pulp coupled with CCE led to a final residual xylan content of approximately 5% and 2%, respectively, at 60 and 100 g/L soda concentrations.

The strategies explored in this chapter resulted in high purity pulp with narrow molecular weight distribution that met the requirement for dissolving pulp grade.

Some drawbacks include the need to use refining equipment made of chemical-resistant materials to avoid wear in the simultaneous refining-CCE treatment. Also, for the fines fractionation, the challenge was the tedious process of fines fractionation.

Chapter 4: Cellulose solubility Studies

Overview of chapter

One of the objectives of this study was to produce from paper-grade pulp, high purity cellulose fibers with high reactivity to dissolution. To accomplish this, a coupling of mechanical refining treatments with chemical (CCE) and enzymatic (xylanase) treatments were applied. The goal was to determine the extraction conditions that achieved high xylan removal and simultaneously improved the reactivity of the resulting cellulose fibers. In order to obtain these conditions, the fibers were subjected to mechanical refining with different technologies, and the xylan extraction was performed at 60 and 100 g/L NaOH. The activation of cellulose fibers prior to dissolution has been reported in the literature. This process involves the chemical, enzymatic and mechanical treatment applied to improve cellulose solubility. Mechanical treatments like ball milling, steam explosion, Valley beater refining, and PFI milling have been reported to enhance dissolving pulp reactivity to xanthation (Budtova & Navard, 2017; Gehmayr et al., 2011; Köpeke et al., 2008; H. Li et al., 2018; Miao et al., 2014; Tian et al., 2014; Zhou et al., 2018). In these reports, the already produced dissolving pulp is subjected to additional treatments (activation) to facilitate dissolution, which means additional production costs. In the present study, the idea was to produce dissolving pulp with high reactivity by ensuring that the hemicellulose removal processes employed also improved the dissolution potential of the resulting dissolving pulp.

In the previous chapters, several strategies were explored to improve the purity of paper-grade cellulose by removing the residual hemicellulose content. Mechanical refining pretreatment showed promise with a xylan removal degree of over 80%. In this chapter, the effect of the different xylan removal strategies on the reactivity of the extracted cellulose was assessed by the degree of swelling in NaOH solution, Cupriethylene diamine solution, and the solubility in NaOH. These results were then compared with the reactivity to xanthation (Fock reactivity). Since cellulose swelling precedes dissolution, the swelling degree could predict the

reactivity of the cellulose fibers. The influence of the crystallinity index and degree of polymerization on reactivity was also discussed.

4.1. Effect of refining and soda concentration on the swelling of cellulose fibers

The high water- absorption and retention capacity of mechanically refined cellulose could improve the degree of swelling of the cellulose fibers in aqueous solvents. This is of particular interest as swelling is the first step in the dissolution process. To investigate this, the degree of swelling of unrefined and refined cellulose in caustic soda solution of various concentrations was determined at room temperature. Swelling degree was measured on the MorFi analyzer from the change in fiber width when the pulp was placed in the caustic soda solution according to a method developed by (Arnoul-Jarriault et al., 2016). The properties of the unrefined and refined pulps before the swelling test are shown in Table 15. In this instance, the pulp used was not dried before the swelling test.

Table 15. Properties of bleached mixed hardwood pulp before swelling.

Samples	Unrefined pulp	^(a) Refined pulp (Disc pilot)
Fiber length (μm)	685	544
WRV %	103	233
SSA (m ² /g)	0.3	0.6
DP _v	1293	1087

(a)The pulp was refined at a net power of 8kW until an SR° 85.

As expected, a change in the pulp properties was observed with refining. Upon refining, a decrease in the fiber length and degree of polymerization was recorded, and the WRV and SSA doubled as well. These changes in morphology could explain the improved swelling of the refined pulp compared to unrefined pulp in soda solution as seen in Figure 75 where the evolution of the fiber length and width with increasing soda concentration is seen. The refined pulp experienced

more swelling than the unrefined pulp. Also, the swelling increased with increasing soda concentration, and the fiber length decreased slightly. The slight loss in fiber length with the increase of swelling is a general trend observed in studies of swelling (Arnoul-Jarriault et al., 2016; Gomes et al., 2020)

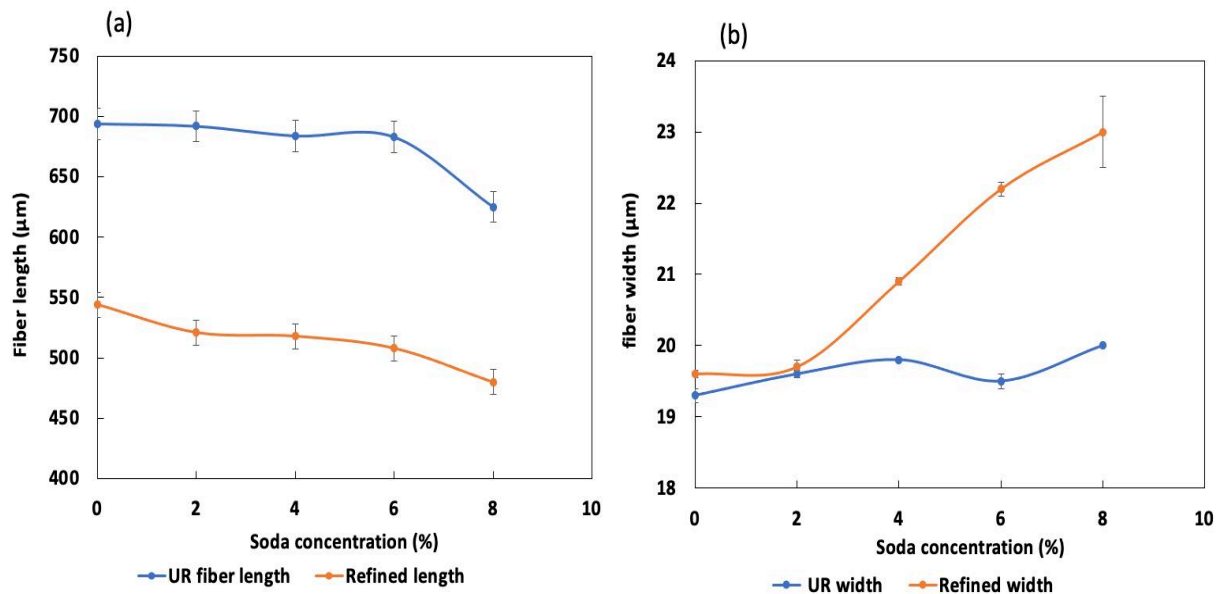


Figure 75. Swelling behavior of unrefined and refined pulp (Disc pilot) at various soda concentration.

Figure 76 shows optical microscopy images of unrefined and refined pulps after 2 min in 0.25 M CUEN. It can be seen that the short fibers, which are more populated in the refined pulp, swell more homogeneously than long fibers. Swelling and ballooning were well observed in the unrefined pulp. The dissolution by ballooning is associated with a restriction in the outer fiber wall (primary (P) and secondary (S1) layers). Other dissolution pathways involve the dissolution by the unwinding of the helical cellulose structure in the secondary layer (S2, S3) and the dissolution by fragmentation, both resulting from more homogeneous swelling, and are made possible by the absence of the P and S1 layers or by the use of strong solvents that resist the effect of the outer layers (Navard & Cuissinat, 2006).

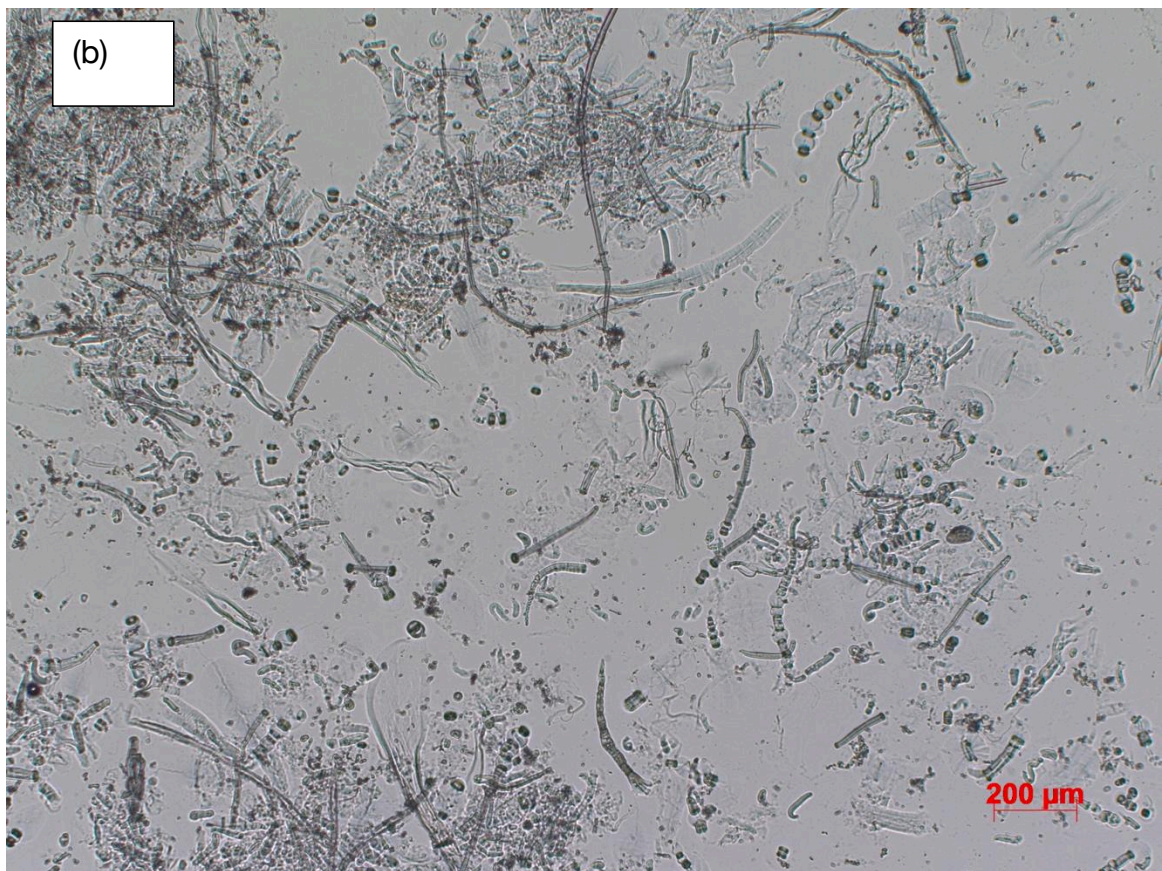
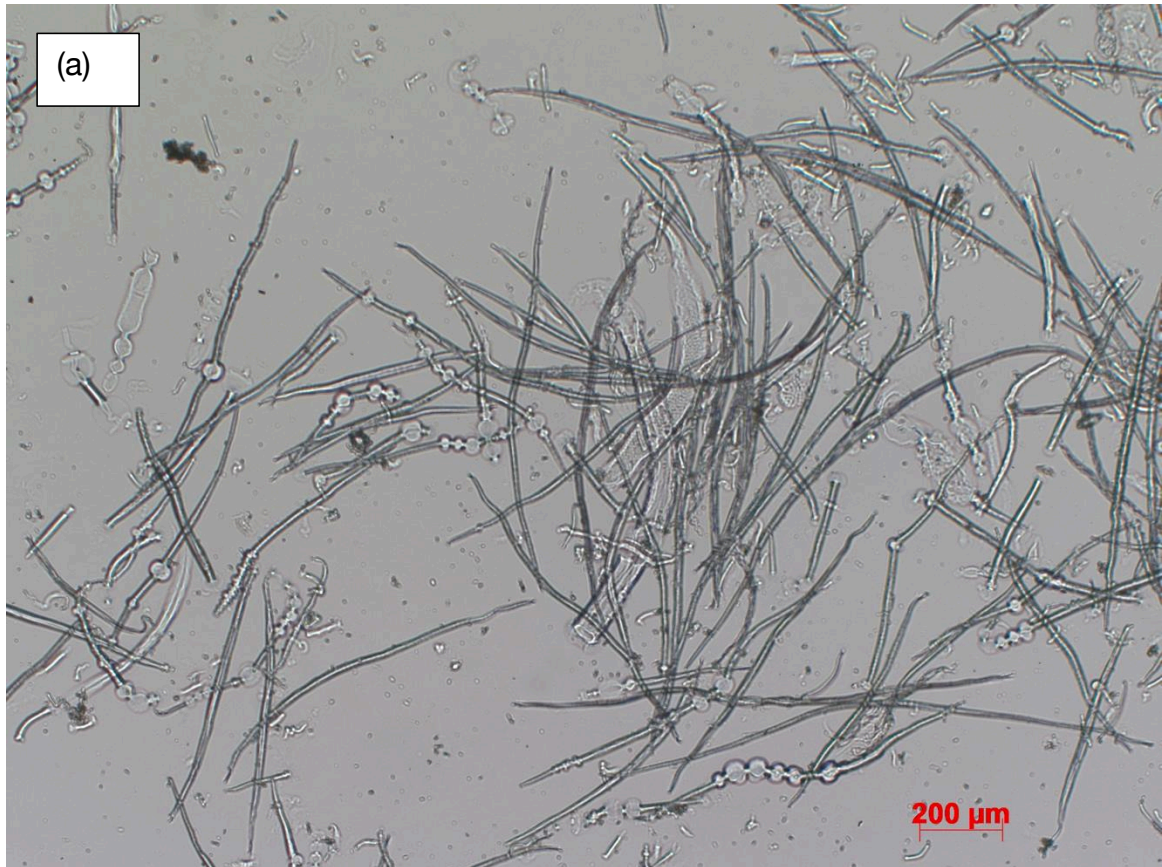


Figure 76. State of unrefined (a) Valley beater refined pulp (SR° 85) (b) after a stay of 2 min. in 0.25M CUEN solution.

Compared to the unrefined pulp, the restrictions in the outer layer of the refined pulp are minimized by the refining action, leading to dissolution with less ballooning and more homogeneous swelling.

4.1.1. Influence of the pretreatment strategy on the swelling of cellulose fibers in 12% NaOH solution

In order to better understand the influence of mechanical pretreatment on cellulose swelling in NaOH solvent, freeze-dried cellulase treated pulp (50 U/g pulp) and pulp refined to the same degree ($^{\circ}$ SR-85) by different technologies (PFI, Valley beater, and Disc pilot), were treated with 12% NaOH at 1% pulp consistency for 30 min at room temperature. As shown in Figure 77, a decrease in fiber length was observed for all the samples regardless of the treatment strategy employed. Likewise, the degree of swelling represented by the gain in fiber width (Figure 78) increased for all the samples but more substantially for the refined pulps.

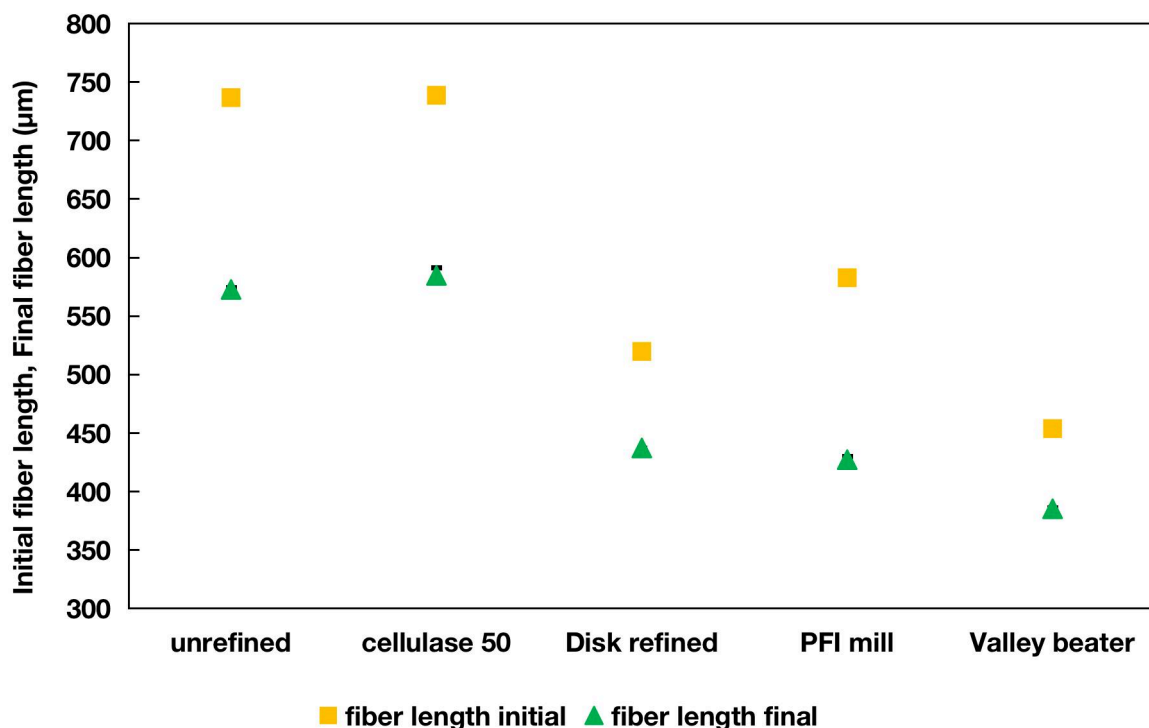


Figure 77. Effect of pretreatment strategy on swelling in 12% soda assessed by variation in fiber length (cellulase 50: represents pulp treated with cellulase at a dosage of 50 U/g pulp).

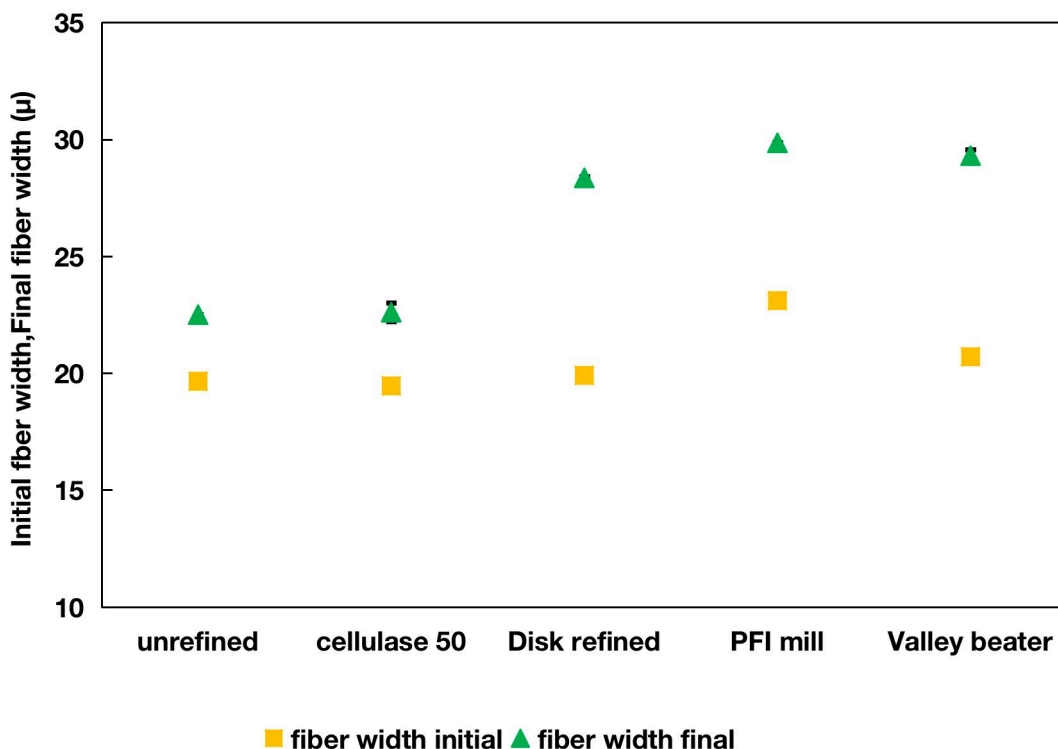


Figure 78. Effect of pretreatment strategy on swelling in 12% soda assessed by variation in fiber width (cellulase 50: represents pulp treated with cellulase at a dosage of 50 U/g pulp).

Under these conditions (12% caustic soda, 1% pulp consistency, with continuous stirring for 30 minutes) the variation in width for the disc-refined pulp was 42% against 17% shown earlier in Figure 75, (obtained under the following conditions; 8% caustic soda, 5% pulp consistency, with intermittent stirring for 30 minutes). The considerably higher swelling obtained in the second scenario (Figure 78) was obviously due to the different conditions operating during the swelling process. Firstly, it is known that in cellulose pulps, swelling in the interfibrillar and intrafibrillar areas reaches a maximum between NaOH concentrations of 10 and 12% (Richter & Glidden, 1940). In addition, the lower pulp consistency (1% versus 5%) and better mixing enhanced the swell test performance.

The cellulase-treated pulp did not swell as much as the mechanically crefined pulp. The higher swelling of the mechanically refined pulp could be attributed to the external and internal fibrillation effect of the refining action, which

causes a kind of peeling off of the fiber wall layer, creating new surfaces which ultimately improve accessibility.

According to (Navard & Cuissinat, 2006) the outer layers of the cellulose fiber wall (primary and S1 layers) are more resistant to dissolution than the inner layers. Their conclusion was based on observations (ballooning effect) made when cotton and wood fibers were dissolved before and after detachment of the outer layers by enzymatic treatment. As mechanical refining disrupts the surface of the fibers (external fibrillation), this could explain the increased swelling recorded for refined pulps. On the other hand, with reference to what is claimed in the literature (Köpeke et al., 2008; H. Li et al., 2018; J. Li et al., 2018; Miao et al., 2015) better swelling of the cellulase degraded pulp was expected. It could be that the cellulase dosage was not sufficient to see an effect. In fact, the DP was still above 1000 which is much higher than in most of the other studies.

The swelling behavior of the pulps, determined by the increase in fiber width was consistent with the modification of pulp properties brought about by the pretreatment, in particular, the water retention value, the specific surface area, the crystallinity index (CI) and the average fiber length (Table 16).

Table 16. Difference in the morphology of bleached mixed hardwood pulps (unrefined, refined and cellulase treated).

Pulp Samples	Unrefined	Valley beater	PFI	Disc pilot	Cellulase
Fiber length (mm)	0.68	0.43	0.54	0.54	0.68
SSA (m ² /g)	0.4	1.3	1.0	0.6	-
WRV (%)	103	268	237	233	105
CI (%)	75	64	68	72	76
Fine % (wt)	20	70	37	-	-
DPv	1293	1192	1221	1087	1021

4.1.2. Effect of pretreatment strategy on swelling of extracted cellulose fibers in 0.16 M CUEN

Cupri-ethylenediamine (CUEN) solution (0.5M) is a known solvent for cellulose fibers. It is commonly used to determine the viscosity of cellulosic pulp, which indicates

the chain length (degree of polymerization). It was found that dilution of the CUEN solution to 0.16 M swells the fibers without dissolution, which facilitates the examination of the swelling behavior of dissolving pulps. Actually, a positive correlation between the Fock reactivity and the degree of swelling of various dissolving pulps determined by measuring the variation in width of the fibers treated in dilute CUEN solution was obtained (Arnoul-Jarriault et al., 2016). In the present study, unrefined and refined pulp extracted with 6 and 10% soda (without drying) were treated in 0.16M CUEN to assess the influence of the hemicellulose elimination treatments on the swelling degree of the cellulose fibers. According to the results shown in Table 17, it appeared that treatments involving mechanical refining had better swelling than without refining. The pulp extracted with 10% soda had less swelling compared to pulp extracted with 6% soda, which could be associated with the formation of cellulose II and the fibril aggregation that occurs with the removal of hemicellulose.

$$\mathbf{Variation\ (\%)} = \frac{(\mathbf{x}_f - \mathbf{x}_i)}{\mathbf{x}_i} \times \mathbf{100} \quad (3)$$

Where x_f represent final fiber length or width (length or width after swelling); x_i represent initial fiber length or width (length or width before swelling)

Table 17. Reactivity of cellulose fibers assessed by determining the variation in fiber width in 0.16 M Cupri-ethylenediamine solution.

Pulp samples	Fiber length (μm)			Fiber width (μm)		
	Initial	Final	Variation (%)	Initial	Final	Variation (%)
^(a) UR-10CCE	623	636	2.1	16.2	16.8	4
^(b) PFI-10CCE	490	448	-9	23.4	27	15
^(c) VB /6CCE	499	485	-3	22.6	24.9	10
^(d) VB 120 min-6CCE	434	407	-6	22.5	27.9	24
^(e) VB 120 min-10CCE	378	368	-3	23.8	27.1	14
^(f) VB 180 min-6CCE	339	340	0.3	26	31.7	22
^(g) VB 180 min-10CCE	320	319	-0.3	27.5	32	16

(a) Unrefined pulp extracted with 10% NaOH

- (b) PFI refined pulp (17,500 revolutions; SR° 85) extracted with 10% NaOH
- (c) Valley beater refined simultaneously with CCE (at 6% NaOH for 60 min)
- (d) Valley beater refined pulp (120 min; SR° 85) extracted with 6% NaOH
- (e) Valley beater refined pulp (120 min) extracted with 10% NaOH
- (f) Valley beater refined pulp (180 min) extracted with 6% NaOH
- (g) Valley beater refined pulp (180 min) extracted with 10% NaOH

To investigate the effect of refining severity of extracted pulp on the swelling degree, the width variation of Valley beater refined for 120 min and 180 min were examined. Even though the fiber morphology of the pulp differed considerably prior to the extraction treatment, similar swelling (variation in width) was obtained for both pulps (VB 120 min and VB 180 min) extracted at 6% and 10% soda concentrations. This could be explained by the fibril aggregation occurring during the dewatering process, which was probably reinforced for the severely refined pulp (VB 180 min). This indicates that although refining improves swelling, the influence of cellulose II and fibril aggregation that occurs with dewatering cannot be neglected. Therefore, to limit this effect, lower soda concentrations could be used for the hemicellulose extraction to prevent the transformation of the crystal lattice of native cellulose to cellulose II and the use of integrated dissolution processes (in the pulp mill) that omit the drying step.

4.2. Influence of conditions of xylan extraction on dissolution performance of cellulose fibers

The dissolution performance of some purified pulps was assessed by the solubility of the freeze-dried samples in 8.5% NaOH at -10°C and Fock reactivity (See methodology chapter for details). The solubility of the pulp in 8.5% soda was determined according to the method proposed by (Isogai & Atalla, 1998) but the freezing temperature was kept at -10°C which was a level where the cellulose solubility was found close to optimum.

From the result obtained, illustrated in Figure 79 the solubility of the untreated and treated pulps was under 40%, which was consistent with results reported in the literature for kraft pulps of a similar degree of polymerization. The influence of mechanical refining and soda concentration on the solubility of the

cellulose fibers is seen. Increasing the soda concentration of the hemicellulose extraction from 60 g/L to 100 g/L decreases the solubility of the resulting pulp. This was not particularly surprising because of the transformation of the native cellulose to cellulose II at high alkali charge and a possibility of aggregative interactions between the cellulose fibrils that occur when hemicelluloses are removed. The lowest solubility (16%) was obtained for the unrefined pulp extracted with 10% soda, while the highest (36%) was obtained when mechanical refining was coupled with sequential xylanase and 6% CCE treatments.

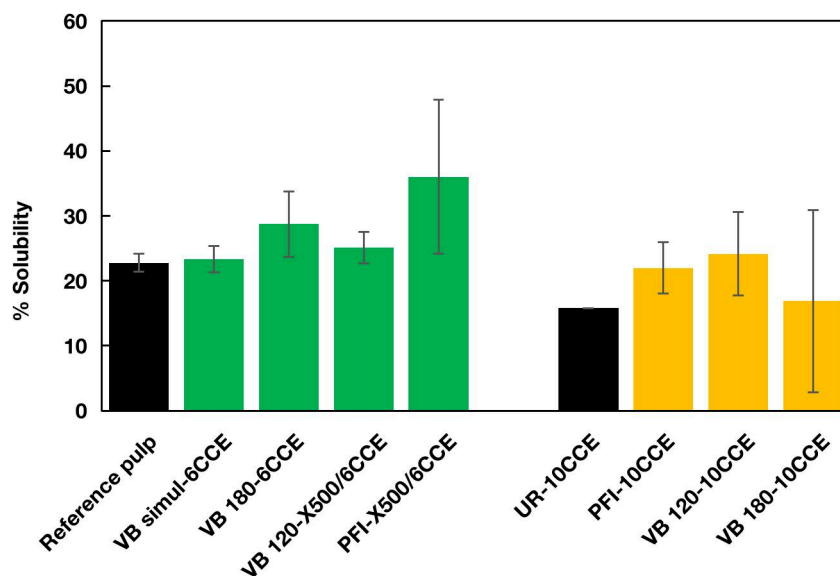


Figure 79. Performance of xylan extraction treatment on the solubility of the resulting cellulose fibers in 8.5% NaOH at -10°C. {Reference pulp is the starting pulp without any treatment, VB 120 represent Valley beater (120 min), VB 180 represent Valley beater (180 min), 6CCE and 10CCE represents the soda concentration of the CCE treatment (60 and 100 g/L NaOH respectively, X500 represents the xylanase dosage (500 U/g pulp)}.

When the Fock reactivity of the purified pulp was determined, a trend similar to that observed for solubility in 8.5% NaOH was observed (Figure 80). Higher Fock reactivity was recorded for the pulp extracted with 6% soda compared to those extracted with 10% soda. Values of Fock reactivity in the range of 60-70% were determined for refined pulp extracted at 6% soda concentration, with and without an additional sequential xylanase treatment.

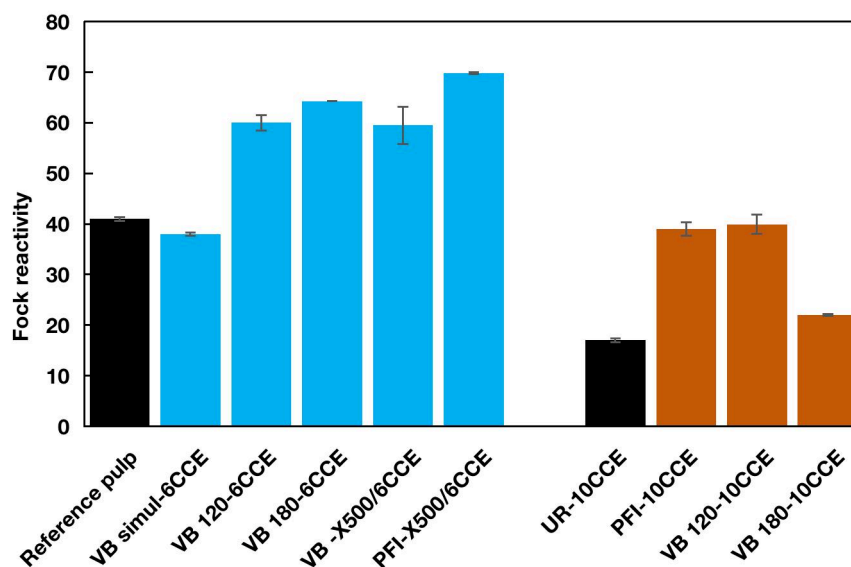


Figure 80. Performance of xylan extraction treatment on the Fock reactivity of the resulting cellulose fibers. {Reference pulp is the starting pulp without any treatment, VB 120 represent Valley beater (120 min), VB 180 represent Valley beater (180 min), 6CCE and 10CCE represents the soda concentration of the CCE treatment (60 and 100 g/L NaOH respectively, X500 represents the xylanase dosage (500 U/g pulp)}.

A lower reactivity to xanthation was recorded for the pulp purified by performing simultaneous refining and CCE at 6% alkali load. This might be explained by the less destructive effect of the simultaneous refining/CCE compared to the sequential treatment (shorter treatment time) noticed previously, and also by the presence of some cellulose II peaks detected by X-ray analysis as illustrated in Figure 81.

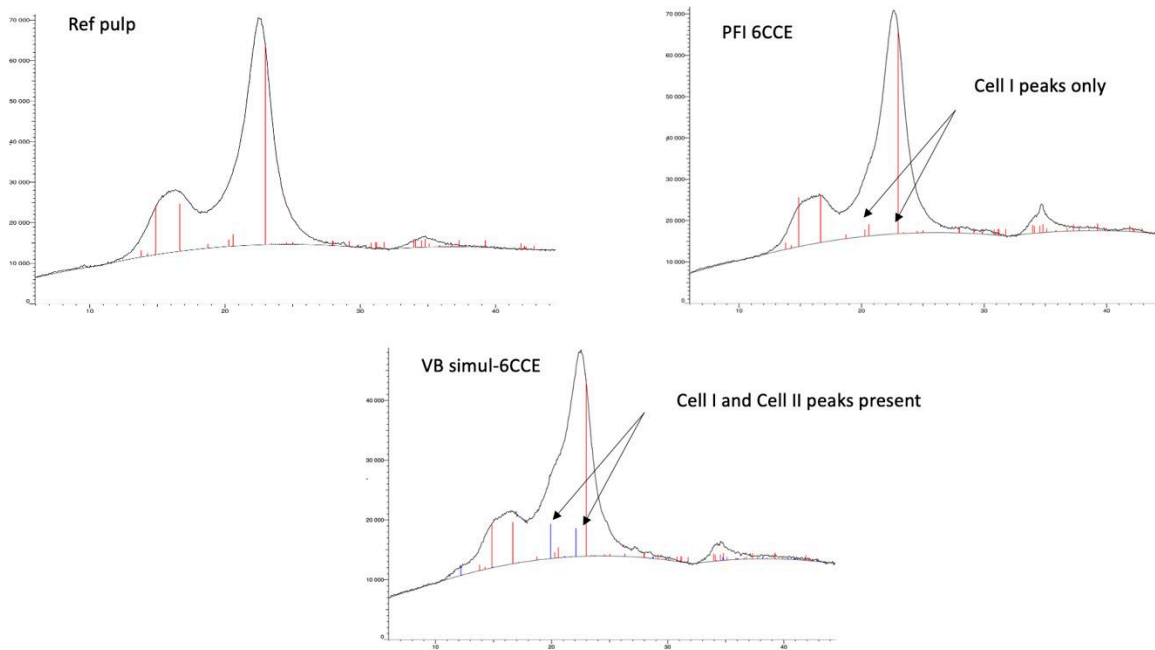


Figure 81. X-ray diffractograms of reference pulp (without any treatment), PFI refined pulp extracted with 6% soda (PFI-6CCE) and pulp obtained by simultaneous Valley beater refining and CCE at 6% soda (VB simul-6CCE); red peaks represent cellulose I, while blue peaks represent cellulose II).

For the pulps extracted with 10% soda, higher Fock reactivity was obtained for pulps refined prior to the CCE treatment compared to the unrefined pulp. In fact, the Fock reactivity is substantially increased except for the (VB 180-10 CCE), where extreme mechanical refining was applied before the CCE treatment. Since the Fock test was performed on dried cellulose fibers, the poor reactivity to xanthation might be explained by two occurrences: Firstly, the effect of external fibrillation of both fines and fibers brought about by mechanical refining, which intensifies aggregation on drying; and secondly, the effect of cellulose II which favors fibril densification and aggregation on dewatering. Apparently, extreme refining favors the transformation of the crystal lattice of native cellulose to cellulose II during subsequent CCE, as shown by the diffractograms in Figure 82.

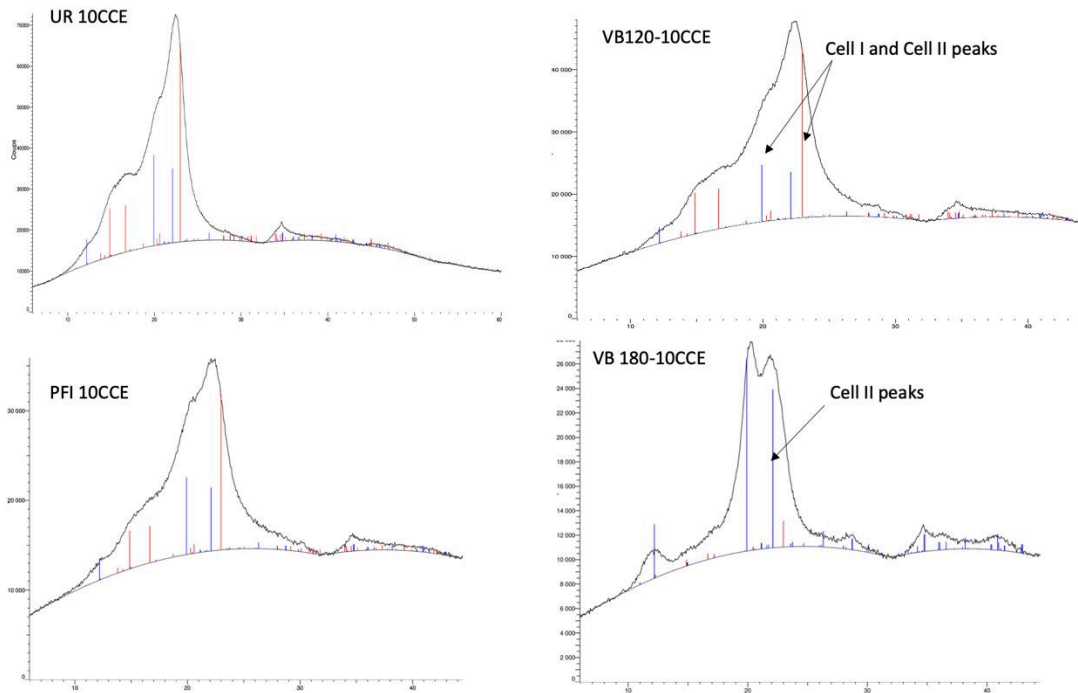


Figure 82. X-ray diffractograms of unrefined pulp extracted with 10% soda (UR 10CCE), PFI refined pulp extracted with 10% soda (PFI-10CCE), Valley beater refined pulp extracted with 10% soda (VB 120-10CCE), Valley beater refined pulp (extremely refined) extracted with 10% soda (VB 180-10CCE); red peaks represent cellulose I, while blue peaks represent cellulose II).

4.2.1. Correlation of swelling behavior of cellulose fibers in CUEN, with solubility in 8.5% NaOH at -10°C and Fock reactivity.

The standard method for determining the reactivity of cellulose fibers in the laboratory is the Fock test. It is a long, tedious process that involves the use of several toxic chemicals. Consequently, some alternatives have been proposed in the literature (Arnoul-Jarriault et al., 2016; Ceccherini & Maloney, 2019). These methods investigated the swelling behavior and rheological properties of cellulose fibers in CUEN. One of these methods was developed in our laboratory, and a correlation was obtained with the Fock test. The influence of mechanical refining pretreatment and alkali loading used for the CCE stage on the dissolution performance of bleached mixed hardwood kraft paper pulp was assessed by three methods; (i) swelling behavior in CUEN determined by the MorFi apparatus (Arnoul-Jarriault et al., 2016) (ii) solubility in 8.5% soda at -10°C (Isogai & Atalla, 1998) and

(iii) Fock reactivity (Tian et al., 2013). Correlations between swelling in CUEN and dissolution performance was determined.

Table 18 shows the values obtained in (%) for the variation in width, solubility in 8.5% NaOH, the Fock reactivity, the crystallinity index (CI), the xylan content and the degree of polymerization of some purified pulp. We did not find a logical connection between the influence of the crystallinity index and the degree of polymerization on the overall performance of the cellulose fiber during dissolution. The pulp with the highest CI and DPv (VB 180-10CCE) had a low Fock reactivity (22%), but an even lower value (17%) was obtained for the extracted unrefined pulp with similar DPv and CI. In (Figure 83 a, b and c) the correlation between the Fock reactivity and the other methods (solubility in 8.5% NaOH at -10 °C and variation in width) was illustrated. This result shows that both methods can be used in the laboratory to assess the reactivity of cellulosic fibers to dissolution in the viscose process. Solubility measurement in 8.5% NaOH at -10 °C is simple and no special equipment is required other than a cooling bath. One disadvantage to using this method is the difficulty in filtering the heterogeneous gel-like substance obtained after the freezing and thawing process. Swelling measurement in CUEN solution is also simple. However, it requires the use of the MorFi fiber analyzer.

Table 18. Suitability of some upgraded cellulose fibers to dissolution assessed by different methods.

Samples	Variation in width (%)	Fock reactivity (%)	Solubility in NaOH (%)	Crystallinity index (%)	DPv	Xylan content (%)
UR 10CCE	4	17	16	70	1362	7
VB 120-10CCE	14	40	24	63	1328	3
PFI 10CCE	15	39	22	59	1329	4
VB 180-10CCE	16	22	17	73	1383	1
VB 180-6CCE	22	64	29	63	1286	5
VB simul/6CCE	10	38	23	70	1309	4
VB 120-6CCE	24	60	Nd ^(a)	69	1328	7

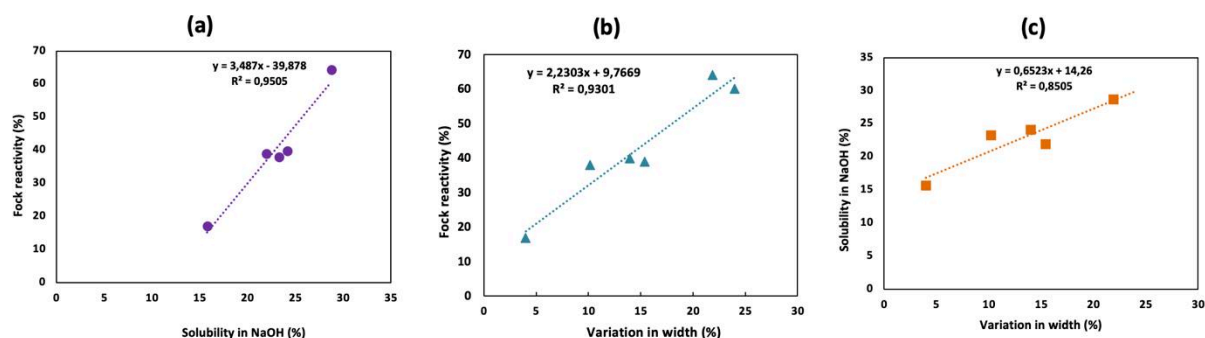


Figure 83. Correlation between different methods of assessing cellulose fiber reactivity in aqueous solvent systems.

4.2.2. Effect of some hemicellulose removal strategies on Fock reactivity

Different strategies of hemicellulose removal from paper pulp were investigated in this study to produce high purity cellulose for use as dissolving pulp. The influence of refining technology, refining severity, soda concentration, treatment sequences that include xylanase, fines fractionation and cellulase pretreatment coupled with CCE on the reactivity of the resulting pulp to xanthation (Fock reactivity) are presented in Figure 84. From these results, some general trends can be drawn on the effect of purification processes on the cellulose dissolution index for the viscose process (Fock reactivity), even though some interactions between the individual process steps are overlooked. On the effect of cold caustic extraction and the quantity of caustic soda on Fock reactivity, it can be seen that irrespective of the treatment strategy applied, pulp extracted with 10% caustic soda had a low reactivity compared to pulp extracted with 6%. This result was not unexpected as the susceptibility of alkali treated pulps to structural modifications like cellulose II formation and fibril aggregation that result in collapsed pores, fiber shrinkage and ultimately reduce accessibility especially at soda concentrations higher than 8% have been reported (Dinand et al., 2002; Ferreira et al., 2020). Although the dissolution index (Fock) was significantly diminished when the CCE was performed with 10% NaOH for both unrefined and mechanical refined pulps, the effect was more pronounced in unrefined pulp with the lowest reactivity of 17%. This result demonstrates that mechanical refining as part of the pretreatment was beneficial in

improving cellulose reactivity. It should be noted that pulp extracted with 10% NaOH had fewer hemicellulose (high purity cellulose) compared to the extraction with 6%. Therefore, strategies that will enhance hemicellulose removal at 6% NaOH were explored.

Regarding the influence of refining technology on the dissolution index of the purified pulp, there appeared to be no considerable difference between the performance of PFI and Valley beater refined pulps at the soda concentrations investigated. This is interesting because even though the fiber development progressed differently, evidenced by the morphology of the fibers after refining (WRV, SSA, fines content, fiber length) as previously shown in Table 16, the Fock reactivity did not reflect it. Ideally, the Valley beater refined pulp should by virtue of the superior morphological properties attained by refining, reach a far better dissolution index than the PFI refined pulp but this was not the case. One reason for this observation could be the intensification of fibril aggregation upon dewatering (drying) in the Valley beater refined pulp which contains more fines/fibrils than the PFI refined pulp.

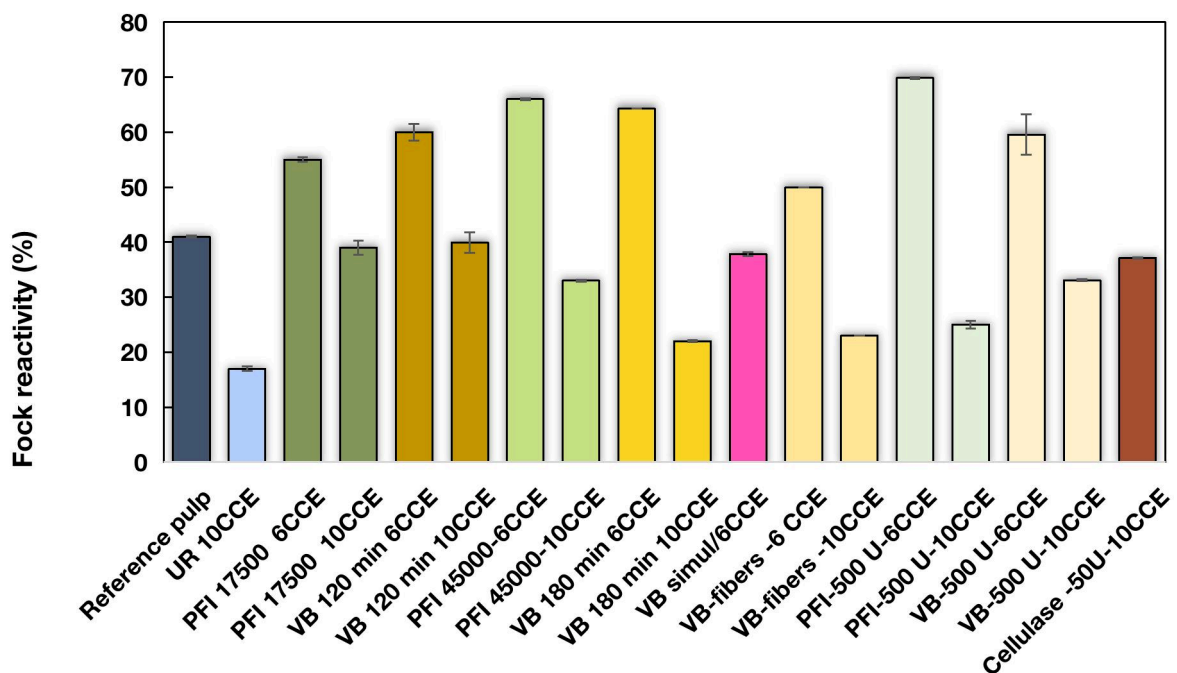


Figure 84. Effect of various hemicellulose extraction treatments on the dissolution of the resulting pulp (reactivity to xanthation).

The implementation of a one-pot simultaneous refining and CCE treatment at 6% NaOH (VB simul/6CCE) was carried out (to limit the formation of cellulose II while maintaining a good hemicellulose extraction), though it achieved a good hemicellulose removal (79%) the Fock reactivity (38%) was lower than the other purification strategies involving sequential refining treatment prior to CCE performed with 6% NaOH. An explanation for this could be the onset of the transformation of crystal lattice to cellulose II which was detected by XRD. This was unexpected as other samples extracted at 6% showed no evidence of cellulose II formation.

The cellulase-treated pulp was obtained by treating unrefined pulp with cellulase at a dosage of (50 U/g pulp) before the CCE treatment and from the result of the Fock reactivity, (37%) it can be said that the performance of the treatment was not impressive although it was better than the value obtained for unrefined pulp (UR-10CCE). The poor performance of the cellulase treatment compared to the result in the literature could be due to the treatment sequence and perhaps enzyme dosage. The effect of fines fractionation of refined pulp prior to a sequential CCE treatment (VB-fiber-CCE) was explored as a means of improving the hemicellulose removal efficiency which was successful with xylan removal 90% and 73% at soda concentrations of 10% and 6% respectively. Based on the result of the dissolution index (Fock reactivity), 55% (VB-fiber-6CCE) and 23% (VB-fiber-10CCE) it can be seen that even though purity is enhanced by this treatment, the Fock reactivity is not improved when compared to treatments involving refining without fines fractionation (VB-120 min).

The best results were obtained in VB-180 min-6CCE, PFI-X500 U-6CCE and VB-X500 U-6CCE with hemicellulose content < 5 and Fock reactivity of 64%, 70% and 60% respectively which is higher than reported in commercial PHK pulp (49%) ([Duan et al., 2016a](#); [Tian et al., 2013](#)).

4.3. Influence of the degree of polymerization (DP_v), crystallinity index, and xylan content on the reactivity of extracted cellulose fibers

According to the literature, cellulose dissolution may be affected by its degree of polymerization (DP) and crystallinity index (CI) (Ferreira et al., 2020; M. loelovich, 2009; Isogai & Atalla, 1998; Liu et al., 2019). In our study, these characteristics varied slightly depending on the purification treatment employed. In this section we investigated the existence of possible correlation with the Fock reactivity. We extended this study to the xylan content.

The impact of xylan content, DP_v and CI on the Fock reactivity of some extracted pulp samples is shown in Figure 85. No relationship between residual xylan content and the Fock reactivity was observed probably because the samples used in the study had low xylan content suitable for dissolving applications (with the highest at 6%). However, there are some contradicting reports regarding the influence of hemicellulose on the dissolution process of cellulose fibers. Some studies claim that hemicelluloses act as some sort of obstacle or barrier that restricts the penetration of solvent molecules (Budtova & Navard, 2016), while other studies insist that the hemicellulose content of the pulp does not affect solubility, especially in NaOH-water solvent systems (Isogai & Atalla, 1998). According to (M. Y. loelovich, 2016), the removal of the hemicellulose fraction enabled an aggregative interaction between the neighboring microfibrils (co-crystallization), which reduces the accessibility.

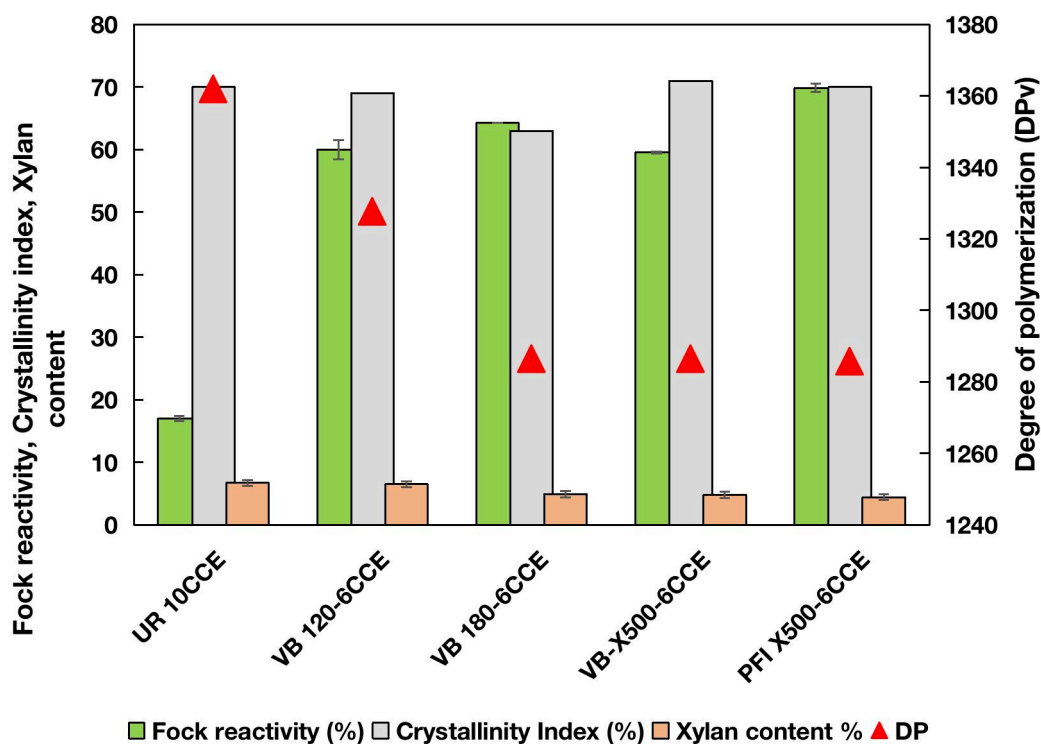


Figure 85. Effect of DPv, CI and xylan content on the Fock reactivity of some extracted pulps

Considering the influence of the chain length (degree of polymerization) on the Fock reactivity, it was observed that the control pulp (UR 10CCE) with the highest DPv value (1368) had the lowest reactivity while the pulp with the highest reactivity had a slightly lower Dpv value (1286). However, this was not enough to conclude on the matter as there might exist other influences contributing to the reactivity of the pulp. In a study by (Ferreira et al., 2020) they reported that the molecular weight of the pulp alone was not a sufficient factor to determine the reactivity of cellulose but that the supramolecular properties were a more important predictor of reactivity. In contrast, several studies have shown a relationship between the intrinsic viscosity (an indication of chain length) and the Fock reactivity especially when cellulase was applied (Duan et al., 2016b; Liu et al., 2019; Miao et al., 2015).

Regarding the influence of crystallinity index (CI) on the dissolution index (Fock), a clearer connection is seen in Figure 86. Here, for better comparison, the samples presented were all refined by the same technology (Valley beater) and the

only other factor at play was the NaOH concentration used for the CCE. Based on the result, a correlation between the Fock reactivity and the CI is seen particularly when the CCE treatment was carried out at 6% NaOH. At this soda concentration, there was no influence of cellulose II on the outcome of the result and so, we see that the soda treatment alone results to a slight decrease in the CI (UR 6CCE), which is further decreased when mechanical refining was applied prior to the CCE (VB 120- 6CCE). Increasing the severity of the refining also led to more decrease in the CI (VB 180-6CCE). This loss in CI from 75% in (UR 6CCE) to 63% in (VB 180-6CCE) resulted to a corresponding gain in the Fock reactivity from 41% (UR 6CCE) to 64% in (VB 180-6CCE).

On the other hand, the relationship between the crystallinity index and Fock reactivity was not apparent when the extraction was carried out with 10% NaOH because of the influence of cellulose II, and other modifications at the supramolecular level particularly fibril aggregation and co-crystallization. As shown in Figure 86, performing the CCE at 10% NaOH decreased both the Fock reactivity and CI but the effects associated with the presence of cellulose II (which is susceptible to fibril aggregation) outweighed the benefit of the loss in CI. In the case of refined pulp extracted with 10% NaOH (VB 120-10CCE) the CI experienced further decrease without a corresponding increase in the Fock reactivity when compared to the reference pulp. Upon further increase of the severity of the refining treatment prior to the CCE at 10% NaOH (VB180-10CCE), a substantial gain (from 63% to 73%) in the CI probably brought about by aggressive fibril aggregation was observed.

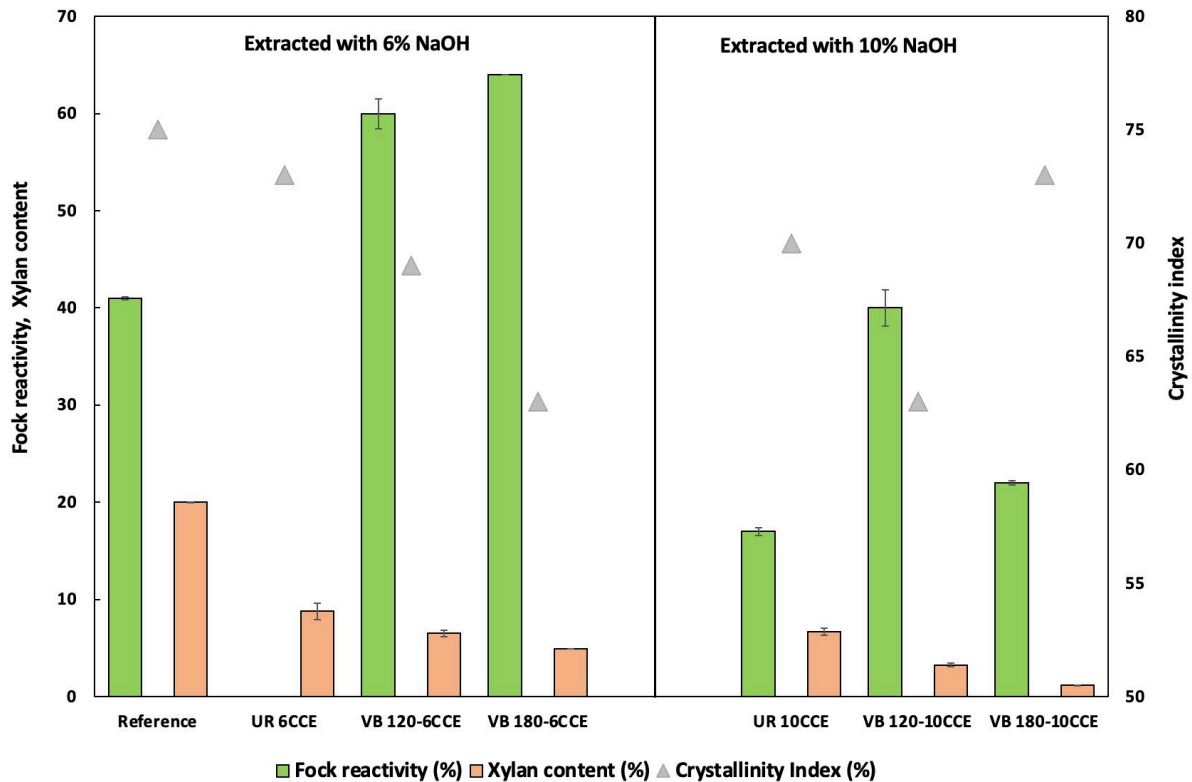


Figure 86. Effect of the crystallinity index (CI) on the Fock reactivity {Reference pulp is the starting pulp without any treatment, UR represents unrefined pulp, VB 120 represent Valley beater (120 min), VB 180 represent Valley beater (180 min), 6CCE and 10CCE represents the soda concentration of the CCE treatment (60 and 100 g/L NaOH respectively)}.

4.3.1. Effect of CCE treatment and drying method on the formation of cellulose II

Among the parameters influencing the Fock reactivity (indicating the extent of dissolution in the viscose process) we showed above that refining and the amount in caustic soda in CCE were the most important. We already discussed the effect of refining. As to the influence of caustic soda on reactivity, we simply mentioned that it was because of the possible formation of cellulose II. When cellulose fibers come in contact with a strong NaOH solution, a series of changes occur. First is the swelling of the fibers that facilitates the dissolution of hemicelluloses if present, then the transformation of native cellulose to Na-cellulose. After washing/neutralization, the cellulose chains undergo an irreversible reorganization to an antiparallel alignment known as cellulose II. Depending on the severity of the treatment, the conversion is either partial (presence of cellulose I and cellulose II) or complete (only

cellulose II). Studies show that the transformation of cellulose I to cellulose II is accompanied by a decrease in the crystallinity index (Dou & Tang, 2017; Ferreira et al., 2020; Janzon, Puls, et al., 2008; Oh et al., 2005). The loss of crystallinity with strong soda treatment was attributed to the conversion of some of the crystalline regions to the amorphous cellulose (Oh et al., 2005). The X-ray diffraction patterns of cellulose fibers after the different degrees of refining treatment, followed by cold caustic extraction treatments at 6 and 10%, are presented in Figure 87. For samples, a, b, and c, (Figure 87) refined by different technology to the same extent, the evolution of the diffractogram of the pulps extracted with 0 to 100 g/L NaOH followed a similar trend. At soda concentrations of 0 and 60 g/L, the diffraction patterns were consistent with the typical structure of cellulose I. However, at 100 g/L, two additional reflexes associated with cellulose II appeared at 12.3° and 20.3° (Figure 88). These additional peaks were observed to be even more prominent when the refining severity was increased (Figure 87 d and e). The result indicated that a change in the morphology of the cellulose fibers leading to increased accessibility by disrupting the fiber organization, and increasing the fragility/brittleness of the fibers by severe mechanical action could intensify the conversion of native cellulose to cellulose II. Thus, under the same extraction conditions (10% CCE), more areas of the native cellulose crystal lattice of refined pulp are transformed to cellulose II.

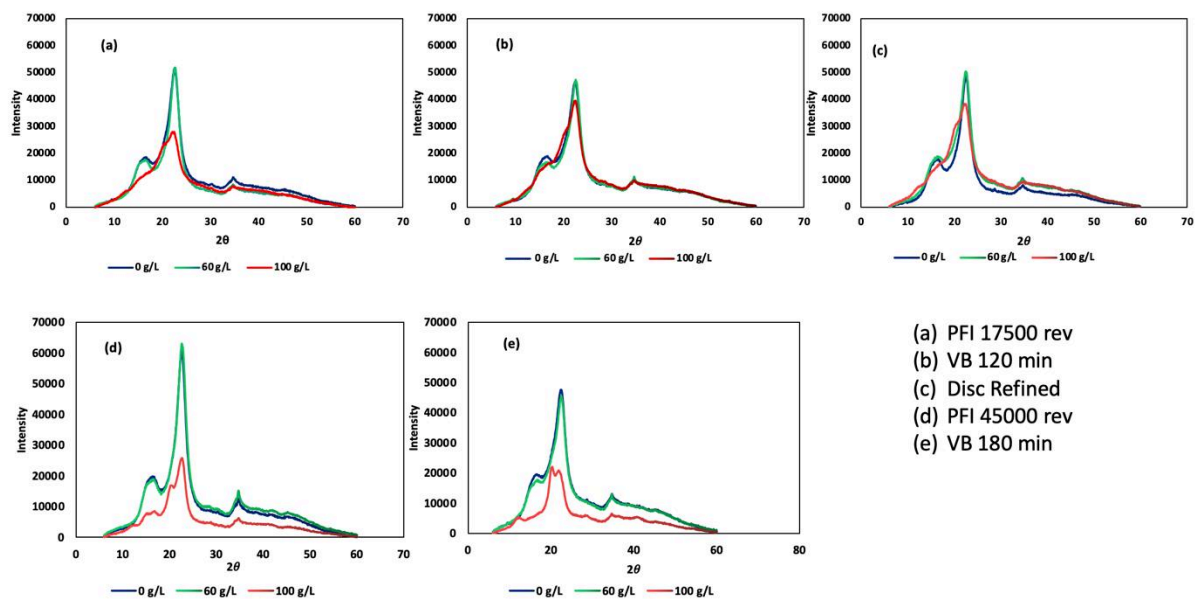


Figure 87. Effect of the mechanical refining and CCE treatment on the evolution of native cellulose X-ray diffraction spectra.

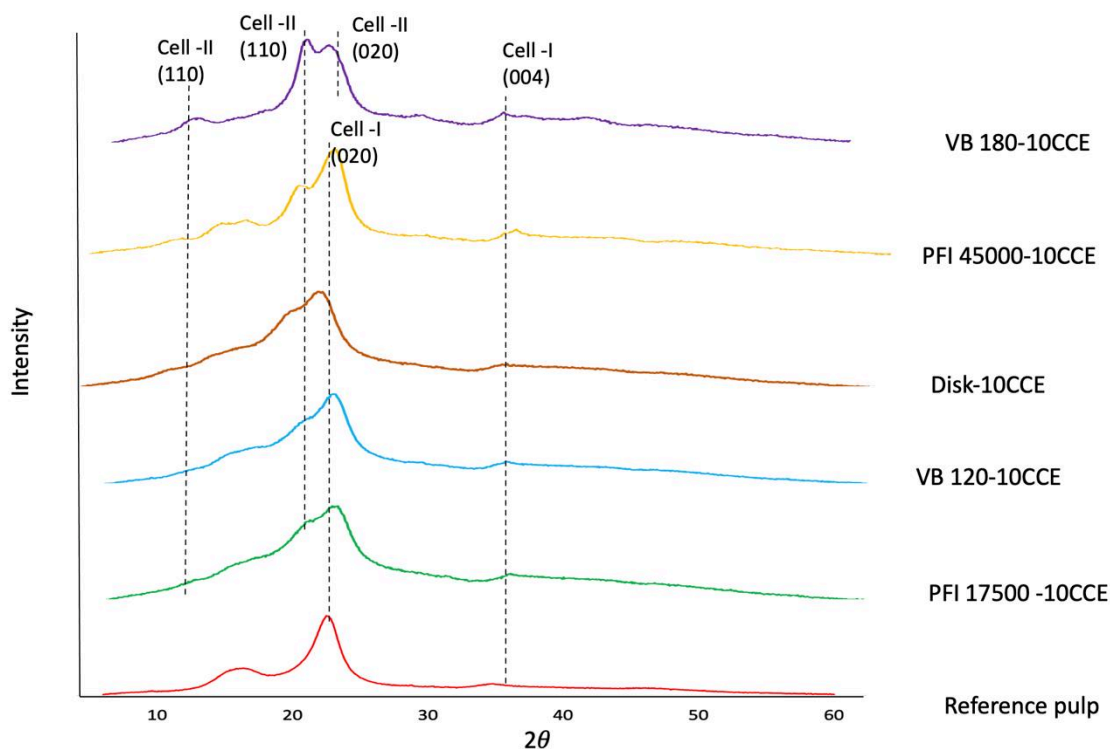


Figure 88. X-ray diffractograms of the reference pulp, PFI refined pulp (17500 rev) extracted with 10% soda (PFI-17500-10CCE), PFI refined pulp (45000 rev) extracted with 10% soda (PFI-45000-10CCE), Valley beater refined pulp extracted with 10% soda (VB 120-10CCE), Valley beater refined pulp (extremely refined) extracted with 10% soda (VB 180-10CCE), Disk refined pulp extracted with 10% soda (Disk-10CCE); red peaks represent cellulose I, while blue peaks represent cellulose II).

To further verify this observation, the supramolecular structure of unrefined and Valley beater refined (VB 120 min) pulps extracted with 0 %, 6 %, and 10 % soda were analyzed by solid-state NMR spectroscopy (^{13}C -CP/MAS-NMR). Typically, the chemical shift ranges assigned to C-1 (106-108 ppm) and C-6 (64-66 ppm) are used to evaluate the transformation of native cellulose to cellulose II, particularly at stronger NaOH treatments (>12 %). However, for NaOH solution of lower strength (7-10 %), the apparent change signaling cellulose II is observed at C-6. In Figure 89 for both unrefined and refined pulps, the C-6 signal at 66 ppm with a slight shoulder at 64 ppm was altered with the formation of cellulose II. The C-6 signal at 64 ppm increased remarkably while the signal at 66 ppm saw a drastic reduction.

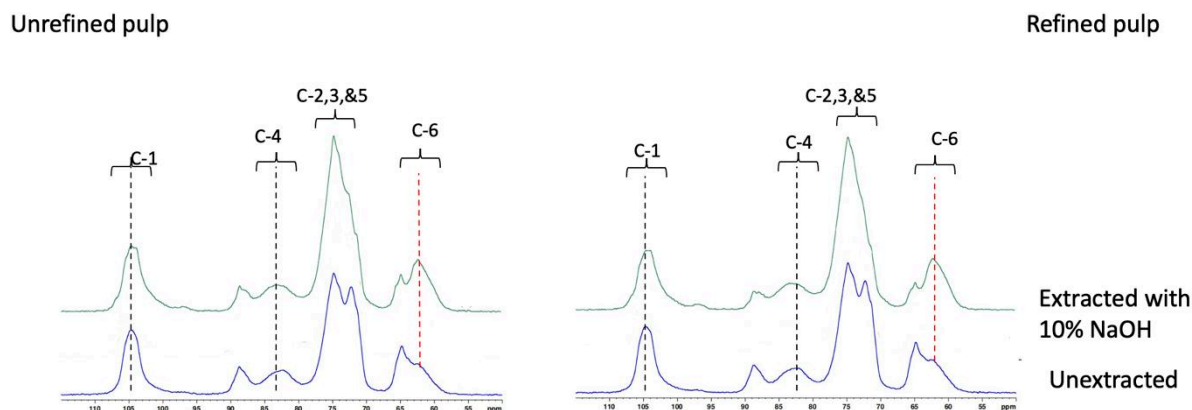


Figure 89. ^{13}C -CP/MAS-NMR spectra of unrefined and refined pulp extracted at 0 and 10% NaOH.

The values of the crystallinity index and cellulose II content estimated from the spectra are shown in Table 19. First of all, the crystallinity index decreased with refining (0% CCE) and after the extraction treatment (10% CCE), the loss in crystallinity became more pronounced especially in the refined pulp. Most importantly, the cellulose II content was 16% higher in refined pulp than unrefined pulp. This was in agreement with the observation made from the X-ray diffraction results. Thus, increased accessibility and the fragile state of the cellulose fibers brought about by mechanical treatment, facilitates the transformation of more regions of native cellulose to cellulose II.

Table 19. supramolecular properties of some pulps obtained by ^{13}C -CP/MAS-NMR.

Sample	Cell II (%)	CI (%)	I/S(crystallites)
Unrefined pulp_0% CCE	-	56	1.54
Refined pulp_0% CCE	-	53	1.54
Unrefined pulp_10% CCE	56	48	1.94
Refined pulp_10% CCE	65	39	1.89

The occurrence of cellulose II is of paramount importance on fiber reactivity. In our measurements on swelling (12%), dissolution in NaOH, Fock, the pulp was dried prior to be tested. In fact, this represents the common practice in industry.

Dissolving pulp is prepared in a pulp mill and then, is sold in the dry state (as any market pulp) to processing units carrying out dissolution and regeneration in the form of threads or other materials. The dry cellulose II hydrogen bond network is denser than the cellulose I and therefore is less accessible.

In addition, the drying method employed also had a significant effect on the CI. The influence of drying method on unrefined and refined pulp, is shown in (Figure 90). Apparently, the fibril aggregation/recrystallization that occurred during air drying was intensified, so that the benefits of mechanical refining were nullified as evidenced by the high crystallinity index values (80%). When cellulose fibers were freeze-dried, the values of CI obtained were lower for unrefined pulp (75%) and for refined pulp (64%). Notably, the loss in CI due to the drying method was 7% for unrefined pulp and 20% for refined pulp. Therefore, freeze drying preserves to some extent the modifications brought about by refining. To further elucidate the impact of the drying method on the morphology of the fibers, the SEM images of air dried and freeze-dried samples of the same refined pulp is presented in (Figure 91). We see that the air-dried fiber surfaces are smooth while the freeze-dried fibers surrounded by the fibrils generated during refining. The increase in crystallinity index, observed in the air-dried fibers can be attributed to the severe fibril aggregation which would be reflected in the reactivity of the pulp to further processing.

Having established that there was a correlation between Fock reactivity and CI, especially in the absence of cellulose II (Figure 86). It is crucial to consider the influence of drying on CI, which, as shown in Figure 90, could vary with drying strategy. This gain in CI with drying will most probably negatively impact the reactivity of the pulp.

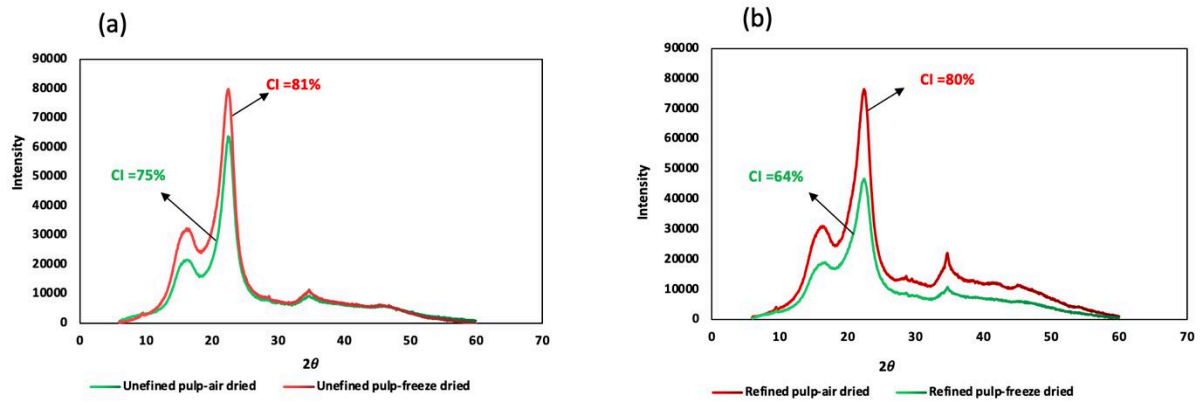


Figure 90. Influence of drying method on the crystallinity index of unrefined (a) and Valley beater refined cellulose fibers (SR° 85) (b).

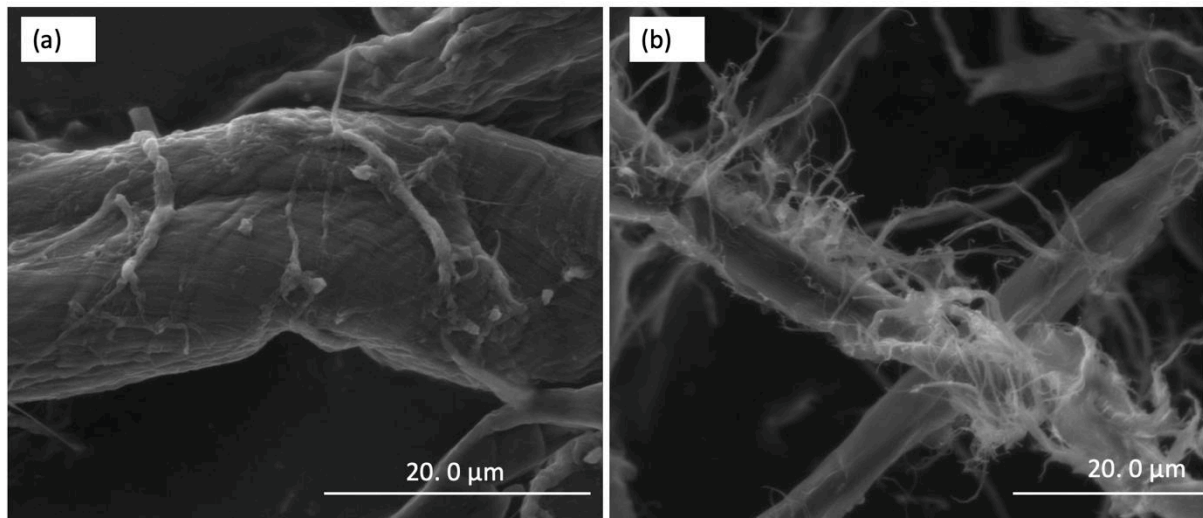


Figure 91. SEM images of air-dried (a) and freeze-dried (b) Valley beater refined pulp (SR° 85).

Conclusions on chapter 4

Fiber swelling is a prerequisite for dissolution thus, the swelling capacity in 12% NaOH and in dilute cupric ethylenediamine (CUEN) solution was determined. From the result, high purity pulp produced from a coupling of mechanical refining prior to CCE had better swelling than unrefined subjected to similar chemical treatments.

Also, Solubility studies performed on the extracted pulp showed that treatments in which mechanical refining was applied had better solubility in 8% NaOH at -10°C and high Fock reactivity than unrefined pulp. Refined pulp extracted with 6% soda had the best result with Fock reactivity ranging from 60-70%, which exceeds those obtained for prehydrolysis kraft dissolving pulp (PHK) (49%). Higher caustic soda charge (10%) did not lead to better Fock reactivity because of the transformation of cellulose I to cellulose II, which was also favored by the refining. The presence of cellulose II is a problem because of the creation of a denser fibril network in cellulose fibers upon drying.

Good correlation was found between swelling measurements, solubility in NaOH, and Fock reactivity. This would make it possible to consider replacing the realization of tedious Fock measurements, made problematic due to the use of CS₂. Finally, the results showed that the crystallinity index was influenced by mechanical refining, the strength of the NaOH used in the extraction process and the drying method. This was particularly interesting because we found a correlation between the Fock reactivity and the crystallinity index.

Chapter 5: Xylan Extraction, Recovery, and Characterization

Overview of chapter

Obtaining a dissolving pulp from a paper pulp is difficult for two main reasons. The first lies in the fact that the xylan molecules retained in the paper pulp would be largely bound to the residual lignin or what remains of it and perhaps also to the cellulose. The second reason is the large quantity to be removed since a paper pulp from hardwoods can contain more than 20% of xylans. The previous chapters have shown that 80-90% of xylans in a paper pulp could be removed by associating the effect of refining with that of alkaline extraction, possibly associated with treatment with a xylanase. As a result, the proposed methods release a large quantity of xylans which can in theory be recovered and upgraded. The advantage of applying an extraction by soda (CCE) is that the xylan molecules are extracted in the polymeric form a priori identical to what they were in the pulp. The aim of this chapter is to study the recovery of these polymers dissolved in sodium hydroxide and to determine their molecular weight distribution (MWD) and their solubility in different solvents in order to provide the data necessary for their valorization.

5.1. Effect of xylan recovery method on solubility

In this study, the first method used to recover the extracted xylan in the CCE filtrate was adopted from the work of (Gong et al., 2017). In this procedure, the xylan was recovered by sequential ethanol extraction, first at 25% (to extract the high molecular weight xylan) and then with 50% ethanol solution (to extract the low molecular weight fraction). After a series of washes with ethanol, the xylan was oven-dried under vacuum at 60 °C (Figure 92a). After drying, the recovered xylan became compact and difficult to handle. Further processing was challenging as the xylan could not be redispersed in water. As a result, a different method for the xylan recovery involving precipitation of the extracted xylan by neutralizing with acetic acid was performed. The recovered xylan was concentrated by centrifugation, purified with methanol, and freeze-dried. As shown in Figure 92 b, the second

method proved to be more suitable and produced samples of xylan in white powder form.

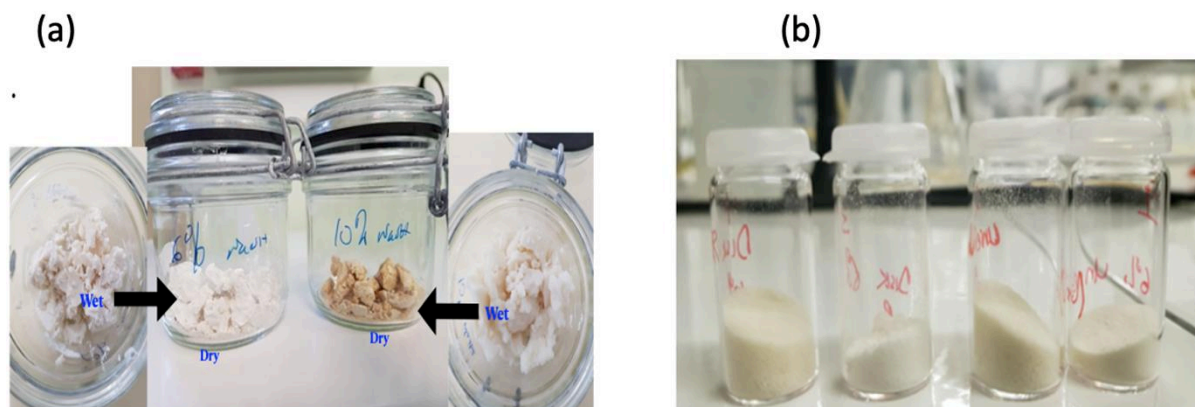


Figure 92. Recovered xylan (a) ethanol precipitated and oven-dried at 60 °C under vacuum (b) precipitated by neutralization with acetic acid and freeze-dried.

The recovered xylan was obtained by this method from unrefined and refined pulp at 6% and 10% soda concentrations. The purpose was to study the effect of refining and the soda concentration on the molecular weight of the recovered xylan. The recovered xylan was easily dispersed but not soluble in water, even at a high temperature (70 °C). In contrast, the commercially available beechwood xylan, directly extracted from wood, was water-soluble. Figure 93 is a picture of the dissolution behavior of the recovered xylan and commercial beechwood in a 6% NaOH solution. The recovered xylan extracted at a high soda concentration (10%) was slightly soluble, while xylan extracted at a lower soda concentration (6%) did not solubilize. According to (Kim et al., 2019), inaccessible xylan recovered from hardwood dissolving pulp contained more Methyl glucouronic acid (MeGlcA) moieties than the accessible xylan. This makes sense since these latter xylan molecules, being hidden in the wall of the fibers, were likely less modified by the kraft cooking reagents. By contrast, accessible xylan has been modified during the kraft cook. Besides, part of the accessible xylan consists of molecules, dissolved in the kraft black liquor under the cooking conditions and which precipitated in and on the fibers during cooling. Thus, it is plausible that they might have undergone more chemical modifications (cleavage of the MeGlcA units) than the inaccessible xylan.

Therefore, the solubility behavior illustrated in (Figure 93) could be explained by fewer MeGlcA units on the accessible xylan extracted with 6% soda compared with the xylan extracted with 10% xylan.

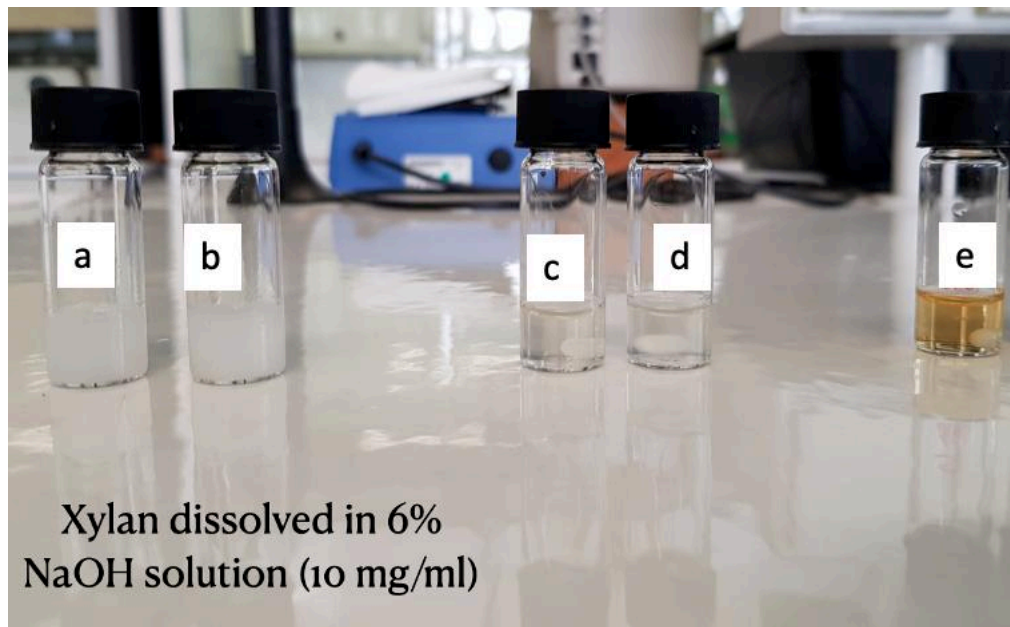
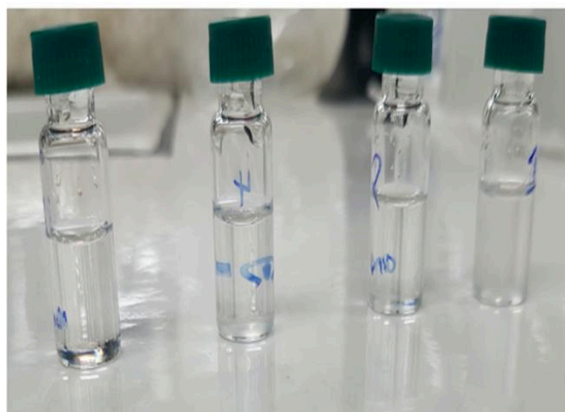


Figure 93. Dissolution in 6% NaOH solution (a) xylan extracted from unrefined pulp with 6% CCE (b) xylan extracted from refined pulp with 6% CCE (c) xylan extracted from unrefined pulp with 10% CCE (d) xylan extracted from refined pulp with 10% CCE (e) commercial beechwood xylan.

However, the recovered xylan was visibly soluble in some organic solvents such as DMSO and DMAc/LiCl (8%), as shown in (Figure 94). This will allow for the measure of their molecular weight distribution.

(a) Dissolution in DMSO



(b) Dissolution in DMAc/LiCl (8%)



Figure 94. Clear solutions of recovered xylans in some organic solvents (10 mg/mL) (a) (from left to right, xylan extracted from refined pulp with 6% CCE; xylan extracted from refined pulp with 10% CCE; xylan extracted from unrefined pulp with 10% CCE; xylan extracted from unrefined pulp with 6% CCE), (b) (from left to right, xylan extracted from unrefined pulp with 6% CCE; xylan extracted from unrefined pulp with 10% CCE; xylan extracted from refined pulp with 10% CCE; xylan extracted from refined pulp with 6% CCE).

The IR spectra of xylan extracted from unrefined and refined pulps at 6 and 10% CCE are shown in Figure 95. The analysis was performed to compare the characteristic IR bands of the extracted hardwood paper pulp xylan with the commercial beechwood xylan. Some difference was observed in the absorption intensity of the samples for the features of OH adsorbed water molecules at 1638 cm^{-1} and 3454 cm^{-1} (Zhiwen Chen et al., 2015; Sharma, Morla, et al., 2020). However, on comparing the spectrum of the commercial wood xylan to that of the bleached paper pulp extracted xylan, some characteristic absorption bands at 1744 cm^{-1} , 1719 cm^{-1} , and 1658 cm^{-1} attributed to C=O stretching in carboxylic acid, C=O stretching in carboxylic acid dimers, and C=O and C-O stretching in carboxylates (COO^-) respectively were visible for commercial wood xylan (Buslov et al., 2009; Zhiwen Chen et al., 2015; Westbye et al., 2008) and much less for the extracted xylans.

This indicates that a large part of the acetyl and glucuronic acid groups in the wood xylan were still present, unlike in the paper pulp xylan, where they are cleaved during the pulping and bleaching stages. The lack of MeGlcA in xylan obtained from bleached paper pulp has been linked to solubility problems, particularly in aqueous solvents (Pinto et al., 2005).

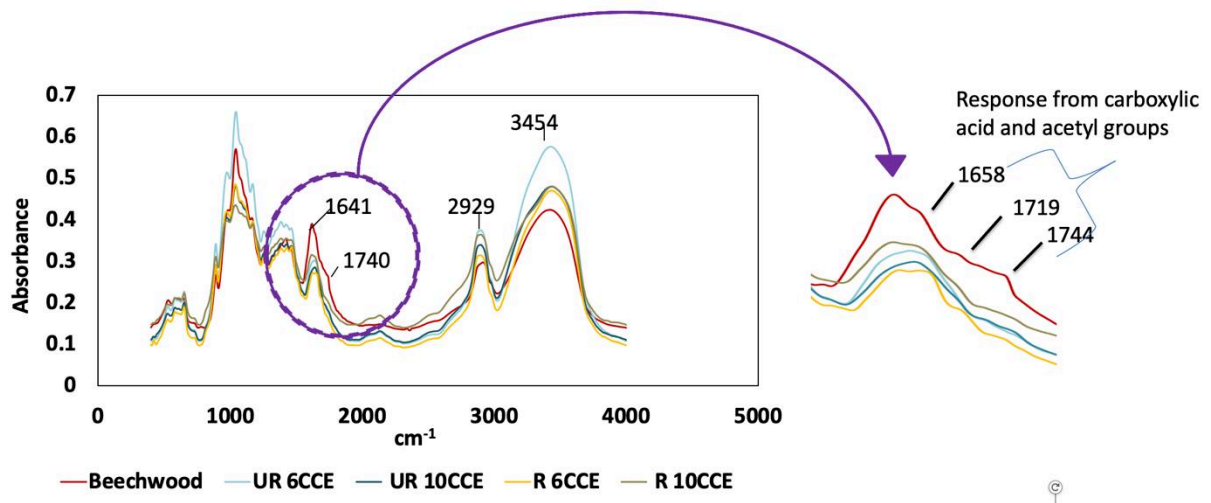


Figure 95. IR spectra of xylan extracted from unrefined and refined pulp with 6% CCE and 10% CCE: (UR 6CCE) represents xylan extracted at 6% CCE from unrefined pulp; (UR 10CCE) represents xylan extracted at 10% CCE from unrefined pulp; (R 6CCE) represents xylan extracted at 6% CCE from refined pulp; (R 10CCE) represents xylan extracted at 10% CCE from refined pulp.

5.2. Molecular weight determination of the recovered xylan

Some studies have shown that hemicellulose extraction conditions influence the chemical characteristics of the extracted xylan (Gomes et al., 2020; Kim et al., 2019). Mechanical refining of pulp prior to xylan extraction has been reported to increase extraction yield as the refining action creates accessibility. Likewise, the soda concentration employed for the extraction should influence the molecular weight of the xylan recovered. Low soda concentrations (5%) would extract lower molecular weight xylan than the high molecular weight xylan extracted at 10% NaOH. To determine the contribution of mechanical refining and extraction conditions on the modification of the molecular weight of the recovered hemicellulose fraction, three commonly used methods for gel permeation chromatography (GPC) in the literature were consulted to determine the best method for molecular weight characterization of bleached hardwood xylan.

5.2.1. Molecular weight determination in aqueous medium

In the first method, the determination was done in an aqueous medium by dissolving the samples with the eluent and filtering through 0.2 μm before injection onto two Shodex OHPak SB 806 M HQ columns placed in series at a temperature of 30 °C. The eluent used was 0.1M sodium nitrate + 0.03% sodium azide at a flow rate of 0.5 ml / min. Detection was performed using a Wyatt refractometer, a Shimadzu UV detector at the wavelength of 280 nm, and a Wyatt 3-angle light scattering detector. Three distinct signals from the light scattering (LS), refractive index (RI), and UV (280 nm) are shown in (Figure 96). The UV signal appeared in all the samples, and in the range of the determination, we observed an overlapping of the UV, RI, and the LS signals between the elution times of 47-52.5 min. Calculation of the molecular weight of the extracted xylan was determined in that region (47-52.5 min), because that was where the RI signal reached a maximum, and it represented the soluble fraction of the sample. The LS detector response reached a maximum outside this region, precisely between elution times of 25-47 min. This broad peak (LS signal) observed in all the samples must represent aggregates that could not be well dispersed. The presence of the strong UV signal in all the samples, especially in the unrefined pulp extracted with 10% soda and in the refined pulp, was unexpected as the starting pulp was bleached. The UV signal detected at 280 nm is typically associated with aromatic structures and it was visible in both aggregates and soluble xylan. This indicates a strong interaction between the xylan molecules and aromatic structures that are most likely lignin carbohydrate complexes (LCC) (Stoklosa & Hodge, 2012; Westbye et al., 2008). The presence of the LCC could explain the difficulties encountered in the total elimination of residual hemicelluloses from the pulp.

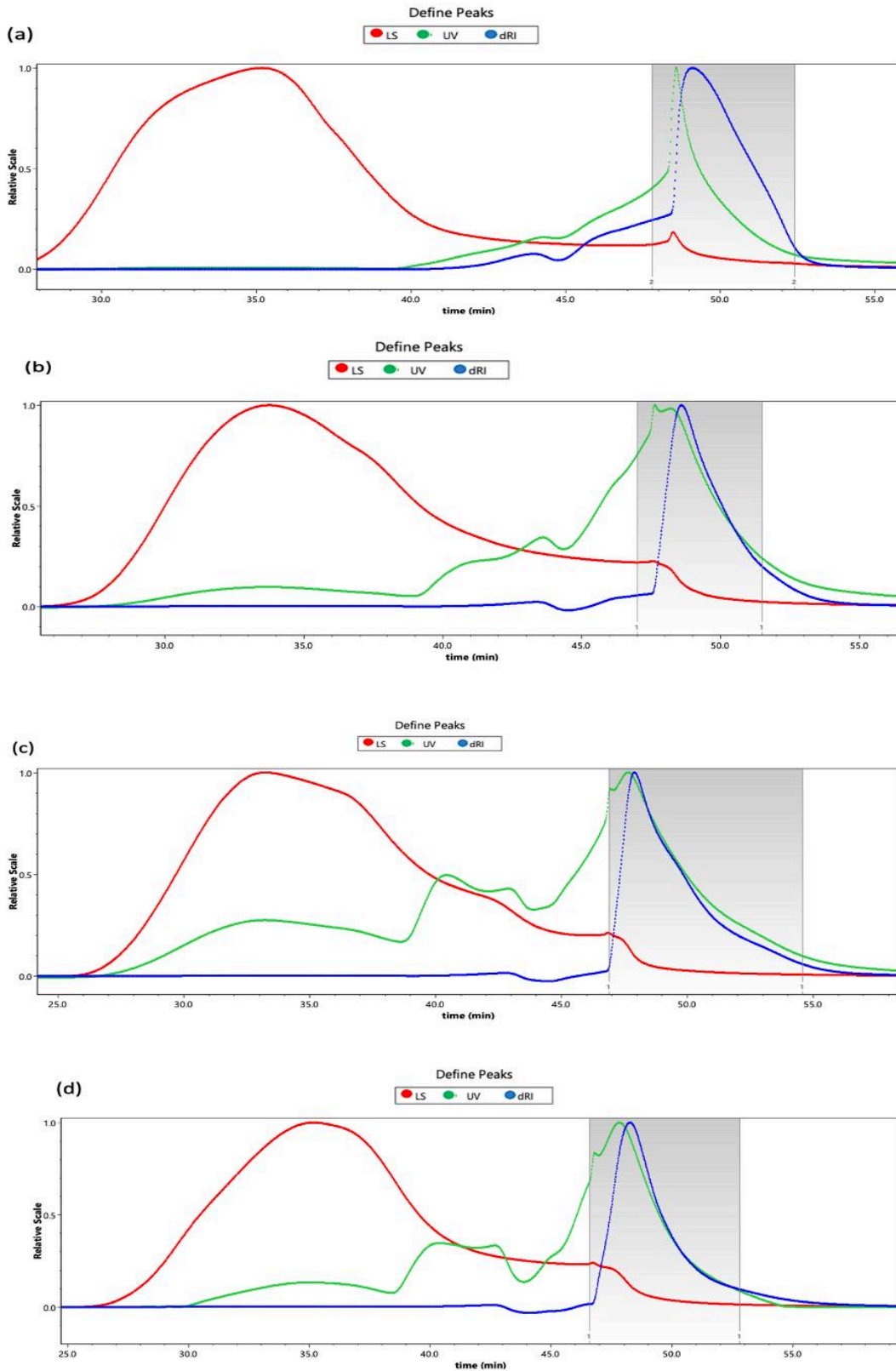


Figure 96. Molecular weight determination of recovered xylan by GPC-MALS (a) xylan extracted from unrefined pulp at 6% CCE (b) xylan extracted from unrefined at 10% CCE (c) xylan extracted from refined pulp at 6% CCE, (d) xylan extracted from refined pulp at 10% CCE.

In Table 20, the average molecular weights, polydispersity index, and number average degree of polymerization is shown. For the unrefined pulp, it can be seen that increasing the soda concentration from 6% to 10% increased the DPn of the extracted xylan. For the refined pulp, refining enabled the extraction of high molecular weight xylan at 6% soda while increasing the soda concentration to 10% coupled with the fragile state of the fibers due to mechanical refining might have degraded the extracted xylan (Kim et al., 2019). Furthermore, since the DP of native xylan (wood xylan) is only about 200, it is apparent that the large quantity of the aggregates and LCC influenced the results of the DP obtained. It is logical to conclude that the results might have been inflated. These values are in the same range as the values obtained for native xylan, as reported by (Vena et al., 2013).

Table 20. Average molecular weight, number average degree of polymerization, and the polydispersity index of xylan extracted from bleached hardwood determined by dissolving xylan in an aqueous medium.

samples	Mn (K Da)	Mw (K Da)	PDI	DPn
UR 6CCE	18.6	23.7	1.27	141
UR 10CCE	48.5	89.1	1.84	367
VB 6CCE	73.3	102.2	1.39	555
VB 10CCE	44.0	65.3	1.48	333

5.2.2. Molecular weight determination in organic medium (direct dissolution in DMAc/LiCl 8%)

The molar weight of the recovered xylan was determined by performing a dissolution in Dimethyl acetamide (DMAc/LiCl 8%) preceded by a series of solvent exchange steps that facilitates the dissolution process (details in the methodology chapter). The analysis was performed with a GPC MAX VE2001, equipped with Viscotek light scattering, RI and UV detectors. Chromatograms obtained for the recovered xylan are shown in Figure 97. By contrast with what was observed in water the distribution is much nicer with less distortion due to aggregates. The condition of extraction slightly influenced the molecular weight distribution as higher

molecular weight xylan were extracted with the coupling of refining and CCE. This becomes apparent when the DPn values were compared. The number average and weight average molecular masses (M_n , M_w), number average DP, and polydispersity index presented in Table 21. As expected, higher masses were extracted with high soda concentration (10%), and the DP values were higher for refined pulp. Also, the polydispersity index obtained was between (1.06-1.18) which was lower than was recorded for the determination in the aqueous phase (1.27-1.84).

Some signals were detected by the light scattering detector that corresponded to aggregates, but they were not as strong as observed in the previous method (GPC carried out in the aqueous phase). The DPn values obtained with this method ranged from 135 - 177 (Table 21), which was slightly lower than reported in some studies ([Hakala et al., 2013](#); [Laine et al., 2016](#)). However, it was consistent with other reports in the literature ([Gehmayr et al., 2011](#); [Gomes et al., 2020](#); [Marques et al., 2019](#)). These values show that after pulping and bleaching the average size of residual xylan is not very far from that in wood. Higher molecular weight xylan appears to have been extracted from the disc refined pulp at 10% CCE compared to the other treatments (valley beater refined pulp extracted at 10% CCE). This could be related to the severity of the refining treatments because the disc refining treatment was not as severe as the Valley beater refining, one can imagine that since the fibers suffered less damage, the extraction at 10% CCE does not degrade the high molecular weight. Although the UV signal (280 nm) was not included in Figure 97, it was detected in all the samples analyzed, which agreed with the finding of the previous method (GPC/aqueous medium).

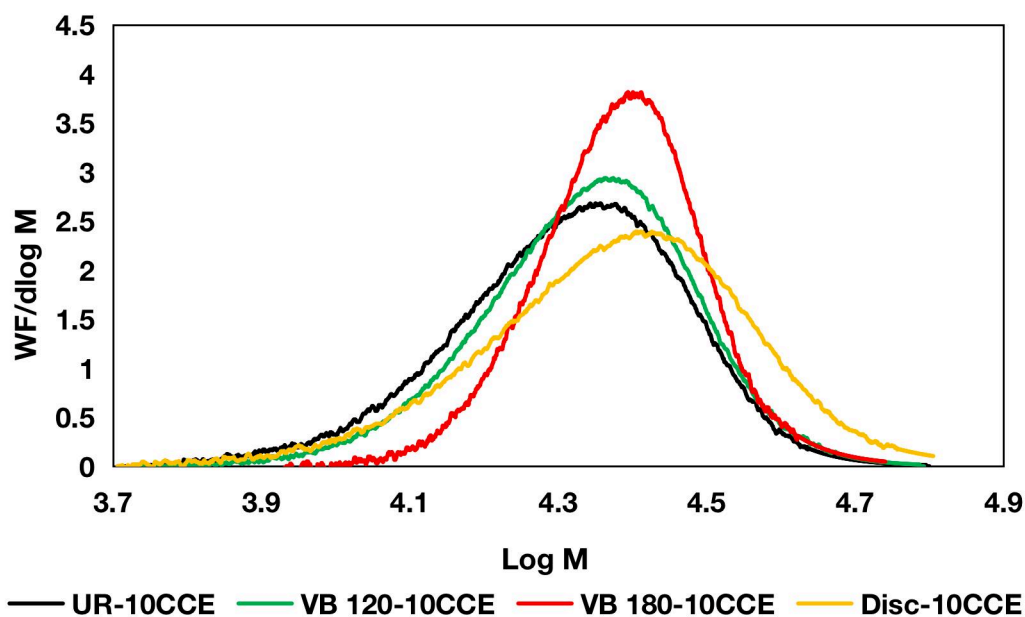


Figure 97. Molecular weight determination of recovered xylan dissolved in DMAc/LiCl (8%) by GPC-MALLS for xylan extracted at 10% CCE (xylan extracted from: Unrefined (UR), Valley beater refined for 120 minutes (VB 120), Valley beater refined for 180 minutes (VB 180), Disc refined (Disc); CCE at 10% soda concentration (10CCE)).

Table 21. Average molecular weight, number average degree of polymerization, and the polydispersity index of xylan extracted from bleached hardwood determined by dissolving xylan in DMAc/LiCl (8%) (Mw of xylose 132 g/mol).

Samples	Mn (Da)	(K Mw Da)	(K DPn	PDI
UR-6CCE	17.9	19.7	135	1.10
UR-10CCE	19.3	21.9	146	1.13
VB 120-6CCE	18.0	19.2	136	1.06
VB 120-10CCE	20.7	23.0	156	1.11
VB180-6CCE	21.1	22.8	160	1.08
VB180-10CCE	23.4	24.9	177	1.07
Disc-6CCE	18.6	20.1	141	1.08
Disc-10CCE	21.8	25.6	165	1.18

5.3. Molecular weight determination in organic medium (xylan carbanilate)

The recovered xylan was derivatized to the carbanilates prior to the GPC analysis. This method was performed in an effort to improve solubility and limit the formation of aggregates. The analysis was performed with a GPC MAX VE2001, equipped with Viscotek TDA 302 triple detector array (RI+DP+LSD) and UV detectors. Figure 98 presents the molecular weight distribution profile of the xylan carbanilate. Firstly, it can be seen that the recovered xylan had a higher molecular weight than the commercial beechwood xylan. Also, higher molecular weight xylan was extracted with 10% soda compared to 6% soda except in (VB 180) sample, which experienced more mechanical refining treatment than the others. The values for the number average molecular weight (M_n), weight average molecular weight (M_w), DP_n , and polydispersity index are shown in Table 22. The highest DP_n values were obtained for the xylan extracted from the Valley beater refined pulp (VB 120 and VB 180). When the severity of the refining treatment was increased (VB 180), the morphological properties of the fibers were changed to improve accessibility so that at 6% CCE, the highest DP was obtained (99). On further increasing the soda concentration, rather than a corresponding increase in the molecular weight of the extracted xylan as observed in the other samples and supported in the literature, a decrease in the molecular weight was recorded. The plausible reason for this is that coupling strong soda extraction (10% CCE) with the fragile state of the fibers resulted in some degradation of the xylan structure. More so, the polydispersity index was low, which agreed with findings in the literature ([Marques et al., 2019](#); [W. Zhang et al., 2016](#)). Still, they were slightly higher than those obtained in the direct dissolution with DMAc/LiCl (8%).

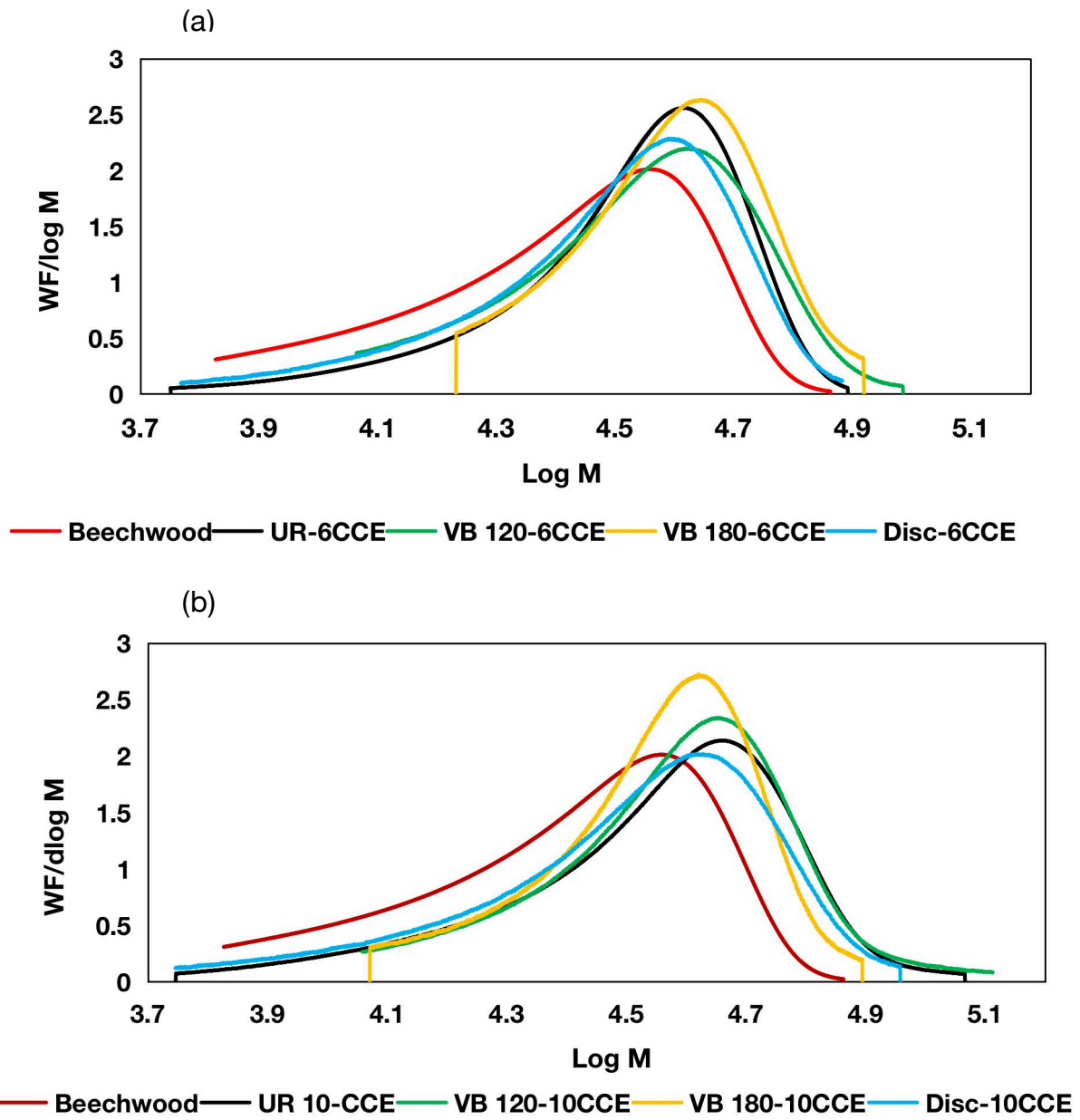


Figure 98. Molecular weight determination of recovered xylan carbanilate determined by GPC-MALLS for xylan extracted at 6 (a) and 10% (b) CCE (xylan extracted from: Unrefined (UR), Valley beater refined for 120 minutes (VB 120), Valley beater refined for 180 minutes (VB 180), Disc refined (Disc); CCE at 10% soda concentration (10CCE)).

Table 22. Average molecular weight, number average degree of polymerization, and the polydispersity index of xylan carbanilate extracted from bleached hardwood determined by GPC-MALLS (Mw of derivatized xylose 370 g/mol).

Sample	Mn (kDa)	Mw (kDa)	DPn	PDI
Beechwood xylan	21.9	28.6	59.1	1.31
UR-6CCE	28.7	35.8	77.7	1.24
UR-10CCE	28.9	39.3	78.2	1.36
VB 120-6CCE	31.3	37.9	84.6	1.21
VB 120-10CCE	33.9	41.7	91.7	1.23
VB180-6CCE	36.5	41.3	98.6	1.13
VB180-10CCE	32.1	37.4	86.8	1.17
Disc-6CCE	26.2	33.7	70.9	1.28
Disc-10CCE	26.3	36.0	71.2	1.37

The UV signal was also detected in the molecular weight characterization of the xylan carbanilates. Just as reported in the GPC-MALS performed in an aqueous medium, an overlapping of the RI and UV signal was seen (Figure 99). This confirmed the presence of lignin-carbohydrate complexes (LCC) in close interaction with the xylan molecules. Additionally, some aggregates were observed, but they were not as pronounced as obtained in the previous procedures.

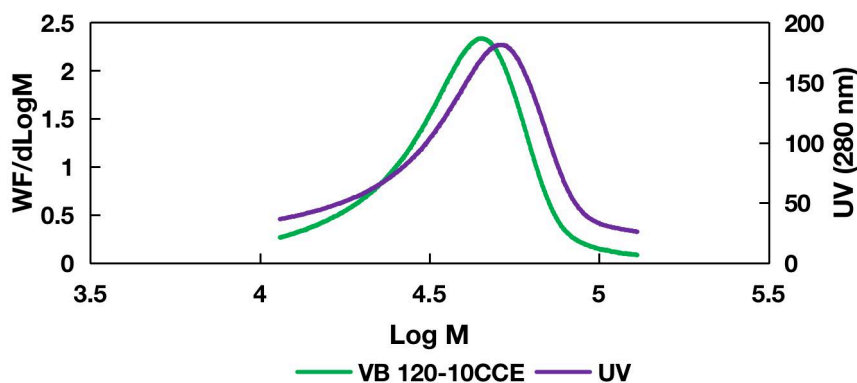


Fig. 99. Molecular weight distribution profile and the UV signal obtained from the xylan carbanilate GPC analysis.

From the result of the analysis of the carbohydrate composition (Figure 100), it was observed that degraded celluloses co-extracted with xylan were detected as glucose in the recovered xylan. In fact, the absence of mannose excludes that the glucose comes from glucomannan. In refined pulps, especially when extracted with 10% soda, the residual cellulose composition in xylan amounts to over 10%. Therefore, glucose detection in the sugar analysis indicated that some loss in the cellulose chain (degradation) occurred during the extraction process. If we recognize the occurrence of cellulose degradation accelerated by the coupling of refining with alkali treatment during the xylan extraction process, then a corresponding xylan degradation in a similar condition cannot be completely ruled out. The presence of low molecular weight cellulose and LCC in the recovered xylan could have contributed to the formation of aggregates and perhaps also responsible for the inflated DP_n values obtained for xylan dissolved in the aqueous medium.–

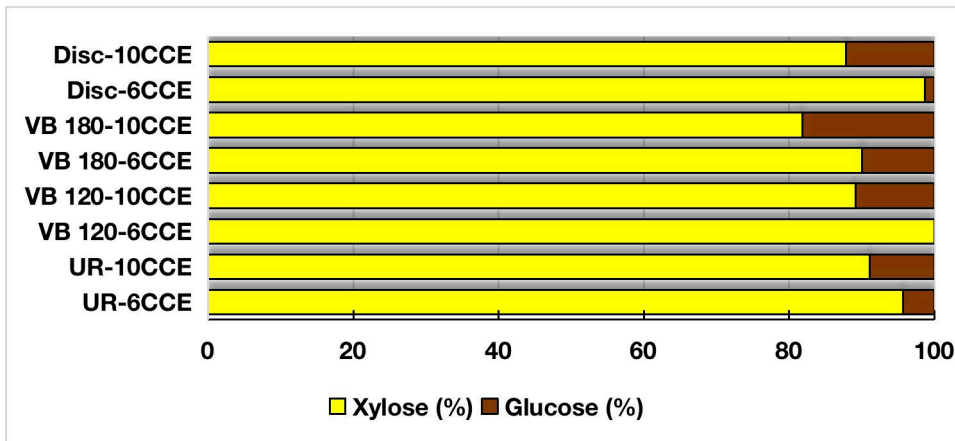


Figure 100. Carbohydrate composition of the recovered xylan.

Figure 101 compares the molecular weight distribution profile of the recovered xylan, extracted pulp (VB 120-10CCE) and the reference pulp. The hemicellulose extracted (xylan) fell within the expected molecular weight region ($10^{3.5}$ and 10^5). In the extracted pulp containing about 3% residual xylan there was a fraction of low molecular weight polysaccharides still in the hemicellulose region. It is unlikely that it only represents residual hemicellulose in the extracted pulp, but it is reasonable to assume that part of this low molecular weight fraction is degraded cellulose.

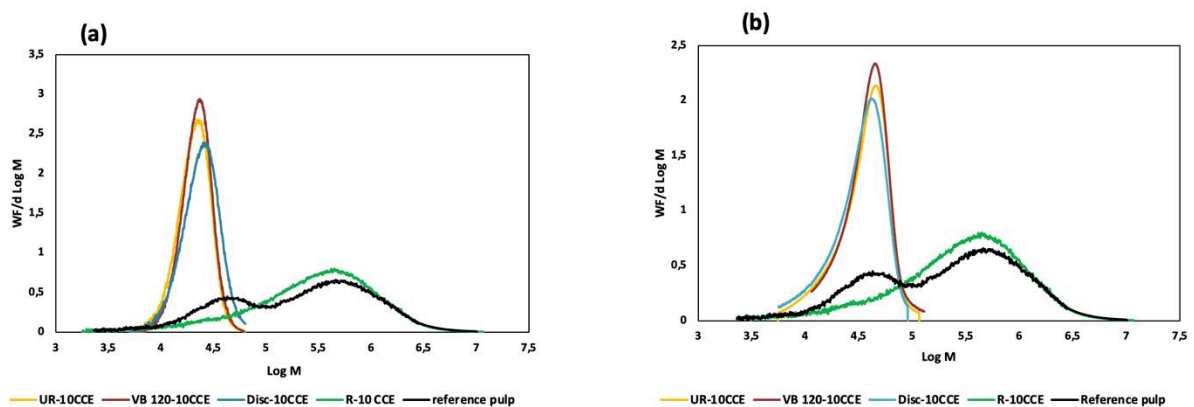


Figure 101. Molecular weight distribution profile of extracted xylan, extracted pulp, and the reference pulp (a) (dissolution in DMAc/LiCl) (b) (dissolution by derivatization- xylan dicarbanilate).

5.4. Molecular structure of the extracted xylan analyzed by MALDI-ToF-MS

The molecular structure of the extracted xylan was further studied by the MALDI-ToF mass spectrometry, which was carried out in linear mode. The MALDI spectrum gives information on the molecular structure of oligomers that make up the polysaccharide. For instance, the molar mass of the repeating unit, type, and quantity of side groups contained in the polymer can be detected. MALDI -ToF-MS is not well suited to the study of high molecular weight polymers. In our case the previous sections indicated that the average DP was above 70 which is rather high. In fact, It was reported that the molar mass of polymers with a broad molecular weight distribution was not accurately determined by MALDI analysis as the high molecular weight fractions were excluded from the analysis so that peaks resulting from high molecular weight fractions are unresolved. It was shown that separating the polymer into fractions by size exclusion chromatography prior to MALDI analysis allowed for better resolution of the high molecular weight fractions ([Jacobs & Dahlman, 2001](#))

The MALDI -ToF-MS spectra of 4 recovered xylan samples are shown in Figures 102 and 103. As depicted, each spectrum was composed of a broad distribution of peaks until an m/z ratio of 6000 (DP around 50). We could see resolved signals of xylan fragments from DP 5 to 50. In Figure 104, the complete spectrum obtained for one of the samples analyzed is shown (unrefined pulp extracted with 6% NaOH). It is seen that peaks corresponding to molar masses much greater than 6000 were detected, but they were of low intensity and unresolved.

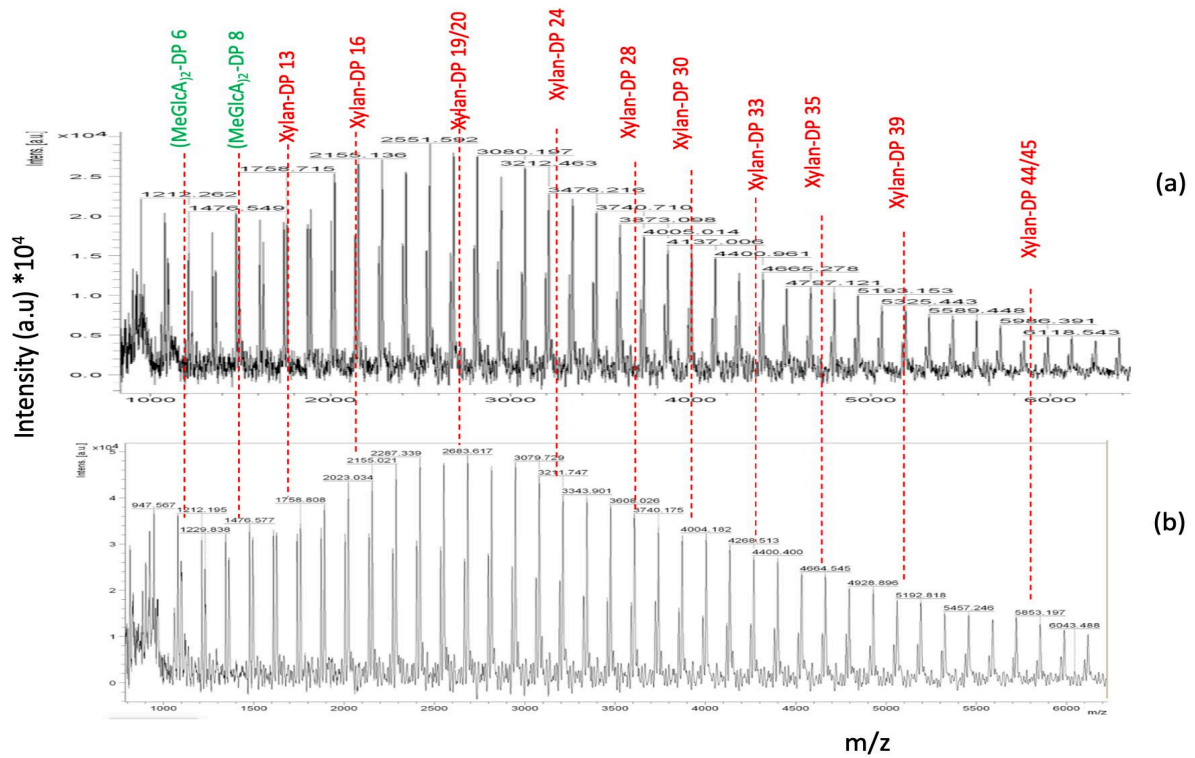


Figure 102. MALDI-ToF-MS spectra of (a) xylan extracted from unrefined pulp with 6% NaOH (b) xylan extracted from unrefined pulp with 10% NaOH.

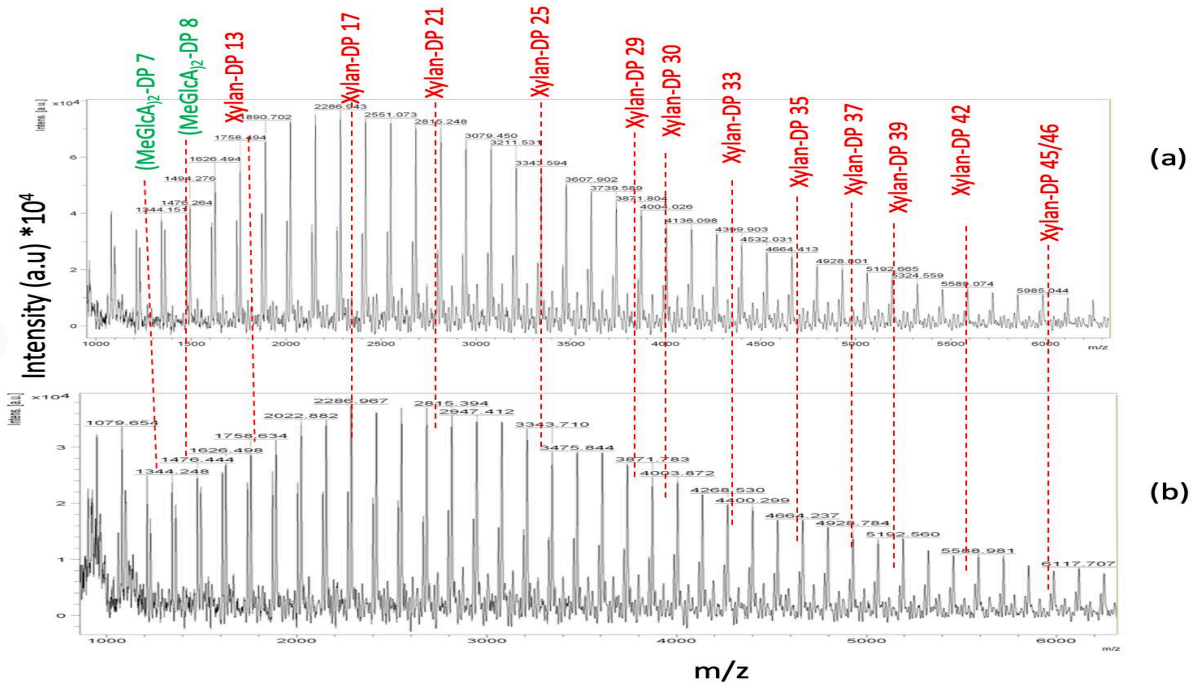


Figure 103. MALDI-ToF-MS spectra of (a) xylan extracted from disc refined pulp with 6% NaOH (b) xylan extracted from disc refined pulp with 10% NaOH.

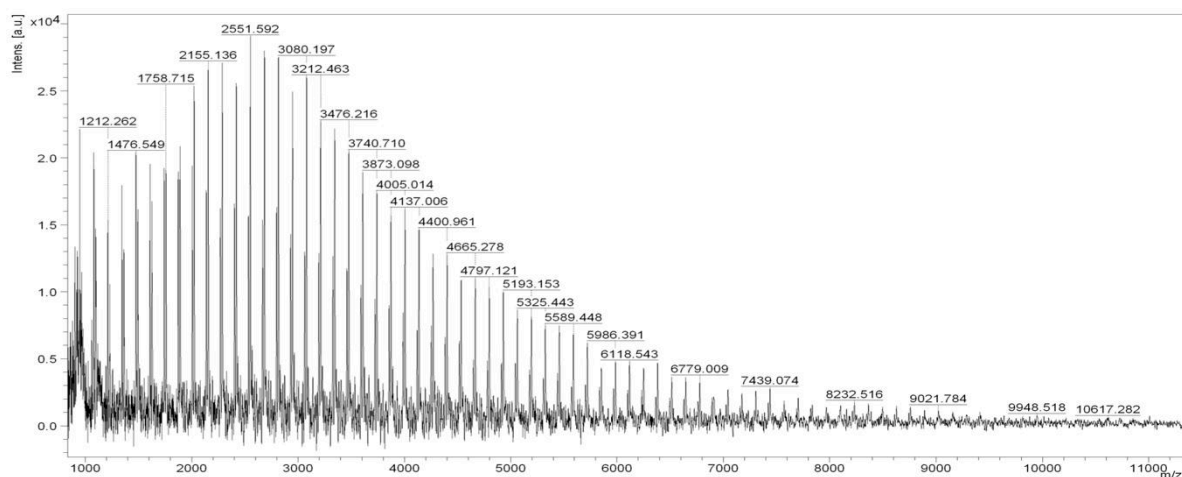


Figure 104. MALDI-MS spectrum of extracted xylan (unrefined pulp extracted with 6% NaOH) showing unresolved peaks contributed by high masses.

The molar mass values of the 4-O-methyl glucuronic acid (MeGlcA) moieties were detected in trace amounts for all the samples, but no acetyl moiety was seen. In particular no xylan molecule of DP higher than 6 carries such MeGlcA group. This agrees with the IR observations and further explains why the xylan was difficult to dissolve (WHISTLER, 1973). Therefore, the data obtained from the MALDI-MS analysis indicated that the xylan recovered was of rather high molecular weight (wide range of DP, up to values much higher than 50) and essentially linear with very few side groups, which is consistent with several literature reports (Jacobs & Dahlman, 2001; Pinto et al., 2005).

Conclusions on chapter 5

Xylan removed from paper pulp by cold caustic extraction combined with refining could be recovered in a rather pure form by precipitation with addition of acetic acid. The size of the xylan molecules was studied by size exclusion chromatography. Dissolution in DMAc/ LiCl (8%) or the derivatization method (xylan carbanilate) enabled good dissolution and reduced the formation of aggregates compared to direct dissolution in alkaline aqueous medium. In addition, depending on the dissolution method (direct or by derivatization), a significant difference was observed in the molecular mass obtained. The DP_n values obtained for the dissolution in DMAc / LiCl (8%) were in the range of 135-177, while they were 71-99 for the xylan carbanilate. Determination by derivatization gave fewer aggregates and is likely to be more accurate. Anyways these values show that the xylan dissolved were of rather high molecular weight. This study found that extraction conditions such as mechanical refining and soda concentration influenced the chain length of the extracted xylan. In fact, the DP of xylan extracted from paper pulp after preliminary refining exhibited a higher value than for the unrefined pulp. Likewise, increasing the caustic soda concentration allowed xylans of greater mass to be dissolved. However, the conjunction of the two effects was not always verified and it appeared that the combination of a powerful refining and a high level of caustic soda charge (10%) could have a degrading effect on the xylan molecules. Therefore, If the preservation of the molecular weight of the xylan is desired, then coupling extreme refining with mild CCE refining (e.g. 6%) would be the best option.

From the MALDI analysis, only traces of MeGlcA units were detected in the extracted xylan, supporting previous reports on the linear form of bleached kraft paper pulp (kraft) xylan.

Chapter 6: Methodology

6.1. Materials

Bleached mixed hardwood kraft dry sheets were supplied by Fibre Excellence St-Gaudens, a paper mill in France. The xylan content, degree of polymerization, and other characteristics of the starting pulp are presented in Table 23. No other hemicelluloses were present in a significant amount except for xylan.

Table 23. characteristic of starting pulp.

Sample	Pulp
Fiber length (mm)	0,685
WRV %	103
DPv	1294
SR°	17
Glucan %	80,5
Xylan%	20

Commercial enzymes purchased from Megazyme were used in the study. The endo-1,4- β -D-xylanase was obtained from *Neocallimastix patriciarum* (E-XYNP) with a specific activity of 600 U/mg protein (on wheat arabinoxylan). According to the supplier, the optimum temperature and pH were 50 °C and 6, respectively, and the molecular weight was approximately 25800 Da. The second enzyme used was cellulase (endo-1,4- β -D-glucanase), obtained from *Bacillus amyloliquefaciens* with a specific activity of 63 U/mg protein (on carboxymethyl cellulose). The molecular weight provided by the supplier was 34300 Da. Both enzymes were supplied as an ammonium sulfate suspension in 0.02% (w/v) sodium azide.

6.2. Mechanical refining

Mechanical treatment was performed on the PFI mill, Valley beater (Voith, Heidenheim, Germany), and the disc refiner pilot. When the refining was performed on the PFI mill, 30 g of the dry pulp was soaked overnight and disintegrated with the Lhomargy blender for 5 min. After that, the pulp suspension was concentrated by filtration until a pulp consistency of 10%. The suspension was then evenly

distributed on the wall of the refining chamber and refined to the desired SR° by controlling the revolutions. On the other hand, for refining on the Valley beater, an equivalent of 440 g (oven-dried weight) of pulp was soaked in 2 L tap water overnight and then drained and disintegrated with a pulper for 10 min. The disintegrated pulp correctly diluted to 22 L (making a pulp consistency of 2%) was then transferred into the beater and refined to the desired Schopper-Riegler value (°SR). Three refining loads, 3 kg, 4.5 kg, and 5.5 kg, were selected and tested to determine the load that would produce morphological modifications best suited for optimum hemicellulose removal. Likewise, when the refining was performed on the disc refiner pilot, the pulp was soaked for several hours prior to the refining process. About 10.35 kg (oven-dried weight) of the pulp was dispersed in 345 L of water, making a pulp consistency of about 3%. The refining was carried out at a flow rate of 10.3 and different Pnet values (4kW, 8kW, and 12kW) until the desired SR° was reached. The plate characteristics and other refining conditions applied are shown in Figure 105. At the end of the refining and characterization process, the refined pulp was centrifuged to remove excess water, placed in a polyethylene bag, and refrigerated until further analysis.

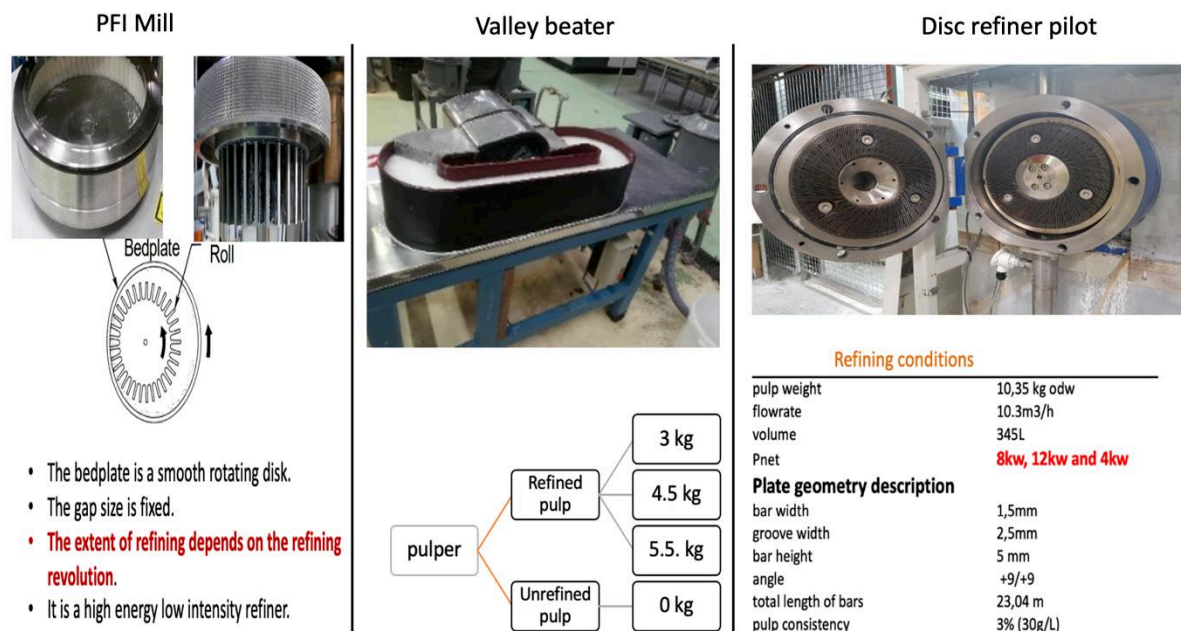


Figure 105. Refiners used for the study.

6.3. Fines removal

To improve hemicellulose removal, the effect of fines fractionation prior to the CCE treatment was investigated using Bauer McNett fiber classifier. The Bauer McNett fiber classifier, which is used in the fractionation of pulps according to weighted average fiber lengths, was adopted for this study. It should be noted that the Bauer McNett classifier was only employed in this study to remove fines. The screen size selected for the study were 28, 48, 65, and 150. In the interest of this study, fines were described as particles that were not retained on the final screen (150). By calculations, these particles had a length of $\leq 0.43\text{mm}$, which was slightly higher than the average length determined by the MorFi (280 mm). The fiber length as determined by the MorFi was used in this study and not the calculated fiber length by the Bauer McNett fiber classifier. A schematic representation of the Bauer McNett fiber classifier is shown in Figure 106. A diluted fiber suspension containing 10 g (odw) of pulp was gradually poured into the first cylinder equipped with screen 28 placed on the side (with an orifice where fibers could pass through into the next cylinder). This process occurred under constant agitation for a period of 20 min.

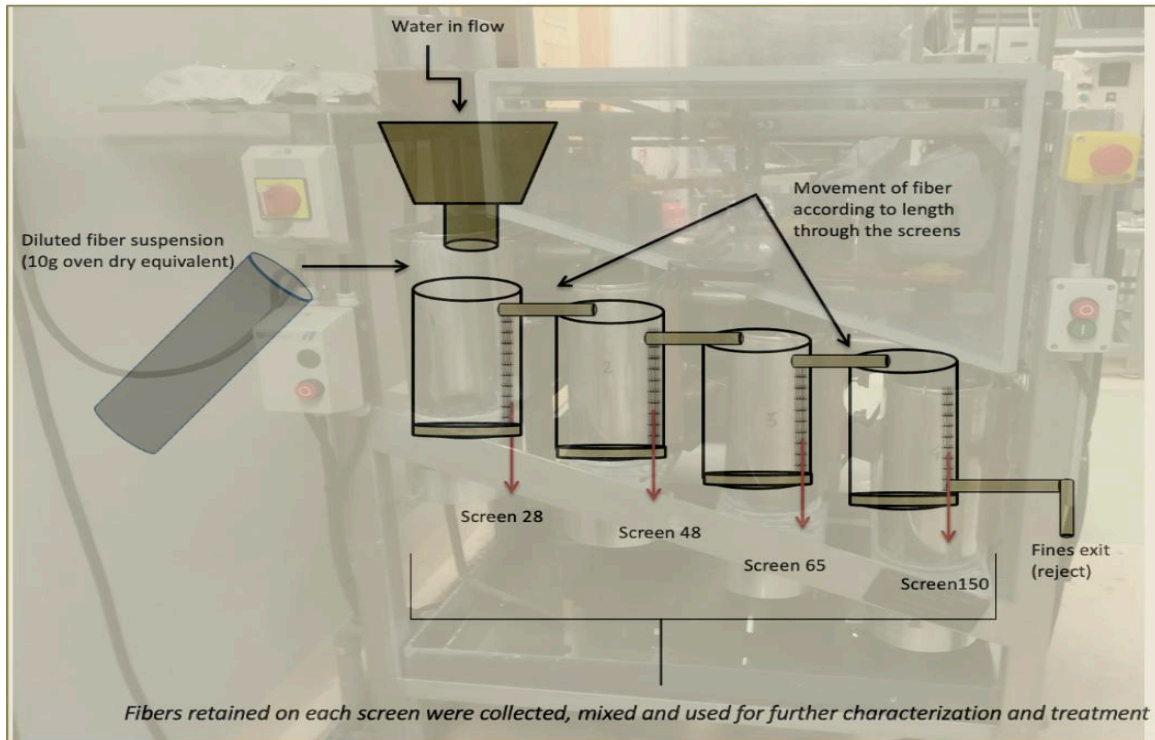
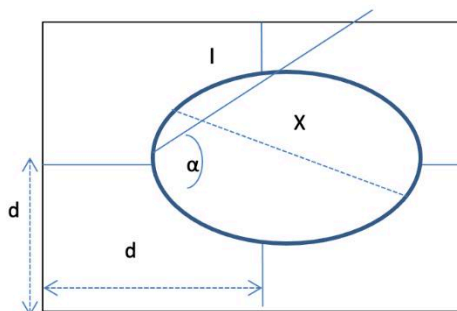


Figure 106. Schematic representation of the Bauer McNett fiber classifier.

$$Fine (\%) = \frac{10 - (m_{28} + m_{48} + m_{65} + m_{150})}{10} \times 100 \quad (4)$$

where m is mass of fiber retained on each screen.

In determining the fiber length from the Bauer McNett fiber classifier, It is assumed that the fiber passes through the screen when the entire disc X is contained in 4 meshes, as demonstrated below.



Therefore, the fiber length is determined as follows;

$$L \leq \frac{4 \cdot d}{\sqrt{\Pi}} \cdot \frac{1}{\cos \alpha} \quad (5)$$

From the above formula

$$L_{min}(\alpha = 0^\circ) = 2.26 \cdot d \quad (6)$$

$$L_{av}(\alpha = 45^\circ) = 3.19 \cdot d \quad (7)$$

$$L_{max}(\alpha = 90^\circ) = \infty \quad (8)$$

Therefore, it is expressed instead as

$$L_{max} = (L_{av} + (L_{av} - L_{min})) d \quad (9)$$

$$L_{max} = 3.19 + (3.19 - 2.26)d = 4.12 \cdot d \quad (10)$$

Since the distribution of the fibers passing through the mesh is not symmetrical, the L_{av} is more suited for determining the fiber length.

6.3.1. Calculation of the average fiber length (L_{av}) of the selected screen sizes

The values of d for all the screen sizes are provided in Table 24

Screen sizes	Calculated average fiber length (L_{av})
28	$L_{av} = 3.19 \cdot d = 3.19 \cdot 0.589 = 1.88 \text{mm}$
48	$L_{av} = 3.19(d_{32}+d_{35}+d_{42}+d_{48})/4 = 3.19(0.495+0.417+0.351+0.295)/4 = 4.97/4 = 1.24 \text{mm}$
65	$L_{av} = 3.19(d_{60}+d_{65})/2 = 3.19(0.246+0.208)/2 = 1.4483/2 = 1.72 \text{mm}$
150	$L_{av} = 3.19(d_{80}+d_{100}+d_{115}+d_{150})/4 = 3.19(0.175+0.147+0.126+0.104)/4 = 0.44 \text{mm}$
200	$L_{av} = 3.19(d_{80}+d_{100}+d_{115}+d_{150}+170+200)/6 = 3.19(0.175+0.147+0.126+0.104+0.088+0.074)/6 = 2.277/6 = 0.38 \text{mm}$

To calculate the average length for the first screen is quite simple as it is strictly based on the formula $L_{av} = 3.19 \cdot d_{28}$; however, for the others, say 48, the mean value of the average length of all the screen sizes between the previous size (in this case 28) and the screen of interest is included.

Table 24. Values for the determination of fiber length by the Bauer McNett fiber classifier.

Screen size	d (mm)	L_{min}^a (mm)	L_{av}^b (mm)	L_{max}^c (mm)
28	0,589	1,33	1,88	2,43
32	0,495	1,12	1,58	2,04
35	0,417	0,94	1,33	1,72
42	0,351	0,79	1,12	1,45
48	0,295	0,69	0,94	1,22
60	0,246	0,56	0,78	1,01
65	0,208	0,47	0,66	0,88
80	0,175	0,4	0,56	0,72
100	0,147	0,33	0,47	0,62
115	0,126	0,28	0,4	0,52
150	0,104	0,24	0,33	0,43
170	0,088	0,2	0,28	0,36
200	0,074	0,17	0,24	0,3

a (L min stands for minimum length)

b (L av stands for average length)

c (L max stands for maximum length)

6.4. Fiber characterization

6.4.1. Fiber morphology analysis

The fiber quality (length, width, fibrillation index, and fines content) was determined by the MorFi fiber analyzer (Techpap, Grenoble, France). About 40 mg of fibers were dispersed in 1L of water before analysis with the device. In this device, fines were classified as fibers of length 200 μ m and less and they are given as the fines % in length. Approximately 5000 fibers were analyzed in each run and the analysis was carried out at least twice for each sample.

6.4.2. Water Retention Value (WRV) determination

The water retention value (WRV) was determined by dispersing 1.2 g of pulp in 1 L of water. Thereafter, the diluted fibers were then transferred to a hand-sheet

maker equipped with a partition, placed on the mesh to allow the formation of 3 evenly sized test pads (fiber mats) as shown in Figure 107a. Each test pad (fiber mat) was then rolled neatly and placed in the centrifuge sample holder (Figure 107b). Centrifugation was performed according to the ISO standard (ISO 23714); (centrifugal force: 3000 g ($g = 9.81 \text{ m/s}^2$), time: 15 min and temperature: 23° C). For each sample, at least 6 determinations were carried out.

After centrifugation, the fibers were retrieved from the sample holder and weighed (m_1) before oven drying at 105° C for 48 hours. At the end of the drying period, the fiber mass was reweighed (m_2).

The WRV was determined by the formula:

$$WRV = \left(\frac{m_1}{m_2} \right) - 1 \times 100 \quad (11)$$

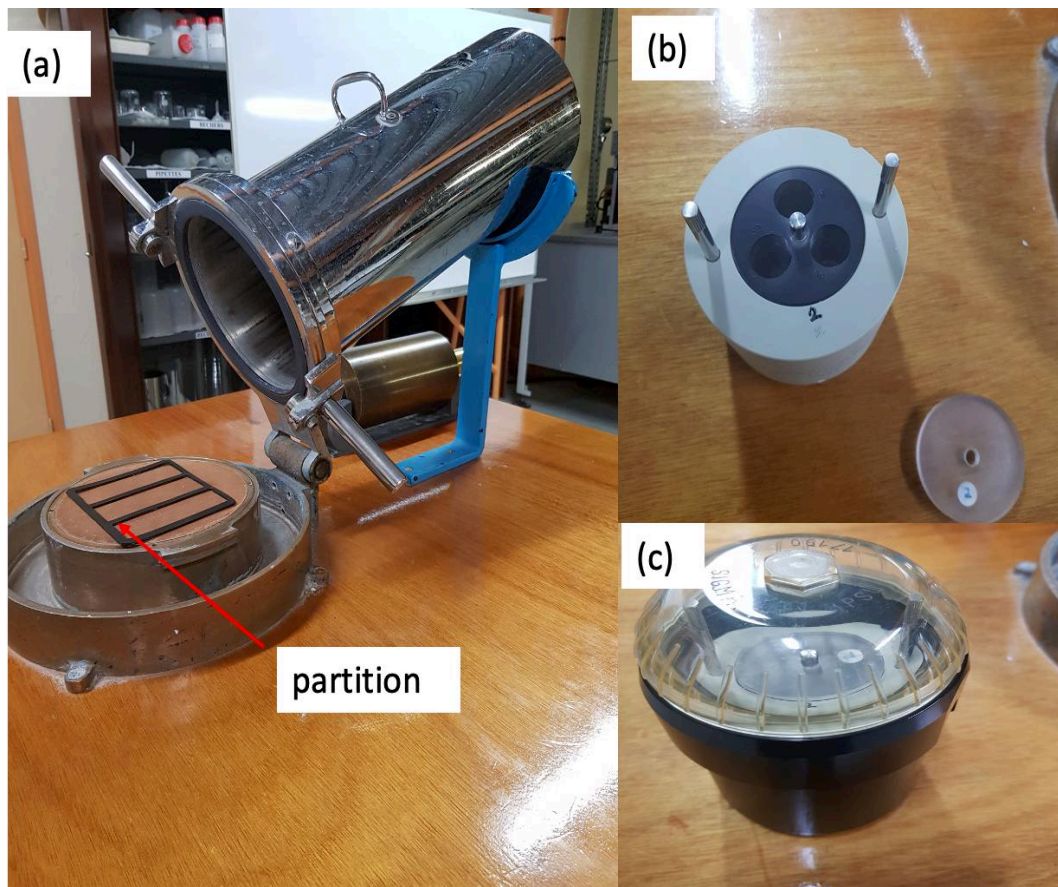


Figure 107. Hand-sheet maker with partition (a), sample holder (b), centrifuge bucket (c) used for WRV determination.

6.4.3. Specific surface area determination (BET)

Pulp specific surface area and total pore volume were determined by the Brunauer-Emmett-Teller (BET) analysis of nitrogen adsorption. The measurements were carried out using the Nova 2200e device from Quantachrome (Grenoble, France). Samples were degassed under vacuum at 105 ° C for 16 hours to remove water molecules adsorbed on the porous surface of the sample prior to determination.

6.4.4. Fiber images

Fiber images of dried fibers were acquired by scanning electron microscopy ESEM (FEI, Tokyo, Japan) while for wet samples, the optical microscopy images were recorded with an Axio Imager M1 microscope (Carl Zeiss, Germany) equipped with an AxioCam MRc 5 digital camera.

6.5. Hemicellulose extraction treatments

6.5.1. Cold caustic extraction

In order to determine the optimum soda concentration for the hemicellulose extraction process, it was initially performed at NaOH concentrations of 20 g/L, 40 g/L, 60 g/L, and 100 g/L. Other conditions chosen for the extraction were pulp consistency of 5%, residence time of 30 minutes, and temperature of 25 °C. At the end of the reaction, the pulp was washed with deionized water to neutral pH. Soda concentrations of 60 g/L and 100 g/L were then chosen for subsequent studies. The resulting pulp was dried by lyophilization. The performance of the CCE coupled with mechanical refining was evaluated by conducting sequential and simultaneous treatments, as shown in Figure 108.

6.5.2. Enzymatic treatment

For the enzymatic extraction of hemicelluloses, pulp samples were treated with xylanase (50 U/g, 300 U/g, 500 U/g) at 3% consistency in a 0.1M sodium phosphate buffer solution. The pH of the buffer was 6, and the reaction was carried out in a plastic bag. The enzyme was first introduced into the buffer solution and thoroughly mixed before pulp addition to ensure uniform distribution. After homogenizing the pulp/xylanase suspension, it was incubated in a controlled water bath at 50 °C for 2 h. The pulp/xylanase suspension was filtered and mixed with deionized water at 90 °C. It was then placed in a water bath maintained at 90 °C for 15 min to deactivate the enzyme. The pulp was washed with deionized water and refrigerated for further analysis.

Similarly, in the enzymatic hydrolysis of celluloses, pulp samples were treated with cellulase (10 U/g, 25 U/g, 50 U/g, 100 U/g, 150, and 250 U/g) at 3% consistency in a 0.1M sodium phosphate buffer solution. The pH of the buffer was 6, and the reaction was carried out in a plastic bag. The enzyme was first introduced into the buffer solution and thoroughly mixed before pulp addition to ensure uniform distribution. After homogenizing the pulp/cellulase suspension, it was incubated in a controlled water bath at 40 °C for 1 h. The pulp/ cellulase suspension was filtered and mixed with deionized water at 90 °C. It was then placed in a water bath maintained at 90 °C for 15 min to deactivate the enzyme. The pulp was washed with deionized water and refrigerated for further analysis.

6.5.3. Simultaneous refining/CCC and simultaneous refining/xylanase treatments

The simultaneous refining-CCE was conducted on the Valley beater and PFI refiner at a soda concentration of 60 g/L. The pulp consistency for the treatment was 2% and 10% for Valley beater and PFI respectively. A refining load of 4.5 kg was used for the Valley beater for 60 min while the PFI was run at 8750 revolutions for about 6 min. At the end of the treatment, the resulting pulp was washed until

neutral pH and freeze-dried. For the PFI refined pulp, the sample was allowed to stand for a total of 30 mins plus refining time.

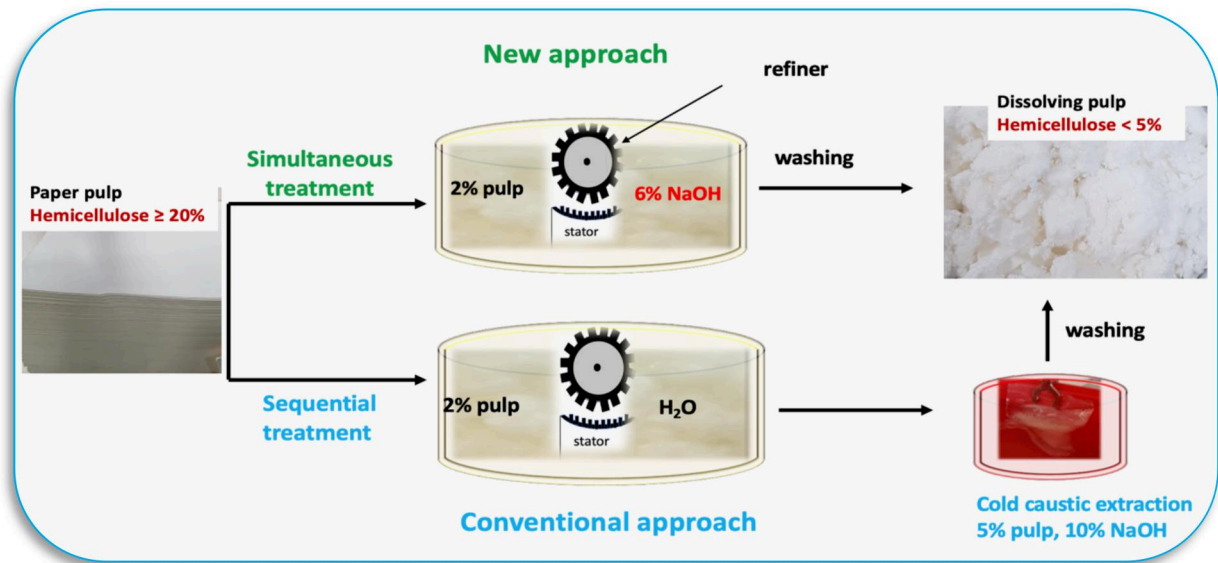


Figure 108. Schematic representation of the simultaneous refining / CCE treatment.

The simultaneous refining/xylanase treatment was performed with the PFI mill. Fibers were mixed with xylanase (50 U/g) at 10% consistency in a 0.1M sodium phosphate buffer solution at pH 6 prior to refining. The refining was run at 17500 revolutions for about 12 min. At the end of the treatment, fibers were incubated in a temperature-controlled water bath for 2 hours at 50 °C. At the end of the treatment, the enzyme was deactivated and the pulp washed prior to the CCE treatment. A schematic representation of the process is shown in Figure 109.

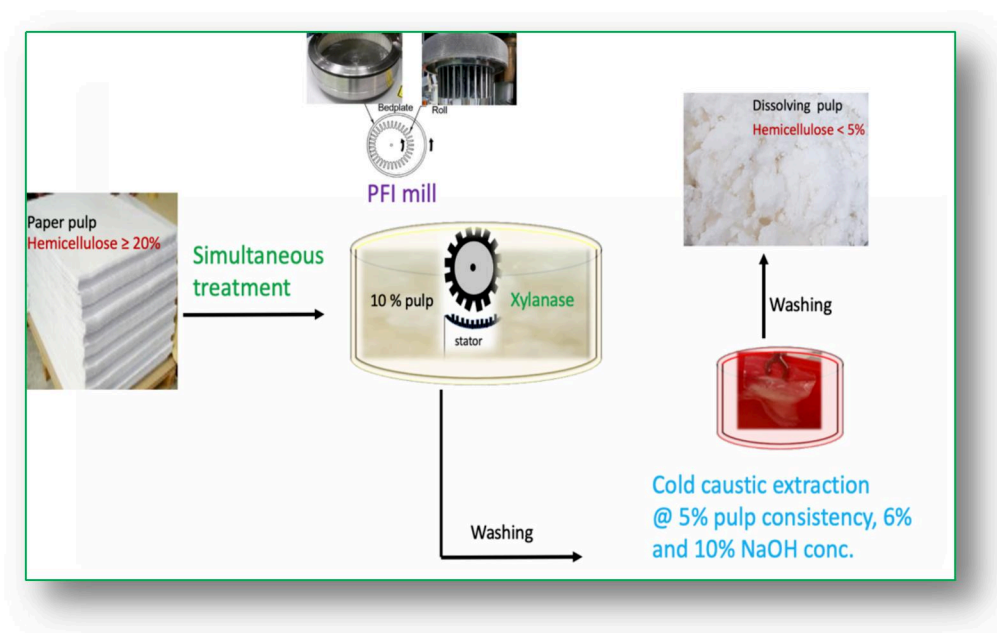


Figure 109. Schematic representation of the simultaneous refining / xylanase treatment.

6.6. Carbohydrate composition

The carbohydrate composition was determined according to the NREL procedure (Sluiter et al., 2004). It involves a two-step acid hydrolysis of the dried pulp first with 72% sulphuric acid at 30 °C for 1 hour, followed by dilution and hydrolysis in an autoclave at 121 °C for another 1 hour. The hydrolysate was filtered, and the monosaccharides were identified and quantified by high-performance anion-exchange chromatography coupled with pulse amperometric detection (HPAEC-PAD) in a Dionex ICS 5000 system equipped with a CarboPac PA column.

6.7. Cellulose solubility study

6.7.1. Cellulose fiber swelling tests

The extent of cellulose fiber swelling in various solvents was determined by measuring the increase in the fiber width with the help of the MORFI apparatus. The MORFI apparatus is a fiber quality analyzer that measures pulp characteristics, including the fiber width. Values of the variation in fiber width indicate the extent of swelling, particularly in the lateral direction. To determine swelling at various soda

concentrations, the pulp samples (unrefined and disc refined) were not subjected to drying before the test. The pulp samples were weighted and mixed with soda at a pulp consistency of 5% and mixed at intervals for 30 min. Thereafter, it was diluted to a concentration of 40 mg/L with water before passing it to the MORFI apparatus. The soda concentrations investigated were 0%, 2%, 4%, 6%, and 8%.

Swelling has been reported to reach a maximum at soda concentrations ranging from 10% to 12%. Therefore, to study the effect of various pretreatment methods on the morphology of cellulose fibers, the swelling test was performed at a pulp consistency of 1%, and soda concentration of 12%, while stirring at 250 rpm for 30 minutes. When the time elapsed, the suspension was diluted to a concentration of 40 mg/L before being analyzed by the MORFI. The samples used in this study were freeze-dried.

Also, the swelling degree of the extracted pulp was determined by reacting it with dilute CUEN solution (0.16 M). This concentration was chosen to favor swelling rather than dissolution. About 40 mg of the pulp (frozen in storage) was dispersed in 2ml of 0.16 M CUEN and agitated at 150 rpm for 10 minutes. After which, the suspension was diluted to 1L and analyzed by the MORFI.

6.7.2. Solubility test of cellulose in aqueous NaOH

The solubility test in aqueous NaOH was performed according to the method proposed by (Isogai & Atalla, 1998). One gram (1 g) of freeze-dried cellulose was dispersed in 26.9 g of water, and 2.5 g NaOH was added making approximately 8.5% NaOH solution. The suspension was thoroughly mixed and cooled to -10 °C and held until completely frozen. The suspension was allowed to thaw at room temperature, after which 20.6 g of deionized water was added to dilute it to 5% NaOH. The gel-like suspension was then filtered to separate the undissolved residue. The filtration was conducted in a 50 ml sintered glass (G2). Before drying, the undissolved residue was washed sequentially with 5% NaOH, 1% NaOH, water, 10% acetic acid, water, and acetone. The solubility was expressed as the % of the dissolved cellulose fibers.

6.7.3. Fock reactivity

Fock reactivity was performed based on the modified protocol proposed by (Tian et al., 2013). The Fock reactivity is determined in stages; Xanthation, regeneration, and quantification of converted cellulose. The pulp used for the experiment was freeze-dried with a moisture content of about 7%. Approximately, 500 mg of the pulp sample were weighed into a pre-weighed 250 mL Erlenmeyer flask with a stopper. Then 50 mL of a 9% (w/w) NaOH solution was added to the flask containing the sample and stirred in a water bath for 10 minutes at room temperature. This was followed by adding 1.3 mL of carbon disulfide (CS₂) to the flask, which was immediately stopped with the stopper, and stirring was continued for 3 hours at a speed of 250 rpm. At the end of the xanthation process, the sample was diluted with deionized water to a weight of 100 g and mixed thoroughly. In order to separate the dissolved cellulose from the undissolved, the suspension was adequately sealed in a special tube adapted for CMR chemicals and centrifuged for 15 minutes at 5000 rpm. To regenerate the dissolved cellulose, 10 mL of the supernatant was collected and transferred to a 100 mL round bottom flask and neutralized with 3 mL of a 20% (w/w) H₂SO₄ solution, which was stirred for 18 hours at 50 rpm (to degas).

To quantify the cellulose reactivity, 20 ml of 68% (w/w) H₂SO₄ was added to the round bottom flask containing the reacted cellulose and stirred for 1 h, followed by the addition of 10 mL of 1/6 M K₂Cr₂O₇, which was refluxed for 1 h to oxidize cellulose. The suspension was then cool to room temperature and diluted to 100 mL. At this point, 20 mL of the oxidized cellulose solution and 5 mL of potassium iodide KI (10% w/w) were transferred into a 250 mL Erlenmeyer flask and titrated against 0.1 N sodium thiosulphate using a starch indicator. The volume of sodium thiosulphate consumed was recorded and used for the calculation as follows;

$$Fock\ Reactivity = \frac{(C_1V_1 - (C_2V_2 \times \frac{100}{40}) \times \frac{1}{6}) \times M \times \frac{1}{4} \times \frac{P_1}{P_2}}{m} \times 100 \quad (12)$$

12)

M is the molecule weight of glucose unit (162 g mol^{-1}),
 m is the oven-dry weight of the pulp sample (g),
 V_1 is the volume of $\text{K}_2\text{Cr}_2\text{O}_7$ added (L),
 C_1 is the concentration of $\text{K}_2\text{Cr}_2\text{O}_7$ solution (mol/L),
 V_2 is the volume of consumed $\text{Na}_2\text{S}_2\text{O}_3$ (L),
 C_2 is the concentration of $\text{Na}_2\text{S}_2\text{O}_3$ solution (mol/L),
 P_1 is the actual mass of the xanthation solution ($\approx 100 \text{ g}$) and
 P_2 ($\approx 10.4 \text{ g}$) is the mass of the 10 mL taken out from the viscose solution.

The ratio (10/2) results from the fact that 20 ml of oxidized cellulose (out of 100 ml) was used for the titration; the ratio (1/6) indicated that each dichromate ion consumed six thiosulphate ions, and the ratio (1/4) represents the consumption of four dichromate ions by each Anhydro glucose unit.

6.8. Molecular weight analysis

6.8.1. Degree of polymerization

The viscosity based-degree of polymerization of the pulp was determined by dispersing the pulp in deionized water, and subsequent dissolution in cupriethylenediamine solution (CUEN) adapted from the TAPPI procedure (TAPPI, 2013). The determination was carried out on dried pulp by weighing 0.25 g of pulp and dispersing it in 25 mL deionized water, followed by the addition of 25 mL of 1 M cupriethylenediamine solution. The suspension was then degassed with nitrogen gas before mixing for 2 hours. After the dissolution, the viscosity was measured by capillary action at 25 °C. The degree of polymerization was then calculated based on the formula proposed by (Sihtola et al., 1963)

$$\eta = 954 \log V - 325 \quad (13)$$

$$DP^{0.905} = 0.75 \times \eta \quad (14)$$

Where V is the viscosity from the capillary method (T230 om-13 (2013)), η is the intrinsic viscosity, and DP is the degree of polymerization.

6.8.2. Molecular weight determination by direct dissolution in 8% LiCl/DMAc solution

Analysis was performed by a Gel permeation chromatography (GPC MAX VE2001), equipped with Viscotek light scattering, RI and UV detectors. The sample was first ground, and 10 mg (freeze-dried) was weighted and swollen in water by mixing at 500 rpm for 2 hours. Then the solvent was exchanged by filtration and washing to methanol and agitated for 1 hour at 500 rpm. Afterward, the samples were again exchanged in Dimethylacetamide (DMAc) and stirred overnight at 200 rpm. The dissolution of the sample was performed in 1ml (8%) LiCl /DMAc solution for at least 1 day, followed by dilution with pure DMAc until a concentration of (0.5%) LiCl/DMAc before analyzing it with the size exclusion chromatography. The samples were filtered through 0.45 μm before being injected into two PL gel columns placed in series at a temperature of 75 $^{\circ}\text{C}$. The eluent used was 0.5% LiCl/DMAc at a 1 ml/min flow rate. In the case of hemicellulose, there was no grinding. A proposed mechanism for the direct dissolution of xylan in LiCl/DMAc is shown in Figure 110 (adapted from (C. Zhang et al., 2014))

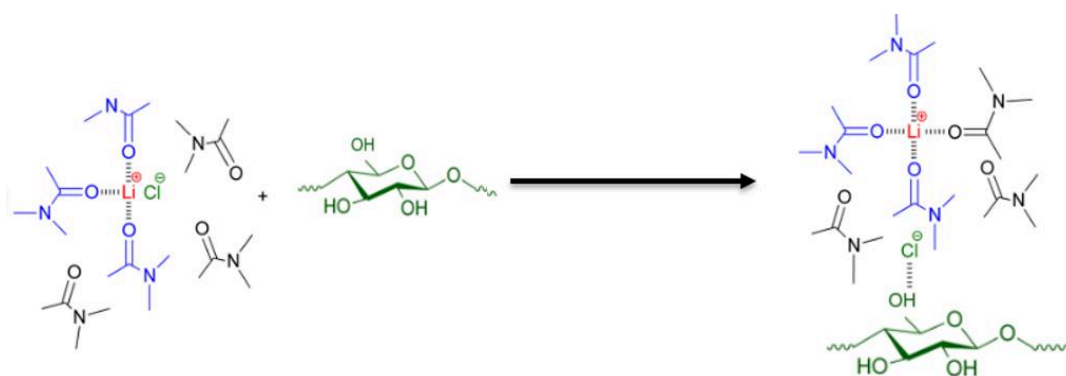


Figure 110. Reaction mechanism for direct xylan dissolution in LiCl/DMAc.

6.8.3. Molecular weight determination by derivatization (xylan dicarbanilate)

For this experiment, the analysis was performed by Gel permeation chromatography (GPC MAX VE2001), equipped with Viscotek TDA 302 triple detector array (RI+DP+LSD) and UV detectors. The molecular weight distribution of the extracted xylan was determined by Gel Permeation Chromatography. About 50 mg (freeze-dried) of the recovered xylan into a 50 mL reagent bottle with a stopper. Then 5 mL dimethyl sulfoxide (DMSO) was added and mixed for 1 hour at 70 °C. At this point, 1 mL phenyl-isocyanate was added, followed by 5 mL DMSO. The solution is sealed and allowed to react for 4 more hours. After a total of 5 hours, the reaction was quenched by adding 1 mL of acetone and cooled to room temperature. The solution was diluted with Tetrahydrofuran (THF) (1:1) and filtered through 0.45 µm before being injected into two Shodex Asahipak columns placed in series at a temperature of 35 °C. The eluent used was THF at a flow rate of 0.4 mL/min. A proposed mechanism for the dissolution of xylan by derivatization to xylan dicabanilate is presented in Figure 111 (W. Zhang et al., 2016).

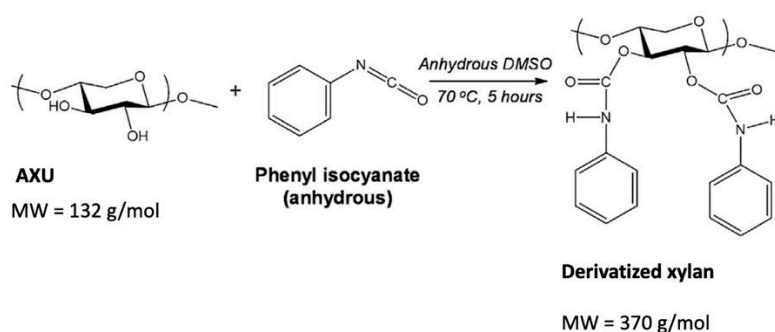


Figure 111. Reaction mechanism for xylan dissolution by derivatization (cabanilation).

Calibration was performed for both device with a narrow polystyrene standard (99 KDa or 105 KDa). For the narrow standard $M_n = M_w$. To validate the calibration, a broad polystyrene standard ($M_n \approx 105$ KDa and $M_w \approx 245$ KDa) is injected. Both standards were purchased from Malvern.

6.8.4. MALDI-ToF MS Analysis

MALDI-ToF MS stands for Matrix-Assisted Laser Desorption Ionization - Time of Flight Mass Spectrometry. It involves the bombardment of the sample embedded in a suitable matrix by a laser beam, which vaporizes and ionizes the sample with minimal decomposition as obtained in conventional mass spectrometry. The ionized molecules are separated based on their mass to charge ratio, with lighter molecules arriving fastest to the detector than heavy molecules. Each peak in the spectrum corresponds to the specific mass of the particle detected. The Time of Flight was detected in the linear and reflector modes. The linear mode detects high molecular mass molecules with a relatively low resolution, while the reflector mode works at a higher resolution, especially for lower masses (oligomers).

The recovered xylan samples were dispersed in water and mixed with the matrix (solvent) (DHB/TA30) before deposition on the MALDI slide. It was allowed to dry at room temperature before the analysis. The analysis was performed by the Bruker Daltonics Autoflex Speed equipment. The solvent (DHB/TA30) is composed of 2,5-Dihydroxy benzoic acid/(TA30) {30:70 (v/v) of Acetonitrile and 0.1% TFA in water respectively}. The determination was done in the positive linear mode. The molecular weight interval between detected oligosaccharides was $m/z = 132$, but they were cationized in the form of sodium $[M+Na^+]$. (Where M: is the mass of oligosaccharide).

6.9. Cellulose II content and crystallinity index determination

6.9.1. Quantification of Cellulose II content and crystallinity index by ^{13}C CP-MAS NMR spectroscopy

The cellulose II content and crystallinity index of samples were quantified by the high-resolution solid-state ^{13}C CP-MAS NMR spectroscopy. Samples were freeze-dried and ground before analysis. This method uses the unique chemical shifts created by the carbon-13 atom of the AGU to distinguish between the various

cellulose polymorphs, quantify the degree of crystallinity and cellulose-II content in pulp samples. The supramolecular structure of cellulose can be examined by analyzing the signals generated by the carbon-13 atoms of the anhydroglucose unit (AGU). Each carbon of the AGU induces resonance at unique chemical shift ranges; atoms C-1(100-110 ppm), C-4 (80-90 ppm), C-2, C-3, and C-5 (70-80 ppm), and C-6 (60-70 ppm). The signals generated by each carbon atom differ according to the type of cellulose: crystalline cellulose, amorphous cellulose, cellulose I, or cellulose II. For the study of crystallinity degree, the C-4 atoms are good indicators, and depending on the extent of crystallinity or disorder; the C-6 could also contribute to the analysis. For instance, fully amorphous cellulose shows no peak at atoms C-4 and C-6, while crystalline cellulose exhibits peaks at C-4 and C-6. The intensity of the peak depends on the degree of crystallinity (Park et al., 2010). The crystalline index is quantified by subtracting the amorphous reference spectrum from that of the sample, where the difference represents the crystallinity degree. Typically, the C-4 signal, separated into two distinct peaks in cellulose, is ascribed to crystalline and non-crystalline domains, assigned 89 ppm and 84 ppm, respectively.

For the quantification of cellulose II, the cellulose I reference spectrum is subtracted from that of the study sample before analyzing the carbon atoms.

According to the Larsson deconvolution method, the C-1 resonance provides information on the determination of small amounts of cellulose II in the sample. The onset of a peak at 106.5 ppm or the widening of the C-1 signal between 100 and 110 ppm indicates the presence of cellulose II. On the other hand, more significant amounts of cellulose II two can be quantified by integration or deconvolution of the C-6 signal. Depending on the extent of cellulose I to cellulose II conversion, the resonance at 65.6 ppm diminishes while that at 62.5 increases. For samples rich in cellulose II or on the complete transition from cellulose I to cellulose II, one narrow peak instead of two is observed at C-6.

6.9.2. Crystallinity index by X-ray diffraction (XRD)

The supramolecular changes resulting from the mechanical and chemical treatments applied were monitored by X-ray diffraction studies. Pulp samples

analyzed were ground to powder by a cryogenic grinder prior to the analysis. The cellulose allomorphs contributing to the crystallinity index were identified and quantified. The analysis was performed with the PANalytical X'Per pro MDP diffractometer (Cu-K α). The calculation of the crystallinity index was done by Segal's method.

$$\mathbf{Crystallinity\ index} = \left(\frac{\mathbf{I}_{cr}}{\mathbf{I}_{cr} + \mathbf{I}_{am}} \right) \times \mathbf{100} \quad (15)$$

Where \mathbf{I}_{cr} and \mathbf{I}_{am} are the intensities of crystalline and amorphous regions of cellulose, respectively.

6.9.3. Fourier transform infrared spectroscopy (FT-IR) analysis

Infrared spectra of the recovered xylan were collected in absorbance mode by the Perkin Elmer Spectrum 65 FT IR Spectrometer. About 4 mg of freeze-dried samples and 176 mg of KBr were pressed into a pellet prior to the determination. For each sample, 16 scans were collected in the range of 4000 – 400 cm⁻¹.

General conclusions and perspectives

About 80% of the dissolving pulp produced globally is used in the manufacture of viscose rayon fibers, most of which are used in the production of textiles. The great interest in viscose textiles is due to their specific properties of comfort, touch, and appearance. Other considerations related to its vegetal and non-fossil origins and the environmental problems associated with cotton cultivation. The growing world population, the basic need for clothing, and the many other uses of regenerated cellulose will secure the future of dissolving pulp. Currently, the two dissolving pulp production processes are Acid Sulfite (AS) and Prehydrolysis Kraft (PHK), which respectively represent 65% and 25% of the global production, with cotton accounting for the remainder (10%). PHK is actually a Kraft process in which some of the hemicelluloses are extracted by acid hydrolysis of the chips before cooking. This is usually done at a high temperature (150 °C) as a separate phase in the cooking reactor, which is a significant change from the traditional Kraft cooking process. The extraction of the hydrolyzed hemicellulose is complex and is generally not carried out.

On the other hand, acid sulfite cooking used to be the traditional method of making dissolving pulp. It is possible to obtain a pulp with a low hemicellulose content by adjusting the conditions. However, for environmental and technical reasons, no new installation will be built using the sulfite process in the future. Current research focuses on transforming kraft paper pulp into dissolving pulp by post-extraction of hemicelluloses essentially by cold caustic extraction (CCE) or by hemicellulose degrading enzymes. This approach provides the kraft mill with the opportunity to switch from paper pulp to dissolving pulp production easily, or vice versa, depending on the market situation since the kraft process is not affected. In addition, the degree of polymerization of cellulose should be higher than after PHK, which would broaden the application spectrum of the dissolving pulp produced. Finally, the process would ensure a higher yield than PHK. However, some serious drawbacks exist, such as the difficulty of achieving low enough hemicellulose content and a loss of reactivity of the cellulose when the cold caustic extraction is

too strong. Despite its advantages, upgrading paper pulp into dissolving pulp is not yet an industrial reality.

This study aimed to achieve a quantitative extraction of the residual hemicellulose in bleached hardwood kraft pulp for use as dissolving pulp but without the drawbacks mentioned above associated with the conventional CCE process. To achieve our goal, mechanical refining was used in conjunction with cold caustic extraction and xylanase treatments. This was done to increase the accessibility of chemical and enzymatic agents to hard-to-reach regions of the fiber for more complete xylan extraction, and improve the reactivity of the pulp towards dissolution.

The first part examined the morphological changes resulting from mechanical refining with three different technologies (Valley beater, PFI, and pilot disc refiner) and the impact on hemicellulose removal when performing CCE and xylanase treatments. We found a positive correlation between refining-induced fiber modification, such as increased water retention value (WRV), specific surface area, fiber shortening, fines generation, and CCE performance. At a soda concentration of 100 g/L, the xylan removal for the Valley beater, PFI, and disc refined pulp were 84%, 82%, and 79%, respectively. This corresponds to 3.3%, 3.6%, and 4.3% residual xylan in the extracted pulp, starting from 20% in the reference paper pulp. Roughly, 50% more xylan could be extracted from the refined pulp compared to the unrefined pulp. In terms of upscaling, it was determined that though the laboratory refiners performed slightly better than the industrial-like refiner, the difference was marginal. Therefore, the risks associated with upscaling would be minimal in this process. Xylanase activity increased also after Valley beater and PFI refining. However final performance was much lower than with CCE, since the xylan removal degree was 38% after valley beater and 24% after PFI refining at a dosage of 500 U/g. The poor performance of enzymatic treatment compared to CCE was probably due the poor solubility of xylan fragments in acidic medium. Although over 60% of the residual xylan in the refined pulp was extracted by performing CCE at a soda concentration of 60 g/L (milder treatment), it did not meet the dissolving pulp

requirements for cellulose purity. Still, this mild condition prevented the conversion of native cellulose to cellulose II, which is often associated with low reactivity after dewatering.

Finally, this study outlined the beneficial effect of fibrillation, fiber cutting and fine production brought about by refining on xylan extraction. This effect was found much more pronounced than that given by cellulase pretreatment proposed by several authors for the same purpose.

In order to improve the extraction performance of CCE further some strategies were therefore examined in the second part of this study. The first consisted of performing a simultaneous refining / CCE on the Valley beater and PFI refiners. The response of residual xylan in the pulp to simultaneous refining / CCE was high already at 60 g/L NaOH, especially for the Valley beater with a xylan reduction of 79% and 61% for PFI against (68%) when the refining was performed prior to CCE. The difference in the performance of the simultaneous treatment on a Valley beater and PFI was not a question of technology but processing condition (consistency of the pulp). The low pulp consistency operated in the Valley beater allowed for a more rigorous and homogeneous mixing compared to the PFI performed at a high pulp consistency of 10%. A subsequent xylanase treatment applied to the pulp resulted in further xylan removal with a total xylan reduction of 84% and 79% for Valley and PFI, respectively, corresponding to a residual xylan content of 3.1% and 4.3%. The xylan removal performance obtained with this treatment (simultaneous refining / CCE at 60 g/L NaOH and xylanase) was similar to the results obtained in the previous part with a stronger NaOH solution (CCE at 10% NaOH after refining). However, we observed that carrying out CCE during refining (Valley beater) favored the formation of some cellulose II. Nevertheless, its content remained much lower than for a CCE at 100 g/L. Simultaneous refining/xylanase treatment was also tested. Unexpectedly, under the conditions used, less xylan removal was obtained compared to sequential treatment. On the contrary, after complementary CCE treatment, refining/xylanase led to better xylan extraction than with sequential treatment. This result can be explained if we

consider that under refining conditions, more xylan chains become accessible and at the same time the homogeneity of the enzyme treatment is increased because of the vigorous agitation. Then, at a given and limited charge of xylanase we may admit that the number of hydrolysis sites per molecule of accessible xylan is reduced, thus increasing the size of the xylan fragments and reducing their solubility in acidic medium. Therefore, applying CCE would dissolve a much bigger part of these fragments. One may expect that this apparent contradictory result would not be obtained at higher charge of enzymes.

Severe refining was also investigated as pretreatment for cold caustic extraction to see if complete removal of the xylans was possible. About 94% xylan reduction was obtained with the Valley beater and 89% for the PFI mill at soda concentrations 100 g/L. Besides, extraction of the Valley beater refined pulp with a mild soda concentration (6%) resulted in 76% xylan removal, satisfying the requirement for dissolving pulp. Thus, indicating that the difficulty in removing xylans from paper pulp by alkaline extraction is essentially caused by accessibility problems.

A third approach explored in this part of the study was the impact of fractionation of fines on xylan removal. One of the advantages of fractionating the fines from refined pulp was the reduction in the initial hemicellulose content of the pulp before chemical or enzymatic treatment since the fines are richer in xylan. As a result, fractionation of the refined pulp coupled with CCE resulted in a final residual xylan content of about 5% and 2%, at soda concentrations of 60 g/L and 100 g/L respectively.

The strategies investigated led to a high-purity pulp with a narrow molecular weight distribution, which met the requirements for dissolving pulp.

In the third part of this study, we investigated the influence of the hemicellulose removal treatment on the reactivity of the resulting pulp. The idea was to develop treatment strategies consisting of mechanical refining, chemical treatment (CCE), and xylanase treatment that enabled both quantitative xylan removal as well as good reactivity to dissolution without the need for additional post-extraction treatments to improve reactivity (which means additional production costs). The reactivity of the extracted pulps was evaluated based on the degree of

swelling in NaOH and dilute cupriethylene diamine solution (CUEN), the solubility in 8% NaOH at -10 °C, and the Fock reactivity. The result obtained showed that hemicellulose removal strategies that included mechanical refining led to better pulp reactivity than unrefined pulp. The best result was obtained with refined pulp extracted with 6% soda (no cellulose II). In addition, we obtained a Fock reactivity ranging from 60 to 70% which exceeded that obtained for the prehydrolysis kraft (PHK) (49%). The good correlations found between pulp swelling, solubility in caustic soda, and Fock reactivity suggest that the tedious Fock test could be substituted by the much simpler swelling and solubility measurements. The negative impact of cellulose II on pulp reactivity is due to the higher number of hydrogen bonds formed under dewatering and drying. This problem would not occur in the ideal case where pulp dissolution is integrated in the pulp mill.

In the last part of this study, the xylans were recovered from the CCE treatment of unrefined and refined pulps extracted at 6% and 10% soda concentrations. Precipitation by addition of acetic acid was the preferred method to obtain xylans in a rather pure form. Xylans were characterized by SEC (size exclusion chromatography) and MALDI-Tof-MS. It was observed that the molecular weight of the extracted xylan as determined by SEC varied depending on the method used to prepare a xylan solution for SEC analysis. The average DP_n varied from 70 to 177. The lowest values were obtained after formation of xylan carbanilate, the highest after direct dissolution in DMAc/LiCl (8%). It was clear that the highest numbers were influenced by the formation of aggregates. Indeed, aggregates composed of certain aromatic compounds, which might be lignin-carbohydrate (xylan) complexes (LCC), were detected. The presence of LCC in paper pulp could be one reason for the difficulty associated with the complete removal of residual xylan. The study also revealed that extraction conditions such as mechanical refining and soda concentration influenced the chain length of the extracted xylan. The DP of the xylan extracted from the paper pulp after coupling mechanical refining and CCE exhibited a higher value than for the unrefined pulp. Likewise, the increase in NaOH concentration made it possible to solubilize xylans of higher molecular mass. However, the association of the two effects (severe refining and a

high load of caustic soda (10%)) appeared to negatively impact the molecular weight of the extracted xylan suggesting that some xylan degradation might have occurred under such severe conditions.

MALDI-MS analysis showed that xylan fragments of wide range of DP were present. Traces of methyl glucuronic acid (MeGlcA) units were found only in the fragments of low DP (lower than 6). Fragments of rather high molecular weight (up to DP values higher than 50) without any side group were detected, which explains also why the xylan was difficult to extract from paper pulp.

To conclude, we developed a new approach to hemicellulose (xylan) extraction from paper pulp consisting of simultaneous refining and CCE treatment. The treatment was performed not only on laboratory beaters (Valley beater and the PFI mill) but also on a pilot scale disk refiner, representative of industrial refining equipments. This approach enabled quantitative removal of hemicellulose at a soda concentration (60 g/L) where no cellulose II was formed. Most importantly, the process produced high purity cellulose of high DP (higher than 1000), and of high reactivity. The dual beneficial effect of refining on xylan removal and pulp reactivity to dissolution was demonstrated. Adding xylanase treatment may either lead to lower content in residual hemicellulose or allow for the application of even lower caustic soda charge. The results show that the production of dissolving grade pulp from conventional hardwood kraft pulp is feasible with the use of existing technologies. This represents a major advantage since a kraft pulp mill may choose to easily shift from paper pulp to dissolving pulp production and vice versa, depending on the market conditions.

Following the promising results obtained from simultaneous refining and CCE performed on the Valley beater; a laboratory scale refiner, It would be interesting in future works to scale up the process in a disc refiner pilot which is an industrial-like refiner. Additionally, it would be interesting to explore ways to recycle the spent NaOH solution used in the process.

The dissolving pulp obtained in the present study exhibited a high DP_v value, which is unusual in conventional processes (sulfite acid and kraft pulp prehydrolysis). Since the Fock reactivity obtained in the study was in the acceptable range, it would be interesting to investigate the effect of high DP (>1000) on the processability and quality of viscose yarn.

References

- Abitz, P., & Luner, P. (1989). The Effect of Refining on Wet Fiber Flexibility and Its Relation-. *Fundamentals of Papermaking*, 1(Transactions of the 9th Fundamental Research Symposium, Cambridge, UK), 67–86.
<https://doi.org/10.15376/frc.1989.1.67.THE>
- Ansell, M. P. (2015). Wood microstructure – A cellular composite chapter 1 in “Wood composites .” 1–28.
- Arnoul-Jarriault, B., Lachenal, D., Chirat, C., & Heux, L. (2015). Upgrading softwood bleached kraft pulp to dissolving pulp by cold caustic treatment and acid-hot caustic treatment. *Industrial Crops and Products*, 65, 565–571.
<https://doi.org/10.1016/j.indcrop.2014.09.051>
- Arnoul-Jarriault, B., Passas, R., Lachenal, D., & Chirat, C. (2016). Characterization of dissolving pulp by fibre swelling in dilute cupriethylenediamine (CUEN) solution in a MorFi analyser. *Holzforschung*, 70(7), 611–617. <https://doi.org/10.1515/hf-2015-0167>
- Asikainen, S., Fuhrmann, A., & Robertsén, L. (2010). Birch pulp fractions for fine paper and board. *Nordic Pulp and Paper Research Journal*, 25(3), 269–276.
<https://doi.org/10.3183/npprj-2010-25-03-p269-276>
- Bäckström, M., Kolar, M. C., & Htun, M. (2008). Characterisation of fines from unbleached kraft pulps and their impact on sheet properties. *Holzforschung*, 62(5), 546–552. <https://doi.org/10.1515/HF.2008.081>
- Bajpai, P. (2014). Industrial Applications of Xylanases. In *Xylanolytic Enzymes* (pp. 69–104). <https://doi.org/10.1016/b978-0-12-801020-4.00008-1>
- Borrega, M., & Sixta, H. (2013). Purification of cellulosic pulp by hot water extraction. *Cellulose*, 20(6), 2803–2812. <https://doi.org/10.1007/s10570-013-0086-1>
- Bossu, J., Eckhart, R., Czibula, C., Winter, A., Zankel, A., Gindl-Altmutter, W., & Bauer, W. (2019). Fine cellulosic materials produced from chemical pulp: The combined effect of morphology and rate of addition on paper properties. *Nanomaterials*, 9(3). <https://doi.org/10.3390/nano9030321>
- Budtova, T., & Navard, P. (2016). Cellulose in NaOH–water based solvents: a review. *Cellulose*, 23(1), 5–55. <https://doi.org/10.1007/s10570-015-0779-8>
- Budtova, T., & Navard, P. (2017). Cellulose in NaOH – water based solvents: a review To cite this version : HAL Id : hal-01247093. *Cellulose Springer Verlag*, 23(1), 6–7.
- Buslov, D. K., Kaputski, F. N., Sushko, N. I., Torgashev, V. I., Solov’eva, L. V., Tsarenkov, V. M., & Larchenko, L. V. (2009). Infrared spectroscopic analysis of the structure of xylans. *Journal of Applied Spectroscopy*, 76(6), 891–897.
- Carr, J. A., Petrokofsky, G., Spracklen, D. V., Lewis, S. L., Roe, D., Trull, N., Vidal, A., Wicander, S., Worthington-Hill, J., & Sallu, S. M. (2021). Anticipated impacts of achieving SDG targets on forests - a review. *Forest Policy and Economics*, 126(November 2020), 102423. <https://doi.org/10.1016/j.forpol.2021.102423>
- Ceccherini, S., & Maloney, T. (2019). Assessing wood pulp reactivity through its rheological behavior under dissolution. *Cellulose*, 26(18), 9877–9888.
<https://doi.org/10.1007/s10570-019-02750-0>

- Celiktas, M. S., & Alptekin, F. M. (2019). Biorefinery concept: Current status and future prospects. *International Conference on Engineering Technologies*, 7–9(2017), 27–32.
- Chen, C., Duan, C., Li, J., Liu, Y., Ma, X., Zheng, L., Stavik, J., & Ni, Y. (2016). Cellulose (Dissolving Pulp) Manufacturing Processes and Properties: A Mini-Review. *BioResources*, 11(2), 5553–5564. <https://doi.org/10.15376/biores.11.2>.
- Chen, J. (2015). Synthetic Textile Fibers: Regenerated Cellulose Fibers. In *Textiles and Fashion: Materials, Design and Technology* (Vol. 2014, pp. 79–95). Elsevier Ltd. <https://doi.org/10.1016/B978-1-84569-931-4.00004-0>
- Chen, X., Kuhn, E., Wang, W., Park, S., Flanagan, K., Trass, O., Tenlep, L., Tao, L., & Tucker, M. (2013). Comparison of different mechanical refining technologies on the enzymatic digestibility of low severity acid pretreated corn stover. *Bioresource Technology*, 147, 401–408. <https://doi.org/10.1016/j.biortech.2013.07.109>
- Chen, Zhiwen, Hu, T. Q., Jang, H. F., & Grant, E. (2015). Modification of xylan in alkaline treated bleached hardwood kraft pulps as classified by attenuated total-internal-reflection (ATR) FTIR spectroscopy. *Carbohydrate Polymers*, 127, 418–426. <https://doi.org/10.1016/j.carbpol.2015.03.084>
- Chen, Zicheng, Zhang, H., He, Z., & Zhang, L. (2019). Current and future markets of dissolving pulp in China and other countries. In *BioResources* (Vol. 14, Issue 4, pp. 7627–7629). <https://doi.org/10.15376/biores.13.2.2861-2870>
- Cherubini, F. (2010). The biorefinery concept: Using biomass instead of oil for producing energy and chemicals. *Energy Conversion and Management*, 51(7), 1412–1421. <https://doi.org/10.1016/j.enconman.2010.01.015>
- Chirat, C. (2017). Use of vegetal biomass for biofuels and bioenergy. Competition with the production of bioproducts and materials? *Comptes Rendus Physique*, 18(7–8), 462–468. <https://doi.org/10.1016/j.crhy.2017.10.002>
- Christov, L. P., Akhtar, M., & Prior, B. A. (1996). Impact of xylanase and fungal pretreatment on alkali solubility and brightness of dissolving pulp. *Holzforschung*, 50(6), 579–582.
- Curmi, H., Chirat, C., Brochier Salon, M. C., & Lachenal, D. (2018). Effect of autohydrolysis on alkaline delignification of mixed hardwood chips and on lignin structure. *Holzforschung*, 72(8), 631–636. <https://doi.org/10.1515/hf-2017-0196>
- de Carvalho, D. M. (2015). Study on the structure and properties of xylan extracted from eucalyptus , sugarcane bagasse and sugarcane straw. <http://kth.diva-portal.org/smash/record.jsf?pid=diva2%3A862284&dswid=-6275>
- Dhiman, S. S., Sharma, J., & Battan, B. (2008). Industrial applications and future prospects of microbial xylanases: A review. *BioResources*, 3(4), 1377–1402. <https://doi.org/10.15376/biores.3.4.1377-1402>
- Dinand, E., Vignon, M., Chanzy, H., & Heux, L. (2002). Mercerization of primary wall cellulose and its implication for the conversion of cellulose I → cellulose II. *Cellulose*, 9(1), 7–18. <https://doi.org/10.1023/A:1015877021688>
- Dou, X., & Tang, Y. (2017). The Influence of Cold Caustic Extraction on the Purity, Accessibility and Reactivity of Dissolving-Grade Pulp. *ChemistrySelect*, 2(35), 11462–11468. <https://doi.org/10.1002/slct.201701551>

- Duan, C., Li, J., Ma, X., Chen, C., Liu, Y., Stavik, J., & Ni, Y. (2015). Comparison of acid sulfite (AS)- and prehydrolysis kraft (PHK)-based dissolving pulps. *Cellulose*, 22(6), 4017–4026. <https://doi.org/10.1007/s10570-015-0781-1>
- Duan, C., Long, Y., Li, J., Ma, X., & Ni, Y. (2015). Changes of cellulose accessibility to cellulase due to fiber hornification and its impact on enzymatic viscosity control of dissolving pulp. *Cellulose*, 22(4), 2729–2736. <https://doi.org/10.1007/s10570-015-0636-9>
- Duan, C., Verma, S. K., Li, J., Ma, X., & Ni, Y. (2016a). Combination of mechanical, alkaline and enzymatic treatments to upgrade paper-grade pulp to dissolving pulp with high reactivity. *Bioresource Technology*, 200, 458–463. <https://doi.org/10.1016/j.biortech.2015.10.067>
- Duan, C., Verma, S. K., Li, J., Ma, X., & Ni, Y. (2016b). Viscosity control and reactivity improvements of cellulose fibers by cellulase treatment. *Cellulose*, 23(1), 269–276. <https://doi.org/10.1007/s10570-015-0822-9>
- Duan, C., Wang, X., Zhang, Y. L., Xu, Y., & Ni, Y. (2017). Fractionation and cellulase treatment for enhancing the properties of kraft-based dissolving pulp. *Bioresource Technology*, 224, 439–444. <https://doi.org/10.1016/j.biortech.2016.10.077>
- FAO. (2020). The World's Forests. In *Forests, biodiversity and people*. Rome. <https://doi.org/10.4060/ca8642en>. <https://doi.org/10.1515/9783035608632-002>
- Fernandes Diniz, J. M. B., Gil, M. H., & Castro, J. A. A. M. (2004). Hornification - Its origin and interpretation in wood pulps. *Wood Science and Technology*, 37(6), 489–494. <https://doi.org/10.1007/s00226-003-0216-2>
- Ferreira, J. C., Evtuguin, D. V., & Prates, A. (2020). Effect of cellulose structure on reactivity of eucalyptus acid sulphite dissolving pulp. *Cellulose*, 27(8), 4763–4772. <https://doi.org/10.1007/s10570-020-03092-y>
- Floe, G. (2011). Dissolving Pulp: The Great Comeback “ It ’ s All About Cotton! ”. TAPPI PEERS Dissolving Pulp Forum, 19. <http://www.tappi.org/content/events/11diss/floe.pdf>
- Friebel, C., Bischof, R. H., Schild, G., Fackler, K., & Gebauer, I. (2019). Effects of caustic extraction on properties of viscose grade dissolving pulp. *Processes*, 7(3), 1–12. <https://doi.org/10.3390/pr7030122>
- Gehmayr, V., Potthast, A., & Sixta, H. (2012). Reactivity of dissolving pulps modified by TEMPO-mediated oxidation. *Cellulose*, 19(4), 1125–1134. <https://doi.org/10.1007/s10570-012-9729-x>
- Gehmayr, V., Schild, G., & Sixta, H. (2011). A precise study on the feasibility of enzyme treatments of a kraft pulp for viscose application. *Cellulose*, 18(2), 479–491. <https://doi.org/10.1007/s10570-010-9483-x>
- Gharehkhani, S., Sadeghinezhad, E., Kazi, S. N., Yarmand, H., Badarudin, A., Safaei, M. R., & Zubir, M. N. M. (2015). Basic effects of pulp refining on fiber properties - A review. In *Carbohydrate Polymers* (Vol. 115, pp. 785–803). <https://doi.org/10.1016/j.carbpol.2014.08.047>
- Gomes, T. M. P., Mendes De Sousa, A. P., Belenkiy, Y. I., & Evtuguin, D. V. (2020). Xylan accessibility of bleached eucalypt pulp in alkaline solutions. *Holzforschung*, 74(2), 141–148. <https://doi.org/10.1515/hf-2019-0023>
- Gondhalekar, S. C., Pawar, P. J., Dhupal, S. S., & Thakre, S. S. (2019). Mechanism

- of xanthation reaction in viscose process. *Cellulose*, 26(3), 1595–1604.
<https://doi.org/10.1007/s10570-018-2213-5>
- Gong, C., Shi, Y., Ni, J., Yang, X., Liu, Y., & Tian, C. (2017). Integration of hemicellulose recovery and cold caustic extraction in upgrading a paper-grade bleached kraft pulp to a dissolving grade. *Journal of Bioresources and Bioproducts*, 2(1), 20–23. <http://www.bioresources-bioproducts.com/index.php/bb/article/view/103>
- Grönqvist, S., Hakala, T. K., Kamppuri, T., Vehviläinen, M., Hänninen, T., Liitiä, T., Maloney, T., & Suurnäkki, A. (2014). Fibre porosity development of dissolving pulp during mechanical and enzymatic processing. *Cellulose*, 21(5), 3667–3676.
<https://doi.org/10.1007/s10570-014-0352-x>
- Gübitz, G. M., Lischnig, T., Stebbing, D., & Saddler, J. N. (1997). Enzymatic removal of hemicellulose from dissolving pulps. *Biotechnology Letters*, 19(5), 491–495.
<https://doi.org/10.1023/A:1018364731600>
- Guo, S., Zhan, H., Zhang, C., Fu, S., Heijnesson-Hultén, A., Basta, J., & Greschik, T. (2009). Pulp and fiber characterization of wheat straw and eucalyptus pulps - A comparison. *BioResources*, 4(3), 1006–1016.
<https://doi.org/10.15376/biores.4.3.1006-1016>
- Hakala, T. K., Liitiä, T., & Suurnäkki, A. (2013). Enzyme-aided alkaline extraction of oligosaccharides and polymeric xylan from hardwood kraft pulp. *Carbohydrate Polymers*, 93(1), 102–108. <https://doi.org/10.1016/j.carbpol.2012.05.013>
- Hua, L., Bibeau, E., He, P., Salcudean, M., Gartshore, I., Olutoye, M. A., Prep, S., Manual, R., Sumida, M., Suzuki, S., Chidi, O. S., Corson, S. R., Husovska, V., Journal, E. I., Vol, T., Engineering, E., Olugbenga, J., Olutoye, M. A., Chidi, O. S., ... Journal, P. T. (2005). Papermaking STOCK PREPARATION – LC REFINING. *New Zealand Journal of Forestry Science*, 3(7), 49–54.
- Hult, E. L., Liitiä, T., Maunu, S. L., Hortling, B., & Iversen, T. (2002). A CP/MAS ¹³C-NMR study of cellulose structure on the surface of refined kraft pulp fibers. *Carbohydrate Polymers*, 49(2), 231–234. [https://doi.org/10.1016/S0144-8617\(01\)00309-5](https://doi.org/10.1016/S0144-8617(01)00309-5)
- Hutterer, C., Kliba, G., Punz, M., Fackler, K., & Potthast, A. (2017). Enzymatic pulp upgrade for producing high-value cellulose out of a Kraft paper pulp. *Enzyme and Microbial Technology*, 102(March), 67–73.
<https://doi.org/10.1016/j.enzmictec.2017.03.014>
- Hutterer, C., Schild, G., & Potthast, A. (2016). A precise study on effects that trigger alkaline hemicellulose extraction efficiency. *Bioresource Technology*, 214, 460–467. <https://doi.org/10.1016/j.biortech.2016.04.114>
- Ibarra, D., Köpcke, V., Larsson, P. T., Jääskeläinen, A. S., & Ek, M. (2010). Combination of alkaline and enzymatic treatments as a process for upgrading sisal paper-grade pulp to dissolving-grade pulp. *Bioresource Technology*, 101(19), 7416–7423. <https://doi.org/10.1016/j.biortech.2010.04.050>
- Ibarra, D., Larsson, P. T., & Ek, M. (2009). Optimization of Treatments for the Conversion of Eucalyptus Kraft Pulp. *Polymers from Renewable Resources*, 1(1), 17–34.
- Ioelovich, M. (2009). Accessibility and crystallinity of cellulose. *BioResources*, 4(3), 1168–1177. <https://doi.org/10.15376/biores.4.3.1168-1177>

- loelovich, M. Y. (2016). Models of supramolecular structure and properties of cellulose. In *Polymer Science - Series A* (Vol. 58, Issue 6, pp. 925–943). <https://doi.org/10.1134/S0965545X16060109>
- Isik, M., Sardon, H., & Mecerreyes, D. (2014). Ionic liquids and cellulose: Dissolution, chemical modification and preparation of new cellulosic materials. *International Journal of Molecular Sciences*, 15(7), 11922–11940. <https://doi.org/10.3390/ijms150711922>
- Isogai, A., & Atalla, R. H. (1998). Dissolution of cellulose in aqueous NaOH solutions. *Cellulose*, 5(4), 309–319. <https://doi.org/10.1023/A:1009272632367>
- Jacobs, A., & Dahlman, O. (2001). Characterization of the molar masses of hemicelluloses from wood and pulps employing size exclusion chromatography and matrix-assisted laser desorption ionization time-of-flight mass spectrometry. *Biomacromolecules*, 2(3), 894–905. <https://doi.org/10.1021/bm010050b>
- Janzon, R., Puls, J., Bohn, A., Potthast, A., & Saake, B. (2008). Upgrading of paper grade pulps to dissolving pulps by nitren extraction: Yields, molecular and supramolecular structures of nitren extracted pulps. *Cellulose*, 15(5), 739–750. <https://doi.org/10.1007/s10570-008-9224-6>
- Janzon, R., Puls, J., & Saake, B. (2006). Upgrading of paper-grade pulps to dissolving pulps by nitren extraction: Optimisation of extraction parameters and application to different pulps. *Holzforschung*, 60(4), 347–354. <https://doi.org/10.1515/HF.2006.055>
- Janzon, R., Saake, B., & Puls, J. (2008). Upgrading of paper-grade pulps to dissolving pulps by nitren extraction: Properties of nitren extracted xylans in comparison to NaOH and KOH extracted xylans. *Cellulose*, 15(1), 161–175. <https://doi.org/10.1007/s10570-007-9154-8>
- Jędrzejczyk, M., Soszka, E., Czapnik, M., Ruppert, A. M., & Grams, J. (2019). Physical and chemical pretreatment of lignocellulosic biomass. In *Second and Third Generation of Feedstocks: The Evolution of Biofuels* (pp. 143–196). <https://doi.org/10.1016/B978-0-12-815162-4.00006-9>
- Jones, B. W., Venditti, R., Park, S., & Jameel, H. (2017). Optimization of pilot scale mechanical disk refining for improvements in enzymatic digestibility of pretreated hardwood lignocellulosics. *BioResources*, 12(3), 4567–4593. <https://doi.org/10.15376/biores.12.3.4567-4593>
- Jong, E. de, Higson, A., Walsh, P., & Wellisch, M. (2011). Task 42 Biobased Chemicals - Value Added Products from Biorefineries. A Report Prepared for IEA Bioenergy-Task, 36.
- Keeble, B. R. (1988). The Brundtland Report: “Our Common Future.” *Medicine and War*, 4(1), 17–25. <https://doi.org/10.1080/07488008808408783>
- Kerekes, R. J. (2005). Characterizing refining action in PFI mills. *Tappi Journal*, 4(3), 9–14.
- Kerekes, R. J. (2015). Perspectives on High and Low Consistency Refining in Mechanical Pulping. *BioResources*, 10(4), 8795–8811. <https://doi.org/10.15376/biores.10.4.8795-8811>
- Kim, C. H., Lee, J., Treasure, T., Skotty, J., Floyd, T., Kelley, S. S., & Park, S. (2019). Alkaline extraction and characterization of residual hemicellulose in dissolving

- pulp. *Cellulose*, 26(2), 1323–1333. <https://doi.org/10.1007/s10570-018-2137-0>
- Kirk, T. K. (1988). *Biochemistry of Lignin Degradation By Phanerochaete chrysosporium*. FEMS SYMPOSIUM (PLENUM PRESS), 43, 315–332.
- Köpcke, V. (2008). Improvement on cellulose accessibility and reactivity of different wood pulps. *Cellulose*.
- Köpcke, V. (2010). Conversion of Wood and Non-wood Paper- grade Pulps to Dissolving-grade Pulps. <http://www.diva-portal.org/smash/get/diva2:373492/FULLTEXT01.pdf>
- Köpeke, V., Ibarra, D., & Ek, M. (2008). Increasing accessibility and reactivity of paper grade pulp by enzymatic treatment for use as dissolving pulp. *Nordic Pulp and Paper Research Journal*, 23(4), 363–368. <https://doi.org/10.3183/npprj-2008-23-04-p363-368>
- Kral, P., Klimek, P., & Mishra, P. K. (2015). Effect of refiner plate pattern design on refined fibre size distribution—a time series study. *Drvna Industrija*, 66(1), 63–67. <https://doi.org/10.5552/drind.2015.1368>
- Kumar, H., & Christopher, L. P. (2017). Recent trends and developments in dissolving pulp production and application. In *Cellulose* (Vol. 24, Issue 6, pp. 2347–2365). Springer Netherlands. <https://doi.org/10.1007/s10570-017-1285-y>
- Laine, C. (2005). Structures of hemicelluloses and pectins in wood and pulp. Department of Chemical Technology, Doctor of(October), 63. <http://lib.tkk.fi/Diss/2005/isbn9512276909/>
- Laine, C., Asikainen, S., Talja, R., Stépán, A., Sixta, H., & Harlin, A. (2016). Simultaneous bench scale production of dissolving grade pulp and valuable hemicelluloses from softwood kraft pulp by ionic liquid extraction. *Carbohydrate Polymers*, 136, 402–408. <https://doi.org/10.1016/j.carbpol.2015.09.039>
- Lee, J. Y., Kim, C. H., Kwon, S., Lee, M. S., & Min, B. G. (2016). Representative effects of valley beater and disk refiner on pulp fibers. *Palpu Chongi Gisul/Journal of Korea Technical Association of the Pulp and Paper Industry*, 48(5), 37–44. <https://doi.org/10.7584/JKTAPPI.2016.10.48.5.37>
- Li, H., Legere, S., He, Z., Zhang, H., Li, J., Yang, B., Zhang, S., Zhang, L., Zheng, L., & Ni, Y. (2018). Methods to increase the reactivity of dissolving pulp in the viscose rayon production process: a review. In *Cellulose* (Vol. 25, Issue 7, pp. 3733–3753). Springer Netherlands. <https://doi.org/10.1007/s10570-018-1840-1>
- Li, J., Hu, H., Li, H., Huang, L., Chen, L., & Ni, Y. (2017). Kinetics and mechanism of hemicelluloses removal from cellulosic fibers during the cold caustic extraction process. *Bioresource Technology*, 234, 61–66. <https://doi.org/10.1016/j.biortech.2017.03.026>
- Li, J., Liu, Y., Duan, C., Zhang, H., & Ni, Y. (2015). Mechanical pretreatment improving hemicelluloses removal from cellulosic fibers during cold caustic extraction. *Bioresource Technology*, 192, 501–506. <https://doi.org/10.1016/j.biortech.2015.06.011>
- Li, J., Ma, X., Duan, C., Liu, Y., Zhang, H., & Ni, Y. (2016). Enhanced removal of hemicelluloses from cellulosic fibers by poly(ethylene glycol) during alkali treatment. *Cellulose*, 23(1), 231–238. <https://doi.org/10.1007/s10570-015-0800-2>

- Li, J., Zhang, H., Duan, C., Liu, Y., & Ni, Y. (2015). Enhancing hemicelluloses removal from a softwood sulfite pulp. *Bioresource Technology*, 192(April), 11–16. <https://doi.org/10.1016/j.biortech.2015.04.107>
- Li, J., Zhang, S., Li, H., Ouyang, X., Huang, L., Ni, Y., & Chen, L. (2018). Cellulase pretreatment for enhancing cold caustic extraction-based separation of hemicelluloses and cellulose from cellulosic fibers. *Bioresource Technology*, 251(December), 1–6. <https://doi.org/10.1016/j.biortech.2017.12.026>
- Liu, S., He, H., Fu, X., Wang, Y., Wang, Q., Yang, G., & Chen, J. (2019). Correlation Between Fock Reactivity and Intrinsic Viscosity of Dissolving Pulp During Cellulase Treatment. *Journal of Wood Chemistry and Technology*, 39(4), 296–303. <https://doi.org/10.1080/02773813.2019.1565867>
- Lumiainen, J. (2000). Refining of chemical pulp. *Papermaking Science and Technology, Papermaking - Part1, Stock Preparation and Wet End. Book 8. Volume 8*, 87–121.
- Luukko, K., & Maloney, T. C. (1999). Swelling of mechanical pulp fines. *Cellulose*, 6(2), 123–136. <https://doi.org/10.1023/a:1009256307149>
- Lyytikäinen, K., & Backfolk, K. (2017). Refining of birch kraft pulp before or during xylanase treatment - Effect on carbohydrate release and retention behavior. *Nordic Pulp and Paper Research Journal*, 32(1). <https://doi.org/10.3183/npprj-2017-32-01-p087-096>
- Marques, A. I., Serrano, M. de L., Alves, A. M. B., & de Sousa, A. P. M. (2019). Isolation of xylans from bleached Eucalyptus kraft pulp by antisolvents precipitation. *Cellulose*, 26(3), 1977–1992. <https://doi.org/10.1007/s10570-018-1941-x>
- Mayr, M., Eckhart, R., Winter, H., & Bauer, W. (2017). A novel approach to determining the contribution of the fiber and fines fraction to the water retention value (WRV) of chemical and mechanical pulps. *Cellulose*, 24(7), 3029–3036. <https://doi.org/10.1007/s10570-017-1298-6>
- Miao, Q., Chen, L., Huang, L., Tian, C., Zheng, L., & Ni, Y. (2014). A process for enhancing the accessibility and reactivity of hardwood kraft-based dissolving pulp for viscose rayon production by cellulase treatment. *Bioresource Technology*, 154, 109–113. <https://doi.org/10.1016/j.biortech.2013.12.040>
- Miao, Q., Tian, C., Chen, L., Huang, L., Zheng, L., & Ni, Y. (2015). Combined mechanical and enzymatic treatments for improving the Fock reactivity of hardwood kraft-based dissolving pulp. *Cellulose*, 22(1), 803–809. <https://doi.org/10.1007/s10570-014-0495-9>
- Monica Ek, Göran Gellerstedt, G. H. (1993). *Pulp and Paper Chemistry and Technology Volume 2. In Standardization News (Vol. 22, Issue 8)*. <https://pdfs.semanticscholar.org/88df/c949855eeceb73fa4667eb69b79e043c9951.pdf#page=11>
- Motamedian, H. R., Halilovic, A. E., & Kulachenko, A. (2019). Mechanisms of strength and stiffness improvement of paper after PFI refining with a focus on the effect of fines. *Cellulose*, 26(6), 4099–4124. <https://doi.org/10.1007/s10570-019-02349-5>
- Navard, P., & Cuissinat, C. (2006). Cellulose swelling and dissolution as a tool to study the fiber structure. 7th International Symposium “Alternative Cellulose: Manufacturing, Forming, Properties,” 7 pages. <https://hal-mines->

paristech.archives-ouvertes.fr/hal-00579326

- Oh, S. Y., Dong, I. Y., Shin, Y., Hwan, C. K., Hak, Y. K., Yong, S. C., Won, H. P., & Ji, H. Y. (2005). Crystalline structure analysis of cellulose treated with sodium hydroxide and carbon dioxide by means of X-ray diffraction and FTIR spectroscopy. *Carbohydrate Research*, 340(15), 2376–2391. <https://doi.org/10.1016/j.carres.2005.08.007>
- Olejnik, K., Skalski, B., Stanislawska, A., & Wysocka-Robak, A. (2017). Swelling properties and generation of cellulose fines originating from bleached kraft pulp refined under different operating conditions. *Cellulose*, 24(9), 3955–3967. <https://doi.org/10.1007/s10570-017-1404-9>
- Page, D. . (1989). The beating of chemical pulp- the action and the effects. In *Fundamentals of papermaking* (Vol. 1).
- Park, S., Baker, J. O., Himmel, M. E., Parilla, P. A., & Johnson, D. K. (2010). Cellulose crystallinity index: measurement techniques and their impact on interpreting cellulase performance Sunkyu. *Biotechnology for Biofuels*, 3(10), 1–10. <https://doi.org/10.1080/02773818608085213>
- Peciulyte, A., Karlström, K., Larsson, P. T., & Olsson, L. (2015). Impact of the supramolecular structure of cellulose on the efficiency of enzymatic hydrolysis. *Biotechnology for Biofuels*, 8(1), 1–13. <https://doi.org/10.1186/s13068-015-0236-9>
- Pere, J., Tammelin, T., Niemi, P., Lille, M., Virtanen, T., Penttilä, P. A., Ahvenainen, P., & Grönqvist, S. (2020). Production of High Solid Nanocellulose by Enzyme-Aided Fibrillation Coupled with Mild Mechanical Treatment. *ACS Sustainable Chemistry and Engineering*, 8(51), 18853–18863. <https://doi.org/10.1021/acssuschemeng.0c05202>
- Pinto, P. C., Evtuguin, D. V, & Neto, C. P. (2005). Structure of hardwood glucuronoxylans: Modifications and impact on pulp retention during wood kraft pulping. *Carbohydrate Polymers*, 60(4), 489–497. <https://doi.org/10.1016/j.carbpol.2005.03.001>
- Pouyet, F., Chirat, C., Potthast, A., & Lachenal, D. (2014). Formation of carbonyl groups on cellulose during ozone treatment of pulp: Consequences for pulp bleaching. *Carbohydrate Polymers*, 109, 85–91. <https://doi.org/10.1016/j.carbpol.2014.02.082>
- Przybysz, P., Dubowik, M., Małachowska, E., Kucner, M., Gajadur, M., & Przybysz, K. (2020). The effect of the refining intensity on the progress of internal fibrillation and shortening of cellulose fibers. *BioResources*, 15(1), 1482–1499. <https://doi.org/10.15376/biores.15.1.1482-1499>
- Richter, G. A., & Glidden, K. E. (1940). Cellulose sheet swelling effect of temperature and concentration of sodium hydroxide solutions. *Industrial & Engineering Chemistry*, 32(4), 480–486.
- Roselli, A., Asikainen, S., Stepan, A., Monshizadeh, A., Von Weymarn, N., Kovasin, K., Wang, Y., Xiong, H., Turunen, O., Hummel, M., & Sixta, H. (2016). Comparison of pulp species in IONCELL-P: Selective hemicellulose extraction method with ionic liquids. *Holzforschung*, 70(4), 291–296. <https://doi.org/10.1515/hf-2014-0313>
- Roselli, A., Hummel, M., Monshizadeh, A., Maloney, T., & Sixta, H. (2014). Ionic liquid extraction method for upgrading eucalyptus kraft pulp to high purity

- dissolving pulp. *Cellulose*, 21(5), 3655–3666. <https://doi.org/10.1007/s10570-014-0344-x>
- Roux, J., Bloch, J., & Olejnik, K. (2017). Refining Impulse Controls the Morphological Modifications of Fibers. *Trans. of the XVIth Fund. Res. Symp.*, i, 175–194. <https://doi.org/10.15376/frc.2017.1.175>
- Schild, G., & Sixta, H. (2011). Sulfur-free dissolving pulps and their application for viscose and lyocell. *Cellulose*, 18(4), 1113–1128. <https://doi.org/10.1007/s10570-011-9532-0>
- Seth, R. S. (2003). The measurement and significance of fines: Their addition to pulp improves sheet consolidation. *Pulp & Paper Canada*, 2, 47–50. <https://www.pulpandpapercanada.com/paptac/PDFs/SethFeb42.pdf>
- Sharma, K., Khaire, K. C., Thakur, A., Moholkar, V. S., Goyal, A., & Goyal, A. (2020). Acacia Xylan as a Substitute for Commercially Available Xylan and Its Application in the Production of Xylooligosaccharides. *ACS Omega*, 5(23), 13729–13738. <https://doi.org/10.1021/acsomega.0c00896>
- Sharma, K., Morla, S., Khaire, K. C., Thakur, A., Moholkar, V. S., Kumar, S., & Goyal, A. (2020). Extraction, characterization of xylan from *Azadirachta indica* (neem) sawdust and production of antiproliferative xylooligosaccharides. *International Journal of Biological Macromolecules*, 163, 1897–1907. <https://doi.org/10.1016/j.ijbiomac.2020.09.086>
- Shen, L., Worrell, E., & Patel, M. K. (2010). Environmental impact assessment of man-made cellulose fibres. *Resources, Conservation and Recycling*, 55(2), 260–274. <https://doi.org/10.1016/j.resconrec.2010.10.001>
- Sieminsky, A. (2014). *International Energy Outlook*. Outlook, November, 70–99. <http://www.informaworld.com/openurl?genre=article&doi=10.1080/01636609609550217&magic=crossref>
- Sihtola, H., Kyrklund, B., Laamanen, L., & Palenius, I. (1963). Comparison and conversion of viscosity and DP-values determined by different methods. *Paperi Ja Puu*, 45(4a), 225–232.
- Sindhu, R., Binod, P., & Pandey, A. (2016). Biological pretreatment of lignocellulosic biomass - An overview. *Bioresource Technology*, 199, 76–82. <https://doi.org/10.1016/j.biortech.2015.08.030>
- Sixta, H. (2008a). Pulp Properties and Applications. In *Handbook of Pulp* (Vol. 2, pp. 1009–1067). <https://doi.org/10.1002/9783527619887.ch11>
- Sixta, H. (2008b). Pulp Purification. In *Handbook of Pulp* (Vol. 2, pp. 933–965). <https://doi.org/10.1002/9783527619887.ch8>
- Sluiter, A., Hames, B., Ruiz, R. O., Scarlata, C., Sluiter, J., Templeton, D., & Energy, D. of. (2004). Determination of Structural Carbohydrates and Lignin in Biomass. In *Biomass Analysis Technology Team Laboratory Analytical Procedure* (Issue April).
- Somboon, P. (2011). Quality developments in pulp fibers using conventional papermaking laboratory beaters and an industrial pilot refiner. *Kasetsart Journal - Natural Science*, 45(5), 883–890.
- Stoklosa, R. J., & Hodge, D. B. (2012). Extraction, recovery, and characterization of hardwood and grass hemicelluloses for integration into biorefining processes. *Industrial and Engineering Chemistry Research*, 51(34), 11045–11053.

- <https://doi.org/10.1021/ie301260w>
- TAPPI. (2013). Viscosity of pulp (capillary viscometer method). TAPPI T230 Om-13, 1–9.
- Tian, C., Zheng, L., Miao, Q., Cao, C., & Ni, Y. (2014). Improving the reactivity of kraft-based dissolving pulp for viscose rayon production by mechanical treatments. *Cellulose*, 21(5), 3647–3654. <https://doi.org/10.1007/s10570-014-0332-1>
- Tian, C., Zheng, L., Miao, Q., Nash, C., Cao, C., & Ni, Y. (2013). Improvement in the Fock test for determining the reactivity of dissolving pulp. *Tappi Journal*, 12(11), 21–26.
- Van Hai, L., Park, H. J., & Seo, Y. B. (2013). Effect of PFI mill and Valley beater refining on cellulose degree of polymerization, alpha cellulose contents, and crystallinity of wood and cotton fibers. *Palpu Chongi Gisul/Journal of Korea Technical Association of the Pulp and Paper Industry*, 45(4), 27–33. <https://doi.org/10.7584/ktappi.2013.45.4.027>
- Vanholme, R., Demedts, B., Morreel, K., Ralph, J., & Boerjan, W. (2010). Lignin biosynthesis and structure. *Plant Physiology*, 153(3), 895–905. <https://doi.org/10.1104/pp.110.155119>
- Vena, P. F., García-Aparicio, M. P., Brienzo, M., Görgens, J. F., & Rypstra, T. (2013). Effect of alkaline hemicellulose extraction on kraft pulp fibers from eucalyptus grandis. *Journal of Wood Chemistry and Technology*, 33(3), 157–173. <https://doi.org/10.1080/02773813.2013.773040>
- Viikari, L., Oksanen, T., Suurnäkki, A., Buchert, J., & Pere, J. (2000). Cellulases in Pulp and Paper Processing. *Cellulosic Pulps, Fibres and Materials*, 69–80. <https://doi.org/10.1533/9781845698546.69>
- Wang, H., Pang, B., Wu, K., Kong, F., Li, B., & Mu, X. (2014). Two stages of treatments for upgrading bleached softwood paper grade pulp to dissolving pulp for viscose production. *Biochemical Engineering Journal*, 82, 183–187. <https://doi.org/10.1016/j.bej.2013.11.019>
- Wang, S., Lu, A., & Zhang, L. (2016). Recent advances in regenerated cellulose materials. In *Progress in Polymer Science* (Vol. 53, pp. 169–206). Elsevier Ltd. <https://doi.org/10.1016/j.progpolymsci.2015.07.003>
- Westbye, P., Köhnke, T., & Gatenholm, P. (2008). Fractionation and characterization of xylan rich extracts from birch. *Holzforschung*, 62(1), 31–37. <https://doi.org/10.1515/HF.2008.005>
- Wetterling, J. (2012). Modelling of hemicellulose degradation during softwood kraft pulping. 8–9.
- WHISTLER, R. L. (1973). Solubility of Polysaccharides and Their Behavior in Solution. 242–255. <https://doi.org/10.1021/ba-1971-0117.ch014>
- Wiedenhoef, A. C., & Miller, R. B. (2005). Chapter 3. Structure and Function of Wood. In *Handbook of wood chemistry and wood composites*.
- Www.britannica.com. (n.d.). <https://www.britannica.com/science/wood-plant-tissue/Microstructure>.
- Yasumura, P. K. (2012). Multivariate Statistical Evaluation of Physical. 73(March), 59–65.
- Yuan, Z., Wen, Y., Kapu, N. S., Beatson, R., & Mark Martinez, D. (2017). A

- biorefinery scheme to fractionate bamboo into high-grade dissolving pulp and ethanol. *Biotechnology for Biofuels*, 10(1), 1–16.
<https://doi.org/10.1186/s13068-017-0723-2>
- Zhang, C., Liu, R., Xiang, J., Kang, H., Liu, Z., & Huang, Y. (2014). Dissolution mechanism of cellulose in N,N-dimethylacetamide/lithium chloride: Revisiting through molecular interactions. *Journal of Physical Chemistry B*, 118(31), 9507–9514. <https://doi.org/10.1021/jp506013c>
- Zhang, N., Li, S., Xiong, L., Hong, Y., & Chen, Y. (2015). Cellulose-hemicellulose interaction in wood secondary cell-wall. *Modelling and Simulation in Materials Science and Engineering*, 23(8). <https://doi.org/10.1088/0965-0393/23/8/085010>
- Zhang, W., Johnson, A. M., Barone, J. R., & Renneckar, S. (2016). Reducing the heterogeneity of xylan through processing. *Carbohydrate Polymers*, 150(September 2017), 250–258. <https://doi.org/10.1016/j.carbpol.2016.05.013>
- Zhao, L., Yuan, Z., Kapu, N. S., Chang, X. F., Beatson, R., Trajano, H. L., & Martinez, D. M. (2017). Increasing efficiency of enzymatic hemicellulose removal from bamboo for production of high-grade dissolving pulp. *Bioresource Technology*, 223, 40–46. <https://doi.org/10.1016/j.biortech.2016.10.034>
- Zhou, S., Li, Y., Huang, L., Chen, L., & Miao, Q. (2018). Enhanced reactivity of kraft-based viscose-grade dissolving pulp by hollander beating treatment. *BioResources*, 13(2), 2861–2870. <https://doi.org/10.15376/biores.13.2.2861-2870>
- Zhu, J. Y., Wang, G. S., Pan, X. J., & Gleisner, R. (2009). Specific surface to evaluate the efficiencies of milling and pretreatment of wood for enzymatic saccharification. *Chemical Engineering Science*, 64(3), 474–485.
<https://doi.org/10.1016/j.ces.2008.09.026>
- Zink-Sharp, A. (2004). Wood Formation and Properties. *Crystal Research and Technology*, 32(1), 187–193.

Appendix

Scientific contributions

Articles (in international journals)

Ngene, G. I., Roux, J. C., & Lachenal, D. (2022). Influence of Hollander Beater Refining on Xylan Extraction from Hardwood Paper Pulp by Cold Caustic Extraction and Xylanase Treatment. *BioResources*, 17(1), 908–921. <https://doi.org/DOI:10.15376/biores.17.1.908-92>

Ngene, G. I., Roux, J. C., & Lachenal, D. (2022). Xylan Extraction Strategies and the Performance of the Resulting High Purity Cellulose Fiber to Swelling and Dissolution. *Carbohydrate Polymers and Applications technologies*. <https://doi.org/10.1016/j.carpta.2022.100196>

Communications (conference proceedings)

Oral presentations in the following meetings

Ngene, G. I., Roux, J. C., & Lachenal, D. (2021). A New Approach to Xylan Extraction from Paper Pulp by Implementing Simultaneous Mechanical Refining with Chemical or Enzymatic Treatment. 7th EPNOE International Polysaccharides Conference (11-15 October, 2021).

Ngene, G. I., Roux, J. C., & Lachenal, D. (2021). Effect of Valley Beater Refining on Hemicellulose Extraction from Hardwood Paper Pulp. XXV TECNICELPA - International Forest, Pulp and Paper Conference XI CIADICYP (10, 11, 12 March, 2021).

Ngene, G. I., Roux, J. C., & Lachenal, D. (2021). Study of Different Refining Mechanisms on the Extraction of Hemicellulose from Paper Pulp. EPNOE Junior scientists meeting (February 3 - 4, 2021).

A poster presentation

Ngene, G. I., Roux, J. C., & Lachenal, D. (2019). Coupling of Mechanical Refining, Chemical and Enzymatic Treatments on Hemicellulose Removal. Glyco@Alps club meetings 2019.