ABSTRACT

ZAMBRANO GOTERA, FRANKLIN J. Developing and Understanding State-of-the-art Technologies at Nano- and Macroscales to Enhance Fiber Utilization in the Hygiene Tissue Industry (Under the direction of Dr. Ronalds W. Gonzalez, Dr. Richard Venditti and Dr. Hasan Jameel).

In recent years, the hygiene tissue industry has been exposed to multiple challenges related to the increasing cost of raw materials, the shrinking supply of recycled fibers from high-grade recovered papers, the rise in the offering of private labels, changes in consumer values, and growing demand for sustainable products. This situation has escalated the pressure on producers that strive to remain profitable in a highly competitive market.

Various approaches have been implemented to create product differentiation and capture additional value from consumers, such as innovative designs and sustainable branding. Cost reduction has also been among the top priorities for tissue companies. Fiber is the primary cost driver for tissue paper manufacturing accounting for 45% to 59% of the total manufacturing cost. Therefore, focusing on strategies to optimize fiber utilization in the tissue product and offset price volatility of market pulps and high-grade recovered papers offers substantial opportunities to drive cost savings and protect profit margins.

This study explores the development and application of technologies that aim to reduce market effects on the profitability and stability of the hygiene tissue business. In a broad sense, the strategies developed involve reducing manufacturing costs and using alternative fibers to improve the flexibility of the fiber supply chain. This is performed based on a fundamental understanding of the factors that dictate tissue properties so that proper product performance is ensured upon application of the technologies.

The **first study** presents a literature review on the use of micro- and nanofibrillated cellulose (MNFC) in papermaking applications. This study revealed that most of the literature

available focuses on improving the strength of graphic papers and packaging grades with the addition of MNFC. Based on the premise that strength standards are already met for most paper grades and consumers may not necessarily be interested in papers exhibiting enhanced strength, it is proposed that the MNFC reinforcing potential should be instead utilized to reduce the fiber content while delivering the strength commercially required. The lack of holistic studies on the use of MNFC in tissue papers also demonstrated the need to understand the impact of the MNFC on tissue properties.

The **second study** aims to understand the effect of MNFC on the tensile strength, water absorbency, and softness of tissue paper. A comparative investigation was performed with MNFC prepared from various virgin (hardwood and softwood) and recycled fibers, considering the impact of the fiber source on MNFC manufacturing cost and the trade-off with performance. The results showed that MNFC acts as an effective strength enhancer at the expense of a reduced water absorbency, softness, and freeness of the slurry. MNFCs produced from southern bleached hardwood kraft, northern bleached softwood kraft, and deinked pulp exhibited similar performance trends, with the MNFC from the deinked pulp having a significantly lower cost. This suggests that MNFCs with similar fibrillation degrees may be used interchangeably regardless of the fiber source, revealing the possibility to minimize MNFC production costs based on fiber selection.

The **third study** demonstrates the use of extensively refined macro-fibers and MNFC to reduce the fiber content in tissue paper from 10% to 15% without impairing product performance. This strategy for decreasing manufacturing cost, which is referred to as the fiber reduction (FiRe) technology, also relies on a cationic polymer to counteract the adverse effects on drainability of the fiber furnish derived from the highly fibrillated material.

The **fourth study** presents a literature review on the fundamental factors affecting the absorbency of tissue papers (e.g., fiber selection, machine technology, wet-end, and creping chemistry) and methods to improve absorbency. The study also discusses the practical aspects related to the measurement of the absorbent properties of tissue and towel, and the end-of-life of tissue products.

The **fifth study** evaluates the suitability of old corrugated containerboard (OCC) to be upcycled into a high-quality pulp for tissue paper manufacture. OCC was bleached to ca. 75% ISO-brightness using two elemental chlorine-free (ECF) bleaching sequences. The tissue-making properties of OCC pulp were evaluated across each bleaching stage and were correlated with changes in the physicochemical properties of OCC fibers. Overall, bleaching significantly increased tensile index and absorbency rate with adverse effects on bulk and softness and minor impacts on absorption capacity. The performance of bleached OCC was compared to that of deinked pulp (DIP), southern bleached softwood kraft (SBSK), and refined OCC unbleached. The results indicate that the upcycled OCC could serve as an alternative fiber to address the forecasted shortage of high-grade recycled papers in manufacturing recycled tissue grades, as well as a replacement for virgin fibers in manufacturing virgin tissue grades. Refined OCC unbleached could also be suitable for brown tissue grades; however, problems related to low absorption rate and freeness are limiting factors to attain high-performance products.

The **sixth study** explores the application of total chlorine-free (TCF) oxidative treatments, viz., oxygen delignification, alkaline hydrogen peroxide bleaching, and ozonation, to improve the tissue-making quality of OCC pulp while maintaining a high lignin content (kappa number > 50). Compared to tissue sheets made from mechanically refined OCC pulp, TCF treated pulps rendered tissue sheets with higher water absorption capacity and absorption rate

and fiber slurries with higher freeness. These results revealed an opportunity to produce high-performance brown tissue products that could meet consumers' rising interest in unbleached tissue papers, perceived as sustainable. At the same time, they show an alternative for repurposing and adding value to the excess packaging waste likely to remain in the US as a consequence of China's ban on US paper waste imports.

Developing and Understanding State-of-the-art Technologies at Nano- and Macroscales to Enhance Fiber Utilization in the Hygiene Tissue Industry

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DEDICATION

To my wife, parents, and grandparents (also Paula), who never doubted I could reach this and more. The bar still remains high.

BIOGRAPHY

Franklin Zambrano was born in 1992 in San Cristobal, Venezuela. In 2009, he participated in a long-term exchange student program in Germany. This was an opportunity for Franklin to learn a new language, enrich his personal development, and acquire a global social perspective. In 2010, he moved back to Venezuela to pursue his undergraduate degree in Chemical Engineering at the University of Los Andes in Merida. During his senior year, he was a junior research assistant at the Laboratory of Formulation, Interphases, Rheology, and Processes (FIRP), where he researched the breakage of high internal phase water-in-oil emulsions. Following his graduation, Franklin moved to Raleigh NC, to pursue his Ph.D. in Forest Biomaterials at North Carolina State University starting in August 2017. While pursuing his Ph.D., Franklin obtained a Graduate Certification in Nonwovens Science and Engineering from The Nonwovens Institute, Wilson College of Textiles. After graduation, he will move to Wilmington DE, to work for a specialty chemical company in the pulp and paper industry.

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Finally, I am deeply thankful for my wife and family. "Every big accomplishment is a series of little accomplishments," and you have been key in the little ones that make you keep momentum in life.

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1 INTRODUCTION

1.1 Overview of hygiene tissue papers

Tissue papers are lightweight paper products designed for sanitary applications. Based on their end-use, e.g., facial tissue, bath tissue, paper towels, or napkins, tissue papers are formulated to exhibit a wide range of properties (Batra et al. 2000). For example, softness, absorbency, and brightness are desirable for bath and facial tissue, whereas absorbency and strength are more relevant for napkins and paper towels (Zou 2017). Consumers integrate these attributes to evaluate their overall impression of the product and make a final purchase decision (Barnholtz et al. 2011). Occasionally manufacturers will design products with features beyond the basic functionality to satisfy consumer desire and increase market share (Novotny 1988). Consumers that are sensitive to hand feel comfort will likely buy paper towels that are soft, even though softness does not contribute to the performance of paper towels in cleaning and drying surfaces (de Assis et al. 2018b).

The properties of tissue papers are primarily a function of fiber selection, machine technology, and chemical additives (both dry and wet-end chemistry) (de Assis et al. 2018b). Long fibers provide high mechanical resistance and high pore volume to the paper web for superior water uptake, whereas short fibers improve formation uniformity, enhance the tactile perception of the sheet, and provide the web with fine pores for superior water holding capacity (Nanko et al. 2010). Virgin fibers with lower fines content and higher flexibility produce sheets with higher strength and softness compared to recycled fibers (de Assis et al. 2019).

Conventional machine technologies, such as Light Dry Crepe (LDC), rely on wet pressing to promote mechanical dewatering of the paper web until 40–45% before transferring the sheet to the Yankee dryer. Wet pressing densifies the sheet, resulting in tissue papers with

reduced water absorbency and softness. Conversely, advanced machine technologies, such as Through-Air Drying (TAD), remove water (until 40–80% consistency) using hot air blown to the wet paper web, rendering sheets with higher bulk, softness, and absorbency (de Assis et al. 2018b). Final drying of the fiber web to consistencies around 94–98% is achieved in the Yankee cylinder, a steam-heated roll surrounded by a hot air flow confined within a hood (Kullander 2012).

The last step of the tissue manufacturing operation includes creping of the paper web. During the creping process, a creping blade, known as the creping doctor, scrapes off the tissue sheet from the Yankee cylinder. This action compacts the sheet in machine direction, resulting in the textured surface structure characteristic of tissue papers (Donner and Manifold 2008). The mechanical force applied to the web causes delamination of the internal fiber layers, causing rupture and weakening of some of the fiber-to-fiber bonds within the network, buckling of fibers, and exposure of individual fibers on the surface. This action improves the extensibility, bulkiness, compressibility, absorbency, and softness of the final tissue sheet (Pan et al. 2018, 2019; Ramasubramanian and Shmagin 2002).

Finally, softener or debonding agents improve softness of tissue products by reducing strength of the paper web and increasing bulk (Liu and Hsieh 2000). Debonding agents are amphiphilic compounds containing hydrophobic (long-chain esters or amide radicals of etherified hydroxycarboxylic acids) and hydrophilic groups (typically, a quaternary ammonium salt that shows affinity to towards the negatively charged fibers). The underlying mechanism is based on the disruption of hydrogen bonding between fibers in the paper web due to the presence of large fatty alkyl chains linked to the cationic group in the debonder (Poffenberger 1996). Although the debonding action improves softness and the fatty moieties impart a lubricating, soft

feel to the sheet surface, their hydrophobic nature also causes an undesired reduction in absorbency (Parham and Hergert 1980). Some debonder formulations are designed to balance the hydrophobic-hydrophilic balance or include rewet aides to mitigate the reduction in absorbency (Poffenberger 1996). Lotions (silicon and non-silicone-based) are also sprayed onto the surface of the tissue sheet to improve the surface softness component (Park et al. 2019).

1.2 The hygiene tissue market: Global status, challenges and trends

The hygiene tissue market is a highly complex and global market valued at USD 72.8 billion in 2015 (de Assis et al. 2018b). Global tissue production reached 38.7 million tonnes in 2018 with steady growth at a CAGR of 3.5% between 2000 and 2018 (Fastmarkets RISI 2020). In the last decade, tissue manufacturers have been under much pressure to minimize costs and regulate pricing as a result of major challenges related to fiber sourcing, high market competition, increase in private label options, changes in consumer values, and growing demand for sustainable products (Figure 1-1).

Figure 1-1: Major challenges faced by the hygiene tissue industry responsible for strong pricing pressures

The significant disruptions in supply and fluctuation in fiber prices has been attributed to the reduced consumption of printing and writing paper owing to increased digitalization, which has shrunk the supply of high-grade recycled fibers (Gregg 2018). In the US alone, the production of printing and writing paper has declined at a CAGR of 3.3% over the past 10 years (around 35% of the total volume produced in 2010) (FAO 2020). High-grade recycled fibers such as “sorted office paper” and “sorted white ledger” are the primary fiber sources used in the US tissue market (Gregg 2018). About 85% of Away-from-home tissue is manufactured with recycled fibers (only 10% of At-home tissue is manufactured with recycled fibers leaving the vast majority manufactured with virgin fiber). With less post-consumer fiber available and an absence of virgin fiber feed into the recovery cycle, fiber quality has been continually diminished. Over-recycled papermaking fibers result in tissue products with inferior performance, causing an accelerated shift to virgin fibers of higher quality but more expensive, in addition to higher utilization of synthetic additives and enzymatic technologies to help meet product performance specifications (Rager 2018).

Despite high market pulp prices, tissue producers have been continuously exposed to decreasing margins caused by the impossibility to increase retailing prices due to very high market competition (Uutela 2019). Market saturation is becoming a severe problem in some regions, to the point where the announced tissue capacity expansion sometimes exceeds the organic market growth. Projects have been delayed to help diminishing the risk of overcapacity (Uutela 2019). Product commoditization resulting from the lack of consumer-relevant innovation in a mature tissue market and the increase in offering of private labels is also a challenge (Groth 2019; Quilleré 2019). Because of little product differentiation offered by national brands, consumers are increasingly attracted to private label products that offer similar performance at a

lower price, affecting margins of branded tissue products. Such megatrend is referred to as the "middle class retreat" (Quilleré 2019). Private labels have consistently managed to gain market share at the expense of established brands. The retail volume of private labels in the U.S. showed a growth of 4.8% between 2014 and 2019 (Euromonitor International 2019), and today represents approximately 27% of the market share in the retail tissue segment (Uduslivaia 2019). Worldwide private labels accounts for 35% of the total tissue market share (Valmet 2019). This market development is expected to accentuate with the aggressive growth of discount stores, whose business models, based on selected private labels with high perceived value, allows for lower retailing prices while providing high-quality performance (Zambrano et al. 2020).

Effects of global megatrends such as changes in demographic behaviors and ethical living have translated into additional pressures to the tissue market (Quilleré 2019). Behaviors of generational groups such as Millennials, who have considerably increased their purchasing power with approximately $600 billion spent yearly in the US, have remarkably contributed to the growth of private labels (Donnelly and Scaff 2013). Millennials primarily seek value, quality, and experiences in their products, which private labels have successfully managed to offer (Rosenstrauch 2019). It has been reported that 60% of Millennials prefer to purchase private labels over national brands (Fromm et al. 2011). This generation is also known for causing serious disruptions in the napkin industry in recent years (Schossberg 2016). They have been accused of 'killing' the napkins by replacing them for paper towels, which they consider are more functional and multipurpose.

As part of ethical living, the growth of environmental awareness has been a topic of increasing attention for Millennials, who demand the industry to adopt more sustainable practices (Hensley et al. 2020; Quilleré 2019). The industry has responded with an increase in

the offering of products marketed as eco-friendly in the past three years, and some manufacturers have looked at these market trends as an opportunity to create product differentiation. Sustainable tissue products, which are typically manufactured using recycled wood fibers, display significant price premiums, being sold at higher shelf prices (48% for the case of paper towels) compared to tissue products without sustainability labels, while exhibiting poorer performance (e.g., 37% lower water absorbency for the case of paper towels) (Hensley et al. 2020). In addition to using recycled wood fibers, there has also been a growing interest in the use of alternative fibers such as non-woods and agricultural residues for the manufacture of eco-friendly tissue products, which are commonly advertised as being 'tree free' (Janda 2019).

The previous scenario has created a "perfect storm" with significant impacts on the US hygiene tissue industry profitability, where fiber cost has been one of the aspects most critically affected. Fluctuations in fiber prices resulted in an additional USD 450 million burden in 2016, and USD 600 million in 2017 compared to the 2015 base line (Gonzalez et al. 2018). Major factors of uncertainty related to China's bans on recovered paper, unscheduled downtime in market pulp producing mills, switch of paper grade pulp to alternative uses (e.g., dissolving and fluff pulp), changes in global economy and trade policies, and sustained demand in market pulp, threat to further contribute to the high volatility of market pulp prices (Amberla 2019). To worsen problem, the COVID-19 pandemic generated a global shortage of hygiene tissue papers as a consequence of stockpiling by consumers feeling threat by the disease (Garbe et al. 2020). Toilet paper prices increased 15.6% from May 2020 to May 2021 as a result of rising wood pulp prices influenced by global disruptions in supply chains and the post-COVID recovery in China (the biggest buyer of market pulp in the world). Consequently, several US tissue manufacturers

have recently announced price increases to help offset significant commodity cost inflation (Meyersohn 2021).

1.3 Motivation, working hypotheses and thesis structure

Considering the highly dynamic environment surrounding the hygiene tissue industry, it is clear the need of manufacturers to reduce the impact that the previously described market effects could have on the profitability and stability of their businesses.

This dissertation is founded on the basis of two working hypothesis to contribute towards achieving such goal:

- Reducing the fiber content in tissue products without impairing performance can offset price volatility of market pulps
- Incorporating alternative fibers from upcycled waste materials can protect manufacturers from the forecasted shortage of recycled fiber supply

The conceptualization, development, and demonstration of such hypotheses are presented in 8 chapters that integrate this dissertation and whose objectives are described below. Chapter 1, the introduction herein presented, provides (i) an overview of hygiene tissue papers and factors influencing their performance, (ii) a description of the hygiene tissue market including current challenges and trends, and (iii) motivations, working hypotheses, and structure of the present work.

As previously stated, fibers represent the primary cost driver in tissue-making operations; therefore, reducing their utilization provides an opportunity to improve the cost position of tissue manufacturers. Considering the high strengthening potential of micro- and nanofibrillated cellulose (MNFC) and the growing industrial interest in utilizing such bio-based material in commercial operations, in the form of a literature review, Chapter 2 explores the concept of

using MNFC to reduce the basis weight of paper products. Although many studies had reported on applications of MNFC in high-basis weight paper grades (e.g., printing and writing papers, and packaging), the literature review showed a knowledge gap related to the impact of the MNFC addition on the properties of low-basis weight paper grades such as tissue paper.

To fill this gap, Chapter 3 presents a fundamental study on the effect of the MNFC addition on the properties of hygiene tissue papers (e.g., tensile strength, water absorbency, and softness). MNFCs produced from different fiber sources (hardwood, softwood, and recycled) were incorporated into a tissue-making slurry at various concentrations, and tissue handsheets were made thereof. The impact of the fiber source on the trade-off with performance (tensile index vs. water absorbency and softness) and the MNFC manufacturing costs was investigated. The results from this study showed that MNFC is an effective strength additive in tissue paper (strength improvement as high as 66% were attained); however, strength developments of the fiber web were achieved at the expense of a reduction in water absorbency and softness.

Chapter 2 and 3 build the technical foundation for Chapter 4, which presents the development of a technology to reduce the fiber content in tissue papers without impairing product performance and machine runnability. This technology, referred to as the fiber reduction (FiRe) technology, relies on the use of extensively refined fibers, including macro fibers and MNFC, to promote an “excess” strength in the paper web that is offset with a reduction in fiber content (between 10 to 15%). Compared to a high-basis weight control sheet having the desired functional strength, the sheet produced via the FiRe technology exhibits similar strength at a lower basis weight. The reduction in basis weight also redresses the penalties in softness incurred by the additional development of strength. A drainage aid is incorporated in the fiber slurry formulation to compensate for the drainage losses caused by the extensively refined fibers and

the presence of fine cellulosic material; this way, freeness remains at suitable levels for proper machine runnability. The FiRe reduction technology, awarded the Chancellor's Innovation Fund, has been demonstrated successfully at a commercial scale and is currently under evaluation towards commercialization by major global tissue manufacturers.

Recognizing that water absorbency is one of the main price drivers for hygiene tissue products, particularly for paper towels (de Assis et al. 2018a), Chapter 5 reviews the factors affecting absorbency of fibrous assemblies and methods to attain superior absorbency features.

In view of the future scarcity of high-grade recovered papers and the excess of packaging waste likely to stay in the US as a consequence of the total ban on paper waste recently imposed by China, Chapter 6 presents an upcycling strategy to produce ECF bleached pulp from old corrugated containerboard (OCC) for tissue manufacturing. The performance of this upcycled OCC fiber, relating to its tissue-making properties, was compared to that of recycled and virgin fibers commonly used in tissue-making. The fundamental knowledge gained in Chapter 5 was also applied to elaborate on the underlying absorbency mechanisms of OCC fibers across the different stages of the elemental chlorine-free (ECF) bleaching sequence. Finally, considering the new consumer interest towards brown tissue papers (perceived as sustainable) and the performance gap that exists between unbleached and bleached products (Hensley et al. 2020), Chapter 7 investigates different state-of-the-art technologies, namely oxygen delignification, alkaline hydrogen peroxide bleaching, and ozonation, to improve the tissue-making properties of fibers from OCC while maintaining a high-lignin content. This dissertation ends with overall conclusions and suggestions for future work, presented in Chapter 8.

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2 USING MICRO- AND NANOFIBRILLATED CELLULOSE AS A MEANS TO REDUCE WEIGHT OF PAPER PRODUCTS: A REVIEW[1]

2.1 Abstract

Based on publications related to the use of micro- and nanofibrillated cellulose (MNFC) in papermaking applications, three sets of parameters (intrinsic and extrinsic variables, furnish composition, and degree of dispersion) were proposed. This holistic approach intends to facilitate understanding and manipulation of the main factors describing the colloidal behavior in systems comprising of MNFC, pulp fibers, and additives, which directly impact paper product performance. A preliminary techno-economic assessment showed that cost reductions driven by the addition of MNFC in paper furnishes could be as high as USD 149 per tonne of fiber (up to 20% fiber reduction without adverse effects on paper's strength) depending on the cost of papermaking fibers. It was also determined that better performance in terms of strength development associated with a higher degree of MNFC fibrillation offset its high manufacturing cost. However, there is a limit from which additional fibrillation does not seem to contribute to further strength gains that can justify the increasing production cost. Further research is needed regarding raw materials, degree of fibrillation, and combination with polyelectrolytes to further explore the potential of MNFC for the reduction of weight of paper products.

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2.2 Introduction

The global trend toward digitalization has caused a decline in the consumption and production of printing and writing paper grades. Such reduction has been reported to be approximately 15% across the last 10 years with a forecasted drop of 4% over the next five years. Recycled fibers, more specifically “mixed office waste (MOW)” and “white office ledger (WOL)”, are the most used recycled fibers in the hygiene tissue industry (de Assis et al. 2018b). As digitalization continues to force a reduction in production of printing and writing papers, less MOW and WOL are available to produce recycled paper grades. This disruption in fiber supply has resulted in huge increases and fluctuations in fiber prices (Figure 2-1).

Not only has the availability of fiber been decreasing, but the quality of the fiber that is available has been continuously decreasing as well, resulting in weaker paper. Decrease in paper strength is a major concern since quality standards are rising (Fastmarkets RISI 2017a). Papermakers tend to redress this situation by using expensive fibers that are better quality than the low-cost alternatives. Some even resort to the use of synthetic additives, which results in increased costs per tonne of finished product. To meet market expectations regarding paper strength, mechanical refining of recycled and virgin fibers is a common practice in the industry (Hubbe 2007a). However, in the case of tissue products, even though refining helps to develop fiber and web strength, at the same time it makes the sheet denser and more rigid, which negatively affects water absorbency, bulk, and softness of the tissue sheet, which are key properties of the final product (Kullander et al. 2012).

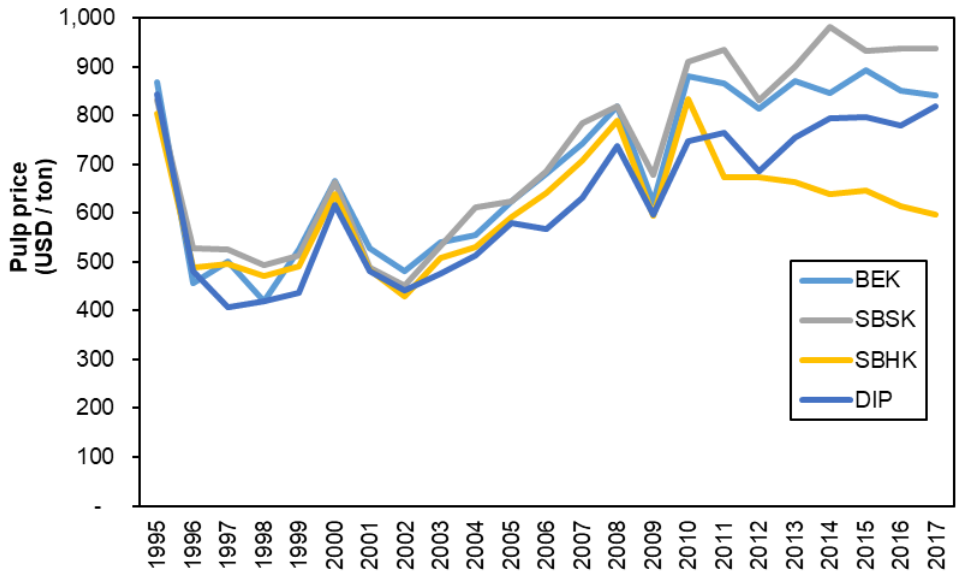

Figure 2-1: Historic fiber cost data for major grades of recycled and virgin fibers: BEK: bleached Eucalyptus kraft; SBSK: southern bleached softwood kraft; SBHK: southern bleached hardwood kraft; DIP: deinked pulp; graph generated with data collected from Fastmarkets RISI (2017b)

There is a pressing need to develop new technologies to face current and future market challenges related to fiber supply, quality, and cost while meeting changes in consumption patterns. Micro- and nanofibrillated (MNFC) has emerged as a promising candidate to generate either high-value applications or low-cost alternatives. Thus far, available reports have been focused on the improvement in tensile strength by addition of MNFC in paper furnishes (Eriksen et al. 2008; He et al. 2017; Taipale et al. 2010). This might be mainly beneficial for poor quality furnishes composed of recycled fibers, where strength properties of such fibers can be insufficient to meet specifications of a paper grade. However, for paper products where strength is not an issue, consumers are not willing to pay a premium for a product that has a superior strength (de Assis et al. 2018a). Therefore, in such cases it makes more sense to consider the gains in strength obtained by MNFC to reduce the fiber content of the paper product instead of

merely developing excess strength. This strategy could potentially allow the production of a lighter-weight version of commercially available papers with properties that are consistent to those available in the market but at a lower manufacturing cost. Moreover, a more rapid adoption of the nanomaterial by the industry can be stimulated given the possible overall economic gain offsetting the high perceived cost of MNFC.

Acknowledging this opportunity, the main goal of this work is to review what is known about factors that affect the ability of highly fibrillated cellulosic materials, such as MNFC, to provide strength and possibly to allow for reductions in the basis weight of various paper products. To accomplish that goal, this review will begin by examining background information concerning nanocellulosic materials and their application in papermaking. To this end, a holistic approach will be used to provide readers with an effective means to rationalize the main variables affecting the performance of MNFC in paper furnishes. Identification of knowledge gaps as potential areas for further research will be emphasized. When considering the factors affecting paper strength – with attention to how the usage of MNFC can augment paper strength – it will be argued that some of the key challenges in research, up to this point, have involved uncertainties concerning the retention of MNFC. Another key challenge, especially when attempting to compare results of different studies, is that chemical aids intended to retain MNFC in the paper may also affect fiber network formation, and therefore the strength of the sheet. After reviewing these factors, two case studies will be considered to highlight economic considerations that may be important relative to commercialization of MNFC as an additive for fiber reduction in papermaking.

2.3 Digging into the cellulose structure: nanocellulose

To enable a better understanding of the potential roles of MNFC as an additive in paper grade applications, this section provides background about MNFC, including its types, some aspects of its chemistry and morphology, and production.

2.3.1 Cellulose and nanocellulose

Cellulose is one of the most important renewable natural biopolymers and is almost inexhaustible as a raw material (González et al. 2014; Siró and Plackett 2010). Wood is the major source of cellulose, but other important natural sources where cellulose is likewise widely distributed are plant fibers (cotton, hemp, flax, *etc.*), marine animals (tunicates), and to a lesser degree algae, fungi, invertebrates, and bacteria (Lavoine et al. 2012). Irrespective of its source, cellulose is a high molecular weight homopolymer whose repeating unit is glucose (French 2017). Cellulose consists of a linear homopolysaccharide composed of β-D-glucopyranose units linked together by β-1-4-linkages (Habibi et al. 2010).

In nature, cellulose is found as assemblies of individual cellulose chains that are formed into fibers. This structure is the result of a hierarchical organization (Figure 2-2). Approximately 36 individual cellulose molecular chains are biologically assembled within biomass into larger units known as elementary fibrils. These elementary fibrils, which are commonly considered as the smallest morphological units in the fibers, are packed into a bundle of larger units called cellulose microfibrils; these are in turn assembled to constitute the original cellulosic fiber (Habibi et al. 2010). In this configuration, each microfibril can be seen as a flexible hair strand made of crystalline cellulose regions linked along the microfibril axis by amorphous domains. The diameter of elementary fibrils is approximately 3 nm (Isogai 2013), whereas cellulose microfibrils have diameters ranging between 20 and 50 nm (Lavoine et al. 2012). Cellulose

particles that exhibit at least one dimension in the nanometer range (1 to 100 nm) are known as nanocellulose (Abdul Khalil et al. 2014).

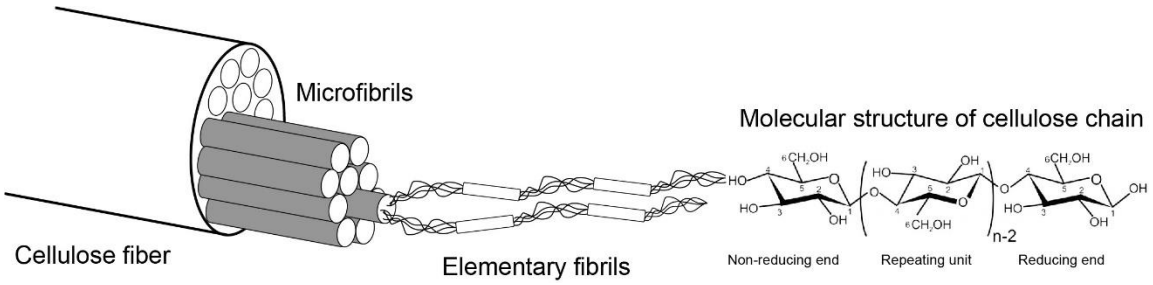

Figure 2-2: Hierarchical organization of cellulose fiber showing molecular structure of cellulose polymer. Figure reinterpreted from Lavoine et al. (2012)

2.3.2 Types of nanocellulose

The manufacturing conditions used to convert macro-scale cellulose into its nano-scale form have a critical influence on the dimensions, composition, and properties of the resulting product. According to the type of treatment applied, two main classes of nanocellulose are distinguished: (i) cellulose nanocrystals (CNC) or cellulose nanowhiskers, which are obtained by acid treatment, and (ii) CNF, also known as nanofibrillated cellulose (NFC), microfibrillated cellulose (MFC), or cellulose nanofibril, which are mainly produced by mechanical disintegration (Nechyporchuk et al. 2014). Table 2-1 summarizes the different nomenclatures found in literature to refer to cellulose nanostructures, as well as typical dimensions and raw materials used for their manufacture. The third type of nanocellulose formed by aerobic bacteria is discussed elsewhere (Ilyas Rushdana et al. 2018; Klemm et al. 2011; Nakagaito et al. 2005).

Table 2-1: Family of Cellulose Nanostructures (adapted from Ilyas Rushdana et al. 2018; Klemm et al. 2011; Siró and Plackett 2010)

Type of Nanocellulose	**Synonyms**	**Average Size**	**Typical Sources**
CNC	Nanocrystalline cellulose (NCC), whiskers, rod-like cellulose microcrystals, bacterial nanocellulose (BNC, synthesized by using bacterial method)	Diameter: 5 to 70 nm Length: 100 to 250 nm (from plants); 100 nm to several micrometers (from tunicates, algae, bacteria)	Wood, cotton, hemp, flax, wheat straw, rice straw, mulberry bark, ramie, MCC, Avicel, tunicin, algae, bacteria, etc.
CNF	NFC, MFC, nanofibril, microfibril	Diameter: 6 to 50 nm Length: several micrometers	Wood, sugar beet, potato, tuber, hemp, flax, etc.

Cellulose nanocrystals consist of rod-like crystals produced through the acid hydrolysis of cellulose fibers (Jonoobi et al. 2015). The acid treatment degrades the amorphous regions of cellulose, leaving the crystalline regions intact (Lavoine et al. 2012). The morphology, dimensions, and degree of crystallinity highly depend on the source of cellulosic material used, as well as on the conditions applied for the nanocellulose production (Habibi et al. 2010). As a general trend, CNC particles exhibit a typical width of 2 to 20 nm, with a length ranging between 100 nm and 250 nm when produced from cellulose fibers, and a crystallinity index that varies between 54 and 88% (Moon et al. 2011). CNC produced from tunicates can reach lengths of several micrometers but they are rarely used in practical systems.

Cellulose nanofibrils consist of a bundle of stretched cellulose chain molecules moderately degraded and with a greatly expanded surface area (Klemm et al. 2011). Unlike CNC, these nanofibrils are comprised of strongly entangled networks that contain both crystalline and amorphous domains. Depending on the production pathway, CNF has dimensions of 5 to 50 nm in width and a length of several micrometers. This range considers the blend of single elementary fibrils and their bundles. As a general estimation, if elementary fibrils have

between 2- and 10-nm-thick fibrous cellulose structure, CNFs are composed of approximately 10 to 50 units of elementary fibrils (Lavoine et al. 2012; Siró and Plackett 2010).

It is worth noting that the many terminologies considered to describe these cellulosic nanomaterials have led to some misunderstanding. Consequently, several technical committees and organizations have initiated standards, *e.g.*, CSA Z5100-14 (2014), ISO/TC 229 (2005), ISO/TC6-TG1 (1947), and TAPPI WI 3021 (2012), for defining the different types of nanocellulose (Nechyporchuk et al. 2016). The irregularity inherent to the mechanical process used to produce cellulose nanofibrils makes standardization a challenging task, as the produced material may consist of a blend of different structures. Chinga-Carrasco (2011) concluded that microfibrillated cellulose obtained by homogenization might be composed of (1) nanofibrils, (2) fibrillary fines, (3) fiber fragments, and (4) fibers. For properly produced MFC materials, nanostructures represent the main component. Other authors claim that CNF can only be obtained from cellulose fibers pretreated using TEMPO-mediated oxidation (Isogai 2013). To avoid possible ambiguities, the authors of this review prefer the term MNFC for considering it broad enough to include the various structures derived from the smallest morphological units of the cellulosic fibers that can have sizes ranging between micrometers and nanometers. However, any reference to external study will consider the terminology used by the corresponding authors.

2.3.3 Production pathways

The most common pathway to produce MNFC is through delamination of wood pulp *via* an intensive mechanical process after chemical or enzymatic treatment (Klemm et al. 2011). According to the nature of the raw material and degree of processing desired, the feedstock can be submitted to chemical treatment before mechanical processing, *e.g.*, TEMPO-oxidation or carboxymethylation, to produce MNFC at higher fibrillation and lower energy consumption

(Islam et al. 2014). Once the purified cellulose pulp is prepared, several methods can be applied for its conversion into highly purified nanofibrils. Typical mechanical procedures used are refining, homogenization (homogenizers and microfluidizers), and grinding. These technologies, which are suitable for upscaling, have been demonstrated to be highly efficient tools used in delamination of the fiber cell wall and subsequent MNFC isolation, despite requiring high amounts of energy (Nechyporchuk et al. 2016).

Depending on the disintegration process, the cellulosic raw material and its pre- and post-treatment (if applied), MNFC with different fibril dimensions and amount of residual microscopic fiber fragments are obtained. Other important changes in features, such as surface chemistry, crystallinity, and degree of polymerization are also influenced by those factors (Abdul Khalil et al. 2012; Nechyporchuk et al. 2014). Therefore, the production pathway should be selected based on a techno-economic assessment and the desired features of the final product (Spence et al. 2010a; b, 2011). Figure 2-3 shows conventional strategies and other alternative paths available for each stage of the manufacturing process of MNFC.

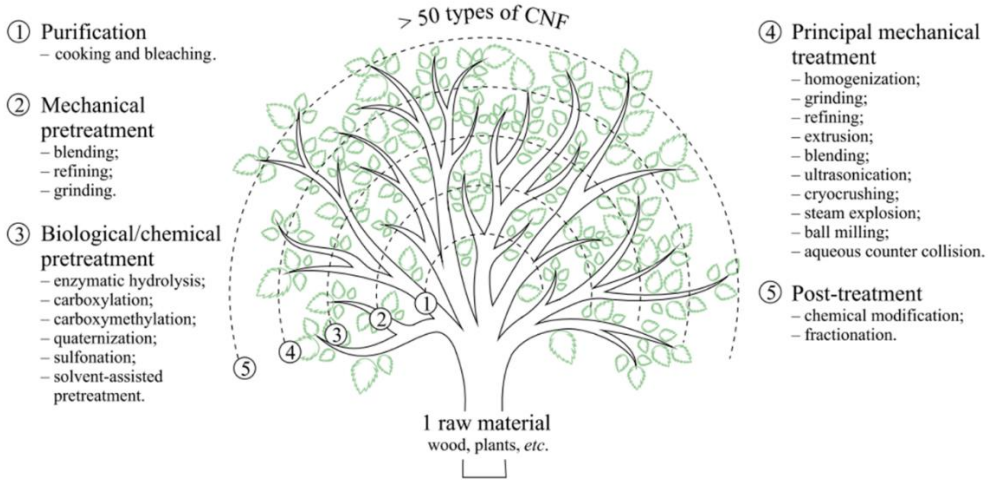

Figure 2-3: MNFC production tree showing general stages and available processing operations (Copyright Elsevier; Nechyporchuk et al. 2016)

From an operational point of view, direct treatment of dry cellulose pulp using mechanical methods alone leads to segments of MNFC having a low degree of polymerization, crystallinity, and aspect ratio, which is a consequence of fiber shredding, rather than elementary fibril delamination. These features can result in poor performance of MNFC when used to improve the mechanical properties of materials. To overcome this situation, production of MNFC can be completed in aqueous dispersions of cellulose with a low concentration (< 5 wt%), which eases the delamination of nanofibrils due to a decrease in the interfibrillar hydrogen bonding energy. At the same time, these operating conditions minimize the potential cutting of fibrils (Nechyporchuk et al. 2016). It is important to note that the high-water absorption capacity exhibited by cellulose nanostructures produces highly viscous dispersions even at low concentrations. Such dispersions can be thought of to have a gel-like structure, which can be difficult to process. For this reason, the dependence of the viscosity on the MNFC concentration is a key factor to consider when evaluating practical yields.

2.4 State-of-the-art applications for the use of micro- and nanofibrillated cellulose in paper making

Before considering evidence that MNFC can help to address some of the challenges introduced above, this section provides a patent perspective regarding the evolution of the applications for MNFC and includes review papers that have discussed the use of MNFC as a papermaking additive.

The study of nanomaterials represents an emerging field that is finding an increasing number of applications in daily consumer commodities (Wijnhoven et al. 2009). Micro- and nanoscale fibrillated cellulose can be introduced to improve the performance of paper products, one of the most promising areas where these bio-nanomaterials can find a commercial niche in a

short term (Osong et al. 2016). This arises as a result of nanocellulose's set of features, such as high abundance, high stiffness, low density, and environmentally friendly nature, all of which can serve as a starting point to provide a final product with exceptional characteristics (Dufresne 2013; Siró and Plackett 2010).

Increasing interest in nanocellulose technology is reflected in the large number of patents available on the topic. Charreau et al. (2012) provided a comprehensive review on the number of patents published every year on cellulose nanoparticles, which included cellulose nanocrystals, microfibrillated cellulose, and bacterial cellulose. Numerous patents regarding micro- and nanofibrillated cellulose have been issued since 2012. A selection of patents specifically looking at MNFC applications in papermaking is presented in Table 2-2 to highlight specific areas of growing interest: coated paper and tissue and towel. For each publication number, the title, current assignee, status, publication year, and application field are indicated. Table 2-2 shows a trend between the application field and the publication year for the group of patents. Coated paper applications correspond to early patents, published between 1994 and 2012, dealing with methods for preparing aqueous suspensions comprising MNFC to be used as coating layers in different fiber-based substrates. A brief patent overview published by Brodin et al. (2014) elaborates on the use of MNFC in the coating of paper.

Table 2-2: Patents issued on micro- and nanofibrillated cellulose applications in papermaking

Application Field	Publication Number	Title of Patent	Current Assignee	Status	Year
Hygiene tissues, towels, napkins and absorbent products	EP2191066B1	Absorbent sheet incorporating regenerated cellulose microfiber	Georgia-Pacific Consumer Products LP	Granted	2016
	US9518364B2	Wet-laid sheet material of a microfibrillated material composition	Stora Enso Oyj	Granted	2016
	US8216425B2	Absorbent sheet having regenerated cellulose microfiber network	Georgia-Pacific Consumer Products LP	Granted	2012
	US8177938B2	Method of making regenerated cellulose microfibers and absorbent products incorporating same	Georgia-Pacific Consumer Products LP	Granted	2012
	US20020162635A1	Softer and higher strength paper products and methods of making such products	Research Foundation of State University of New York	Application	2002
Different paper and paperboard products	US8945345B2	Method for producing furnish, furnish and paper	UPM-Kymmene Oy	Granted	2015
	EP2014828B1	Cellulose-based fibrous materials	Nippon Paper Industries Co., Ltd.; Jujo Paper Co., Ltd.	Granted	2014
	WO2013072550A3	A paper product and a method and a system for manufacturing a paper product	UPM-Kymmene Corporation	Application	2013
	US8377563B2	Additive for papermaking and paper containing the same	Nippon Paper Industries Co., Ltd.; Jujo Paper Co., Ltd.	Granted	2013
	WO2012039668A1	A paper or paperboard product and a process for production of a paper or paperboard product	Stora Enso Oyj	Application	2012
	WO2010131016A3	Paper filler composition	Imerys Minerals Limited	Application	2011
	EP0403849B1	High opacity paper containing expanded fiber and mineral pigment	Weyerhaeuser Co.	Granted	1994

Table 2-3: (continued).

Coated paper or board products, filled papers, dyed papers	WO2013061266A1	Process for producing a dispersion comprising nanoparticles and a dispersion produced according to the process	Stora Enso Oyj	Application	2013
	WO2012163711A1	Process for manufacturing coated substrates	Omya Development Ag	Application	2012
	WO2011056130A1	A coated substrate, a process for production of a coated substrate, a package, and a dispersion coating	Stora Enso Oyj	Application	2011
	WO2011147825A1	Cellulosic barrier composition	Akzo Nobel Chemicals International B.V.	Application	2011
	WO2011005181A1	Barrier layer for a packaging laminate and packaging laminate comprising such barrier layer	Tetra Laval Holdings and Finance Sa	Application	2011
	WO2012066308A3	Composition	Imerys Minerals Limited	Application	2010
	WO2009123560A1	Composition for coating of printing paper	Stfi-Packforsk Ab	Application	2009
	WO2009020239A1	Gas barrier material	Kao Corporation	Application	2009
	WO2007088974A1	Method of imparting water repellency and oil resistance with use of cellulose nanofiber	Kyushu University, National University Corporation	Application	2007
	US6214163B1	Super microfibrillated cellulose, process for producing the same, and coated paper and tinted paper using the same	Tokushu Paper Manufacturing Co Ltd	Granted	2001
	US6214163B1	Super microfibrillated cellulose, process for producing the same, and coated paper and tinted paper using the same	Tokushu Paper Manufacturing Co., Ltd.	Granted	2001
	JPH08284090A	Ultrafine fibrillated cellulose and its production, production of coated paper using the ultrafine fibrillated cellulose and production of dyed paper	Tokushu Paper Mfg Co., Ltd.	Granted	1999
	JP2967804B2	Manufacturing method of preparation and dyed paper for coated paper using ultrasonic microfibrillated cellulose and a method for manufacturing the same, an super microfibrillated cellulose	Tokushu Paper Mfg Co., Ltd.	Granted	1999

Beginning in 2012, the application of MNFC expanded into broader categories, such as consumer products, more specifically tissue and towel grades. Sumnicht, and Sumnicht and Kokko from Consumer Products LP at Georgia-Pacific, submitted several patent applications on the hygiene consumer segment. The first two patents related to a method of making cellulose microfibers by splitting larger fibers of regenerated cellulose in high yield using low-intensity refining and incorporating such microfibers into absorbent sheets to provide strength, softness, bulk, and absorbency to tissue, towel, and personal care products (Sumnicht 2012; Sumnicht and Kokko 2012). A third patent provided more insights into the benefits that can be obtained by using microfibers. This latter invention related to an absorbent sheet made from papermaking fibers (*e.g.*, softwood and hardwood cellulosic pulps) including regenerated cellulose microfibers. When comparing an equivalent sheet prepared without fibrillated cellulose microfiber, the resulting product was claimed to have higher absorbency (+15%), wet tensile (+40%), and a specific bulk (+5%), making it an ideal candidate for applications in tissue papers (Sumnicht and Miller 2016). Goto et al. (2014) at Nippon Paper Group, Inc. filed a patent on fibrous materials with an assembly of microfibrils with a width of 3 μm or more for obtaining sheets with low density and high surface quality in addition to high strength. The product of the invention was claimed for use in different paper grades, including facial tissue, toilet tissue, and paper towels. A recent patent filed by Stora Enso relates to a wet-laid sheet of a microfibrillated material composition intended for hygiene tissue applications Heiskanen et al. (2016).

As pointed out by Charreau et al. (2012), and based on this brief patent review, worldwide corporations owning most of the patents have kept a consistent focus for the last five years, namely, finding high-value applications for MNFC to push value creation. Within this

segment, MNFC is meant to improve water absorbency and tensile strength without affecting other key properties of interest in consumer products such as softness and bulkiness.

In academia, numerous authors have published recent reviews dealing with the use of MNFC as an additive in papermaking. A review was presented by Brodin et al. (2014), who discussed different strategies for incorporating cellulose nanofibrils (CNF) in pulp furnishes and results regarding drainage and paper properties that included density, permeability, strength, and light scattering coefficient. Osong et al. (2016) discussed the critical variables to consider before adding MNFC to pulp furnishes, *i.e.*, production pathways, energy consumption, chemical and enzymatic pre-treatments, and characterization techniques. Meanwhile, Boufi et al. (2016) published a review that highlighted the progress in the field of cellulose nanofibers in papermaking applications and analyzed the effect of CNF according to the type of papermaking furnish.

2.5 Micro- and nanofibrillated cellulose as a paper strength additive in papermaking applications

Micro- and nanofibrillated cellulose products have been shown to be high-performance strength additives in paper and paperboard products (Eriksen et al. 2008; He et al. 2017; Kasmani and Samariha 2019; Konstantinova et al. 2019; Taipale et al. 2010). Improvements in the strength of wet web of base paper after the addition of MNFC have been also reported (Lu et al. 2019, 2020), despite the decrease in the web solid content observed after pressing of the paper sheet containing MNFC (Lu et al. 2019). There are two main features that might explain the MNFC strengthening capacity. First, the surface area expanded by the nanoscale dimensions allows MNFC to act as an effective adhesion promoter. By filling the interstices within the fiber network, fibers can come closer together, increasing the fiber-fiber bonding and thus the total

bonded area. Secondly, the tendency of MNFC to form entangled networks enhances the mechanical properties of the paper. The outstanding intrinsic strength of these nano-networks embedded along larger fibers provides the macroscopic network with points of high resistance, which improves the overall tensile strength (González et al. 2012). Additionally, the similarity found in the chemical structure of both MNFC and cellulosic fibers reduces chances of incompatibility when combining the biomaterials (Balea et al. 2016).

Several studies highlight how MNFC decreases porosity and air permeability when added into the sheet (Brodin et al. 2014; Eriksen et al. 2008; González et al. 2012; He et al. 2017; Sehaqui et al. 2013; Taipale et al. 2010). This decrease in porosity is caused by the MNFC bonding with the fibers in the sheet network, which closes off the porous structure (Brodin et al. 2014; He et al. 2017). Pore blockage increases when the content and fibrillation degree of MNFC used increases (Balea et al. 2019). Taipale et al. (2010) proposed that air permeability indicates the complexity of the resulting network.

The reduction in porosity with the addition of MNFC also correlates with an increase in paper density (He et al. 2017; Sehaqui et al. 2011). Brodin et al. (2014) suggests that MNFC behaves similarly to fines in regard to their ability to close pores in the sheet structure which increases the number of hydrogen bonds. Other studies also report a significant increases in sheet density (Charani et al. 2013; Eriksen et al. 2008; Manninen et al. 2011; Su et al. 2013).

2.5.1 Factors affecting the usage of MNFC as a paper strength additive

The goal of this section is to review the most important factors affecting paper strength when MNFC is added to papermaking furnishes. This must be considered with caution, not only because of very different pulp slurry conditions utilized in different published studies, but also because the efficiency of retention of the MNFC is rarely known or reported in such studies.

Furthermore, in cases where the investigators have employed chemical-based strategies (retention aids or fixatives) to achieve relatively high retention efficiency in the course of their work, there can be profound changes in the uniformity of formation, and such differences can greatly affect the paper's strength and other characteristics.

In light of such uncertainties, results of studies in the absence of chemical additives will be regarded as a good source of information about the direction, but not the extent of resulting changes in paper properties, because in many cases it is not possible to estimate the MNFC content of the paper. By contrast, studies conducted with the participation of cationic polymers will be used as evidence of what magnitude of quantitative changes are possible, with the caveat that large differences in formation uniformity might reduce one's confidence in generalizing the published findings.

Though other reviews have discussed general aspects related to applications of MNFC in papermaking, there are still limitations regarding an integrated comprehension of the colloidal behavior of systems containing MNFC. To address such gap, this review will systematically discuss and analyze the latest studies on applications of MNFC in papermaking. For a better understanding, three sets of main parameters describing the colloidal behavior of systems comprised of MNFC, pulp fibers, and retention aids (or any other additive) are defined. These parameters are (1) intrinsic and extrinsic variables, (2) furnish composition, and (3) degree of dispersion. Any element included in these categories can be expected to affect the paper performance. This approach will give papermakers a clear overview of how to manipulate the MNFC application to tailor the final properties of the paper product.

The intrinsic variables describe the physicochemical nature of each of the components comprising the colloidal system, whereas extrinsic variables refer to the effect of outside parameters, such as temperature. This set can be further divided as follows:

- Properties of MNFC, affected by (i) morphology (a function of the production pathway, the fiber source used for manufacturing, and the intensity of the mechanical treatment applied), and (ii) chemistry (a function of the fiber source used for manufacturing, and the biological/chemical pre- and post-treatment applied, which will dictate the chemical composition).
- Properties of pulp fibers used as the paper matrix, affected by (i) pulp source, (ii) pulping method, (iii) lignin content, and (iv) degree of beating.
- Properties of additives, affected by (i) nature of the additive and (ii) addition strategy, *i.e.*, the sequence of addition used to mix the MNFC, pulp fibers, and additive in the paper furnish.
- Bulk conditions, affected by (i) pH and (ii) salinity.

The furnish composition defines the relative amount of each of the species in the colloidal system, whereas the degree of dispersion relates to the mechanical protocol applied to disperse the species in the bulk of the paper furnish. Table 2-4 shows a breakdown of the sets of parameters previously defined.

Table 2-4: Sets of main parameters describing the colloidal behavior of systems comprising MNFC – pulp fiber – retention aid (or any other additive)

Intrinsic and Extrinsic Variables		
Property of:	**Variable:**	**Determined by:**
MNFC	Morphology	Fiber source* (hardwood *vs.* softwood nanofibers)
		Particle size* (micrometric *vs.* nanometric)
		Degree of fibrillation*
	Chemistry	Fiber source (hardwood *vs.* softwood nanofibers)
		Lignin content (lignocellulosic nanofibers *vs.* cellulosic nanofibers)
		Surface modification (carboxylation (TEMPO-oxidation), carboxymethylation, periodate-oxidation, quaternization, enzymatic hydrolysis)
Papermaking fibers	Source	Virgin (hardwood, softwood) or recycled fibers (deinked pulp)
	Pulping method	Thermomechanical pulping (TMP), chemi-thermomechanical pulping (CTMP), Kraft, Sulfite
	Lignin content	Bleached or unbleached fibers
	Degree of beating	Fiber fibrillation and fines content*
Additives	Type of additive	Polyelectrolytes* (Carbohydrates, amides, amines, quaternary ammonium with cationic or anionic nature)
		Fillers
	Sequence of addition	Pre-mixture of polyelectrolyte and MNFC or direct addition of components into paper furnish*
Bulk	pH	Changes in pH and salinity of paper furnish containing MNFC
	Salinity	
Furnish Composition		MNFC to additive ratio*
		MNFC to pulp fiber ratio
Degree of Dispersion		Degree of MNFC dispersion in paper furnish*

* subjects discussed in this review

2.5.2 Intrinsic and extrinsic variables

2.5.2.1 Fiber source

The type of fiber used for the production of the MNFC has an important influence on the fibrillation development, fines generation, and subsequent performance of the nanocellulosic material (Johnson et al. 2016; Lahtinen et al. 2014; Stelte and Sanadi 2009). At similar levels of mechanical treatment, hardwood cellulose nanofibrils will produce a comparable but slightly weaker film, i.e., lower tensile strength, than softwood cellulose nanofibrils (Spence et al. 2010a; b). Thus, if the tensile strength of the resulting film is used as an indication of the fibrillation degree induced by the treatment, hardwood cellulosic fibers are harder to fibrillate than softwood fibers; i.e., they will require a higher level of pre-treatment and mechanical treatment (Stelte and Sanadi 2009; Vartiainen et al. 2015; Zhao et al. 2017).

Figure 2-4 shows scanning electron microscopy (SEM) images comparing the progression of hardwood fibrillation to the fibrillation of softwood fibers after a given number of passes through a refiner. Similarly, when using CNF as an additive to hardwood-based pulp handsheets, hardwood CNF produces lower tensile and internal bond values compared to softwood CNF at a given fines content (< 86% fines). However, for fines content above 90%, the change in the handsheets properties is independent of the source used for the CNF production (Johnson et al. 2016).

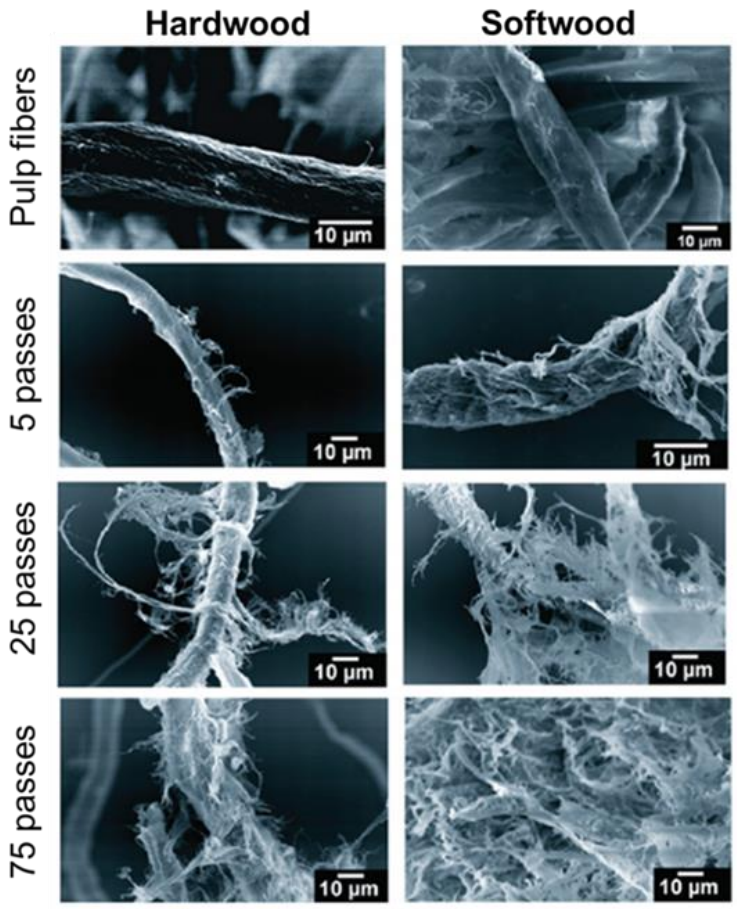

Figure 2-4: SEM images comparing the fibrillation evolution for hardwood and softwood fibers after a given number of passes through a refiner (adapted from Stelte and Sanadi 2009; Copyright 2009 American Chemical Society)

Results from this work suggest that at the nanoscale, the expanded surface area overcomes the chemical component inherent to the fiber source and that such surface area can also drive interaction between the CNF and the fiber network. Further research to assess the influence of different raw materials on the performance of nanocellulose when used as a paper strength additive needs to be conducted.

The chemical composition of the pulp fibers also plays a key role in the fibrillation process. A higher hemicellulose content facilitates the fibrillation of nanofibers during the

mechanical treatment of the pulp (Iwamoto et al. 2008). Also, it is proposed that lignin-containing fibers promote fibrillation because of lignin's antioxidant properties and its ability to stabilize radicals generated from cellulose during the grinding treatment (Ferrer et al. 2012; Solala et al. 2012). Results reported by Spence et al. (2010a; b) support Ferrer's 2012 finding that lignin-containing NFC produces films with comparable properties to their bleached counterparts. Higher lignin content was found to aid in the fibrillation process because the resulting nanofibrils have a higher surface area and lowest size fraction (Imani et al. 2019b). Alternatively, it is suggested that the presence of lignin and hemicellulose hinders the fibrillation process, especially when combined with TEMPO pre-treatment (Herrera et al. 2018). A high content of hemicellulose may be detrimental for the fibrillation, as xylan does not have the C6 that is the oxidation position targeted by the TEMPO catalyst (Syverud et al. 2011). It should be noted that the studies cited here used different pulping processes, e.g., kraft, soda, semi-chemical, to produce the unbleached fibers for MNFC production. Therefore, the discrepancies in performance could be due to the different pulping environments influencing the remaining lignin structure in the fibers. For example, during the kraft process sulfate groups will be added to the lignin structure as it is being degraded, but the sulfate groups are not present in the soda process. Thus far, studies have only concerned themselves with the amount of lignin remaining with the cellulose before fibrillation, which makes it hard to draw a conclusion on how the different degradations of the lignin structure influences fibrillation.

When evaluating papermaking applications, the blending of lignin-containing nanocellulose into fiber sheets improves the overall strength profile; however, it has been shown to be less efficient than using lignin-free nanocellulose (Osong et al. 2014). Before reaching a definitive conclusion, more research should focus on how the presence of lignin alters the

performance and reinforcement capabilities of the MNFC in targeted papermaking applications. For example, there is evidence suggesting that even though lignin-containing MNFC could be suitable as a bulk additive in papermaking, it would make a poor coating additive compared to lignin-free MNFC (Imani et al. 2019a).

2.5.2.2 Particle size (micro vs. nano) and degree of fibrillation

The size of fibrils and the degree of fibrillation, the latter referring to the homogeneity of the fibrillated sample, largely determine the colloidal features of pulp suspensions containing MNFC. The colloidal interactions exhibited by particles at the micro- and nanoscale result from a balance between electrostatic and dispersion forces governing the system. Any change in the degree of fibrillation contributing to increase the surface area will also result in a higher surface charge, directly affecting the colloidal behavior among cellulosic fibrils (Hakeem et al. 2015; Hubbe 2007b; Saarikoski et al. 2017).

The fibril size plays a key role in the resulting properties of paper when MNFC is incorporated in pulp suspensions. The MNFC with a small particle size produces a paper with greater bonding strength and denser structure, but it also results in lower retention. In contrast, MFC with a broader particle size distribution shows less improvement in mechanical properties but more efficient retention in the fiber web (Su et al. 2014). Madani et al. (2011) reduced the average fibril length of MFC from 221 μm to 100 μm by applying a gel fractionation technique. Composite papers formed by 10% addition of MFC to chemical wood pulp showed 25% increase in tensile index for non-fractionated MFC and an additional 10% improvement for fractionated MFC. Eriksen et al. (2008) also reported an increasing tensile index in TMP paper by decreasing the average particle size of MFC. However, the authors also claimed that mechanical processing beyond a specific energy consumption does not translate into a significant further increase in

tensile strength. They observed a drop in tensile index from a maximum value when the degradation of homogenized MFC was successively increased beyond that point. From this study, it is possible to infer that there is an optimal fibrillation degree that will yield a maximum improvement in tensile strength. Any additional energy input beyond this limit will represent an energy loss in the overall energy balance associated with MFC manufacturing. In agreement with this logic, He et al. (2017) concluded that MNFC production should be focused on tailoring the properties of the fibrillated fibers to be incorporated into a specific application, i.e., achieving an optimal degree of fibrillation for a given application, rather than trying to retrofit MNFC, whose dimensions are completely nanoscale, to possible applications.

Fibrillation also has an important influence on the mechanical properties of nanocellulose films. The NFC with a high degree of fibrillation can be more easily dispersed in the bulk suspension prior to sheet formation. As a result, a more homogeneous distribution of the defects and vulnerable locations for initiation of failure within the network is obtained, which consequently improves the strength and rigidity of the nanostructure (González et al. 2014). A reduction in the average fibril size also results in more fiber bridging through both mechanical interaction and H-bonding. However, excessive mechanical treatment has the potential to reduce strength properties due to a possible reduction in the length of the fibrils (Stelte and Sanadi 2009).

The degree of fibrillation influences the dewatering capacity of pulp suspensions and the solid content of the paper after wet pressing. He et al. (2017) described an increase in the drainage time as a function of the degree of fibrillation of CNFs, which was accompanied by an overall reduction in the degree of polymerization, zeta potential, and degree of crystallinity. As the fibrillation of fibers progresses, particles are more easily incorporated into the fiber web.

However, this partially closes the pores between fibers, limiting the ability for the wet web to drain water. The CNFs also hinder drainage due to its increased water retention capacity, which may be the cause of the reduction in solids content observed after wet pressing.

Besides favoring the reduction of the high-energy demand associated with mechanical fibrillation processes, the pre-treatment of cellulose fibers also aims to improve the achievable degree of fibrillation (Isogai 2013). Delgado-Aguilar et al. (2015) evaluated the reinforcing ability of five types of CNFs prepared by different pre-treatments (chemical, mechanical, and enzymatic) when combined with papermaking pulps. The CNFs with a high degree of fibrillation and a large specific area, e.g., TEMPO-oxidized CNF, showed the best performance as paper strength additives. However, it was shown that CNFs with a smaller degree of fibrillation could also induce an equivalent increase in the mechanical properties by using a higher load compared to that of TEMPO-oxidized CNFs. A similar observation was made by Johnson et al. (2016), who claimed that similar values of paper strength could be reached by either adjusting the CNF loading level or the CNF fines content. As shown in Figure 2-5, the authors found that changing the fines content in the CNF from 77% to 94% did not affect the performance in terms of tensile index. This held at all the levels tested for CNF load in the handsheets. The findings also support the idea that there are diminishing returns in strength improvements past a certain MNFC degree of fibrillation.

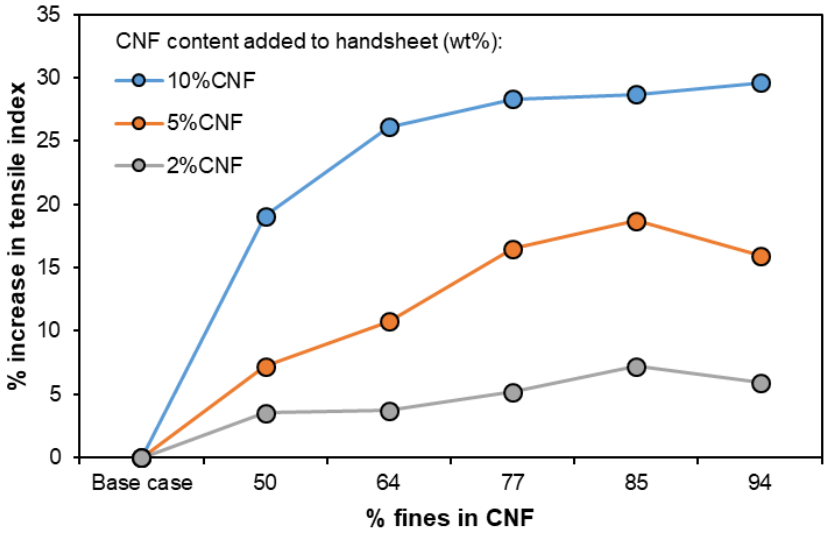

Figure 2-5: Effect of addition of CNF with different fines content on the tensile index of handsheets (no retention aids were used) (adapted from Johnson et al. 2016)

2.5.3 Degree of beating of papermaking fibers

2.5.3.1 Fibrillation and fines content

Mechanical refining of papermaking fibers increases the number of fiber-to-fiber bonds, thus producing a stronger paper. The mechanisms of shearing and compression forces involved in this process completely transform the original characteristics of the fibers. The increase of external fibrillation enlarges the fiber surface area and creates fibrils from the primary and secondary wall. Fines are also produced when the primary and secondary wall fibrils are cut off from the fibers (Smook 2016). These factors might affect the reinforcing features of the MNFC due to a change in the interaction with the pulp fibers in suspension and during the sheet formation.

Several authors have suggested that an increase in the external fibrillation of pulp fibers inhibits the enhancement that MNFC has on fiber-fiber bonding. Su et al. (2013) compared the strength development resulting from the blending of MFC with unrefined fibers and fibers

refined at 10,000 rpm in a PFI mill. The addition of MFC into unrefined fibers resulted in a radical increase in the dry strength in contrast to the dry strength of composites made from the mixture of refined fibers and MFC, which exhibited a small variation despite the MFC content added. Afra et al. (2013) evaluated the effect of NFC addition on the properties of paper made from softwood pulps beaten to 350 and 550 CSF. As a recurrent trend, the increase in the tensile strength of the paper prepared with 550 CSF softwood fibers was greater than the increase obtained with the 350 CSF fibers (~72% vs. ~60%).

González et al. (2012) studied the physical, morphological, and mechanical properties of paper sheets reinforced with TEMPO-oxidized NFC using unbeaten and slightly beaten Eucalyptus slurries. An analysis of that study conducted by Boufi et al. (2016) showed that an addition of 3 wt% NFC produced an increase of approximately 24% in the tensile index, which was similar for both beaten and unbeaten pulps. Conversely, after addition of 6 wt% NFC, the increase in tensile index shown by the unbeaten pulp was 67% while only a 45% increase was obtained for the slightly beaten pulp. A similar trend was found by Taipale et al. (2010). The authors obtained increments of 73% and 35% in tensile index of the paper after adding NFC to a softwood pulp beaten for 10 and 30 min. In this case, a cationic starch dosage of 15 mg/g dry pulp was used.

The presence of fines in pulp fibers might also affect the MNFC performance when added into pulp furnishes. Potulski et al. (2014) reported an increase of 258% in tensile index after the incorporation of microfibrillated cellulose to bleached Eucalyptus pulp with a low refining level (15° SR), compared to an increase of 41% obtained after adding an equivalent amount of MFC to the same pulp but at a higher degree of refining (25° SR). The authors ascribed the difference observed to the fact that the combination of refining and addition of MFC

generates a larger number of fines in the system that imposes limits on increasing the tensile strength of paper. Furthermore, after examining the work by González et al. (2013) covering the effect of the combination of enzymatic treatment (bio-refining) and NFC addition on the mechanical properties of paper, Boufi et al. (2016) stated that González's study supports the theory that the fibrillation of refined pulps is the variable limiting the performance of NFC in papermaking. This is because the bio-refining process does not generate the amount of fines that is typically generated during the traditional pulp refining. It has been also reported that the presence of fines negatively impacts the drainage properties of pulp suspensions containing MFC, even with the presence of cationic polyelectrolytes. Taipale et al. (2010) showed that after removing the fines from a beaten pulp suspension (the pulp was beaten for 60 min), the drainage of the furnish depended less on both the MFC content and type of polyelectrolyte used.

The results just discussed reinforce the hypothesis postulated by Brodin et al. (2014) that CNF shows its best performance in fiber networks where poor fiber bonding is the variable hindering the tensile strength. For that reason, the addition of MNFC in paper furnishes comprised of beaten chemical pulps is less likely to significantly enhance the mechanical properties of paper sheets in comparison to the addition in unbeaten pulp furnishes. It is also worth noting that although the percentage of change in tensile index decreases with the fiber fibrillation, the tensile index value obtained by combining defibrillation of pulp fibers and MNFC addition is greater compared to that obtained when MNFC is simply added to a pulp slurry of unbeaten fibers.

Despite seeing a better MNFC performance when adding it to unbeaten furnishes, several authors have stated that the gains in tensile index obtained by the addition of MNFC to a pulp furnish are similar to what could be obtained by beating the original pulp suspension before the

sheet formation. Sehaqui et al. (2013) studied the mechanical properties of handsheets made of 10% NFC and 90% softwood pulp fibers subjected to varying levels of beating. The authors reported that the addition of NFC to non-beaten pulp fibers had a similar effect on tensile index as beating a 100% softwood fiber furnish because both strategies resulted in a high-density sheet. Hollertz et al. (2017) described the same trend for unbleached kraft pulp sheets containing either carboxymethylated CNF or kraft MFC with different loadings. However, that relationship between tensile strength and density was not found when chemically modified CNFs (periodate-oxidized CNFs and dopamine-grafted CNFs) were introduced into the paper furnish using polyvinyl amine (PVAm) as a retention aid, as shown in Figure 2-6a. In this case, the tensile strength was significantly above the beating curve. Taipale et al. (2010) also stated that the results obtained through the addition of MFC without cationic starch considerably mimicked the results obtained with simply beating the bleached softwood kraft pulp and using no MNFC. As shown in Figure 2-6b, slightly higher tensile strength values were attributed to the MNFC with more fibrils compared to the fibrils present on fibers generated during the beating process. Nevertheless, the combination of carboxymethylated MFC and cationic starch significantly increased the tensile strength compared to the tensile strength seen with just the beaten fibers at the same drainage rate. The underlying mechanisms yielding these results are discussed in the following section of this review.

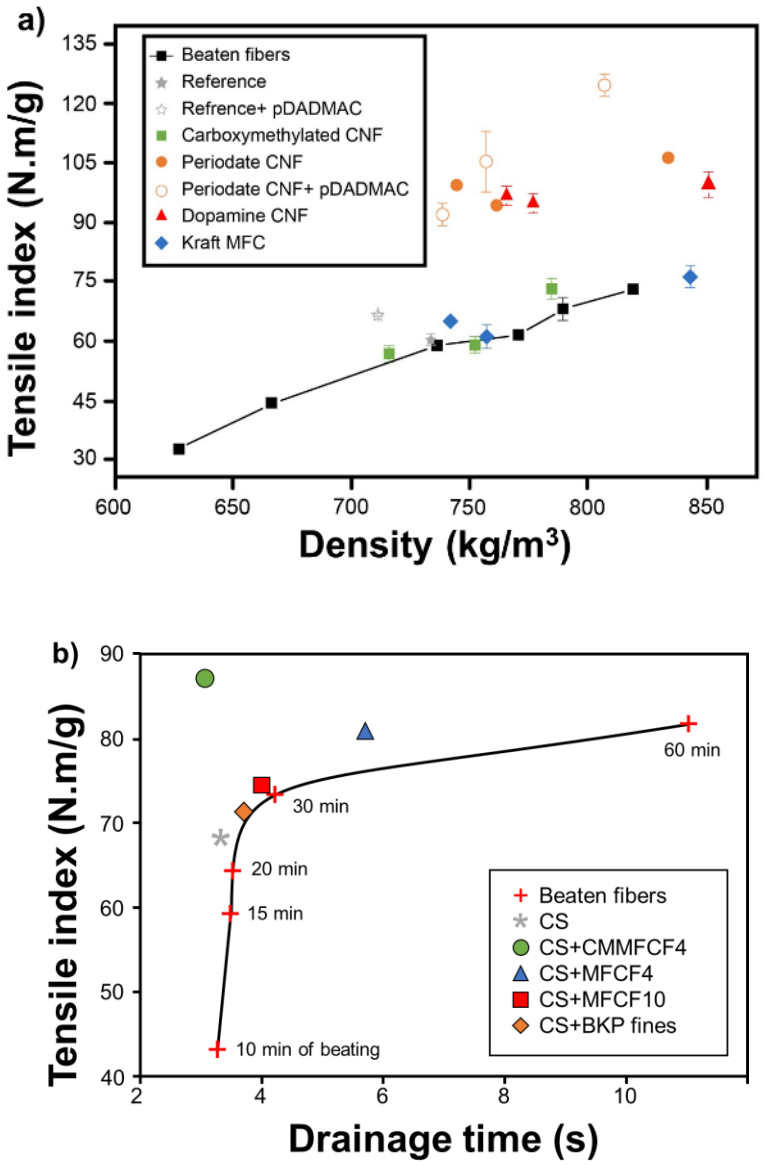

Figure 2-6: Comparison between addition of MNFC and mechanical beating of pulp fibers as strategies to increase the tensile index of paper sheets: (a) different types of chemically modified CNFs added to a 4000 PFI-revs beaten pulp using 2.5 mg/g PVAm as retention aid or, if indicated, polyDADMAC; (b) different types of MFCs added to a 10 min beaten pulp using 15 mg/g of cationic starch (CS) as fixative. F4 and F10 indicates that the pulp was passed through a fluidizer unit either four or ten times respectively. CMMFC is a carboxymethylated MFC sample (adapted from Hollertz et al. 2017; Taipale et al. 2010)

2.5.4 Type and addition point of additive

2.5.4.1 Polyelectrolytes

Polyelectrolytes showing diverse chemical nature and surface charge density are commonly introduced in the pulp slurry to improve the retention of fines particles during sheet formation. Using polyelectrolytes, best-known as retention aids (RA) and dry strength agents (DSA), is considered a proven strategy in conventional paper machine operations. Retention aids represent one of the most suitable ways that researchers are currently focusing on to increase the retention of MNFC in the sheet. In this sense, factors related to the chemical structure of the polyelectrolyte, bulk concentration of both MNFC and retention aids, as well as the sequence of addition, are main variables affecting the system performance.

The typical chemical species studied for their use as retention aids and possibly as dry strength agents are long molecular chain polymers with a cationic nature. Four main families of polyelectrolytes used in combination with MNFC have been identified: (i) carbohydrates, e.g., cationic starch (CS), xyloglucan, and chitosan (CH); (ii) polyvinylamines (PVA); (iii) polyacrylamides, e.g., c-PAM, c-PAM-B; and (iv) cationic polymers with quaternary ammonium, e.g., polyamidoamine-epichlorohydrin (PAE) (Boufi et al. 2016).

The chemical structure of the cationic polymer will influence the way MNFC interacts with it, i.e., the balance between non-electrostatic forces, electrostatic forces, and flocculation mechanism. The use of MNFC in pulp slurries containing polyelectrolytes has been shown to increase the flocculation and stability of the particle flocs. MNFC increases the floc stability in the presence of CS due to the formation of hydrogen bonds, regulates the negative effect of increasing PAM dose on floc stability, and increases the floc size when combined with PVA. Therefore, the particular interaction between MNFC and the cationic polymer will be the crucial

factor affecting the retention of the nanoparticles within the fiber network (Merayo et al. 2017a). Besides improving retention, some polyelectrolytes can also boost the strengthening effect of MNFC by generating synergic effects within the paper web. The most important strength improvements reported in the literature correspond to cases where MNFC has been combined with a polyelectrolyte (Ahola et al. 2008; Boufi et al. 2016; Hollertz et al. 2017; Rice et al. 2018; Taipale et al. 2010; Yousefhashemi et al. 2019). Moreover, the use of retention aids has been shown to improve the dewatering of pulp suspensions containing MNFC (Merayo et al. 2017b). These synergistic behaviors will only occur if the correct retention aid chemistry for a system is implemented.

Merayo et al. (2017b) studied possible synergies between MFC and RAs to improve recycled paper strength while avoiding negative effects on the drainage process. Five different RAs were considered: PVA, CH, CS, c-PAM, and c-PAM-B (which is formed by a formulation of polyamine as coagulant, PAM, and hydrated bentonite clay). As a common feature, all the RAs improved water drainage and retained approximately 90% of the solid particles. A comparison made at the lowest dose tested, which was representative of the dosages used in industrial applications, showed that c-PAM and c-PAM-B were the most efficient in reducing drainage times, followed by CH. The PVA also provided good results with a dosage ten times higher than commercially viable doses. The CS was the least effective in reducing drainage times, especially at low and moderated doses.

Regarding mechanical properties, the addition of MFC using c-PAM-B resulted in the best formation uniformity of the paper and the higher tensile index increase (15%). According to the authors, bentonite, an anionic component found in this RA, kept a good dispersion of MFC in the pulp despite the presence of PAM, which is known for promoting a high floc formation. No

synergy was observed between MFC and c-PAM. The highest values of tensile index were obtained with pulp containing 1% MFC when CH was used as RA. The CH itself did not affect tensile index; however, in combination with MFC, a synergistic effect developed, enhancing the paper strength. The use of MFC and PVA provided a tensile increase of 15% at its highest point, and for the case of CS, addition of MFC showed a negative synergy that decreased the tensile index. The authors claimed that CS might be interacting with MFC in the pulp, resulting in flocs that favor retention but worsen formation uniformity. At the same time, this might decrease the interaction between MFC and fibers. From this study, it is important to note that some RAs required the addition of MFC to the pulp to recover the tensile index that the paper originally shows without the presence of any additive. For example, c-PAMs provided the lowest drainage time at expenses of a high floc formation, which favors faster drainage but hinders fiber bonding. Thus, a balance between flocculation and bondability will also be required in this case, and attention needs to be taken when dealing with additives exhibiting such features.

Similarly, Taipale et al. (2010) studied the effect of the addition of MFC and fines on the drainage of a kraft pulp suspension and its relation with paper strength. Five polyelectrolytes were evaluated for this purpose: three different types of c-PAM, polyDADMAC, and CS. First, contrary to the results obtained by Merayo et al. (2017b), an increase in the drainage time was obtained in the presence of c-PAM and MFC. According to the authors, high molar mass c-PAMs tend to form a thick, loose, and viscoelastic layer with the added MFC that might increase the water retention capacity of the network. Secondly, compacted networks formed by the addition of polyDADMAC allowed faster drainage as the low molar mass high charge density polyelectrolyte adsorbs in a flat conformation leading to thinner layers of polymer and MFC. Finally, highly branched CS with a very high molecular mass only slightly decreased the

drainage. The authors reported a strong dependence between the type of polyelectrolyte and the drainage for suspensions containing fines. As a common trend, it was stated that addition of MFC causes an increase in the strength of the paper, which can be enhanced when CS is used as a fixative. Although a reduction in the drainage rate consistently accompanied this effect, the authors also found that by adding carboxymethylated MFC in combination with CS it was possible to double the tensile strength without decreasing the drainage rate. They attributed this finding to the small size and high-density charge of the anionic MFC that would allow the formation of a thin MFC layer on the CS previously adsorbed onto the fiber surface. As a result, MFC nano-networks would be coating the fibers rather than filling the voids between them, leaving more open pores for water to freely drain from the sheet.

Likewise, Hollertz et al. (2017) showed how cellulose micro- and nanofibrils exposed to different chemical modifications can be effectively used as strengthening additives in papermaking. The authors considered carboxymethylated CNFs as the starting reactant to produce two types of modified CNFs: periodate-oxidized carboxymethylated and dopamine-grafted carboxymethylated. These three different CNF were added to a pulp suspension of unbleached kraft pulp with and without PVAm used as a retention aid. In this case, an increase in the tensile strength index of 56% was obtained with as little as 2 wt% periodate-oxidized CNF added. The authors found that PVAm promotes the adsorption of periodate-oxidized CNF on the fiber surface before dewatering rather than its attachment in the pores between the fibers during dewatering. As a result, a higher dewatering rate was obtained for periodate-oxidized CNF compared to that of the sheets prepared with dopamine-grafted CNF and a conventional kraft MFC. This coating-like conformation is similar to the one reported by Taipale et al. (2010) for sheets made with the addition of carboxymethylated CNF in combination with CS. Therefore,

based on the results obtained from the previous studies, it is possible to state that retention aids affect the conformation of the fibrillated material onto the cellulosic fibers, and the resulting arrangement is what will dictate the extent of improvement in strength and drainage rate obtained in the paper product.

The formulation and addition of cationic polyelectrolyte complexes (CatPECs) onto papermaking furnishes containing MNFC, as well as the pretreatment of the nanofibers with cationic polymers, has also been explored. Schnell et al. (2018) evaluated the efficiency of PECs to improve the reinforcing capacity of lignocellulosic micro/nanofibers (LCMNF) while reducing the drainability problems caused by the fibrillar material. CatPECs were prepared by mixing polyacrylic acid with poly(allylamine hydrochloride). The combination of CatPECs with LCMNF increased the tensile strength of the paper sheet compared to a reference sheet with no additives. The highest improvement (+48%) corresponded to the CatPEC dosage required to reach the charge neutrality of the system (0.75% based on pulp) in a papermaking furnish containing 3% LCMNF. At this dosage, the negative effects on drainage caused by the LCMNF were minimized, and the retention of fines and LCMNF were maximized as determined by the Britt Dynamic Drainage Jar test.

Rice et al. (2018) evaluated the performance of NFC pretreated with cationic starch as a bonding system in 350 g/m^2 handsheets made from bleached kraft pulp (70% hardwood and 30% softwood). NFC pretreated with cationic starch was particularly effective in improving the tensile strength and stiffness of low-refined pulp mixtures (473 mL CSF) compared to high-refined pulp mixtures (283 mL CSF). Such a strategy allowed improved tensile strength at a lower apparent density (higher bulk) of the handsheets, which the authors suggest could be used as a means of substituting the mechanical refining of the pulp mixture in preparation of specific

paper grades. It was proposed that cationic starch enhances the retention of NFC in the paper web and NFC simultaneously acts as an extender for cationic starch, which results in a synergistic action that improves paper strength. At the same time, a “spring-back” effect of the NFC-starch complex due to the elastic character of NFC might help to regain bulk of the paper web after wet-pressing (Hubbe 2019). Additional treatment of the cationic starch-treated NFC with colloidal silica was also employed to promote better dewatering of the pulp slurry.

2.5.4.2 Sequence of addition

The colloidal behavior of systems comprising MNFC, pulp fibers, and polyelectrolytes might be sensitive to the sequence used to introduce each substance into the pulp suspension. However, not many systematic studies assessing the influence of the addition strategy on the final properties of paper have been published. Ahola et al. (2008) studied the differences in addition strategies of CNF and PAE onto cellulose fibers. According to the sequence of addition considered, two configurations were obtained: a bi-layer system for the case where CNF was added to pulp suspension containing the retention aid and nano-aggregates when the CNF was pre-flocculated with the retention aid and then added to the pulp suspension. The adsorption of PAE and nanofibrils as a layer-structure translated into a significant increase in both dry and wet tensile strength of paper. Conversely, cationic aggregates did not significantly improve the paper strength properties. He et al. (2017) investigated the effect of the addition method of cellulose nanofibrils into the wet-end of the papermaking process. Two different addition strategies were assessed: a precipitated calcium carbonate (PCC)-CNF composite filler and a wet-end additive. CS and c-PAM were used to promote binding and improve retention. Handsheets dosed with the composite filler showed a higher solid content than the CNF-added sheets after wet pressing; however, in both cases, a similar tensile strength was obtained.

2.5.5 Furnish composition

2.5.5.1 MNFC to polyelectrolyte ratio

Taipale et al. (2010) reported a linear increase of tensile index with increasing addition of MFC in a pulp suspension containing cationic starch. Conversely, Merayo et al. (2017b) found a decrease in the tensile index with increasing addition of MFC to pulp slurries containing CH, CS, and PVA as retention aids. Moreover, increasing the concentration of retention aid did not cause significant improvements in the tensile index, which even decreased in some cases. For these systems, the results suggest that retention of MFC is not the variable driving the decrease in tensile strength. According to the authors, high concentrations of MFC do not necessarily increase paper strength as the effect of poor paper formation can overcome the reinforcing capacity of MFC. Similarly, Hollertz et al. (2017) stated that retention aids do not significantly increase the fibril content in handsheets prepared using chemically modified CNF and PVAm as a retention aid. The authors rather attributed the self-retention capacity shown by these CNFs to their large size and a high degree of aggregation.

2.5.6 Degree of dispersion

2.5.6.1 Degree of MNFC dispersion in the paper furnish

There is a proportional correlation between the dispersion degree of the species in a pulp suspension and the mechanical properties of the resulting paper sheets. Especially, for colloidal systems comprising MNFC, pulp fibers, and polymers, the energy input provided by hydrodynamic shear will affect the dispersion and thus the distribution of each component within the fiber matrix (Alcalá et al. 2013; Campano et al. 2018). Given the viscous features of the gel in which nanocellulose is normally produced, its homogenization in aqueous medium proves more difficult compared to cases where there is a dilute dispersion of nanofibers (Osong et al.

2016). Furthermore, as the tensile strength of a paper sheet depends mostly on the weakest bonds in the fiber network, a poor distribution of MNFC in the pulp furnish will translate into a non-optimum performance of the fibrillated component when used as a paper strength additive.

Based on this logic, Alcalá et al. (2013) studied the effect of the number of revolutions applied during dispersion on the performance of NFC within an unbleached Eucalyptus fiber matrix. The authors found a gradual decrease in porosity and a linear evolution of density with the addition of NFC. Nevertheless, after achieving the highest increase of density corresponding to samples with 9 wt% NFC, further addition caused a drop in these properties, as shown in Figure 2-7a. The authors claimed that an increase in the NFC content in the paper slurry requires higher energy input to promote a homogeneous dispersion and result in a denser composite with a better interaction between the nanofibrils and the larger fibers. This hypothesis was corroborated after dispersing fiber slurries containing 3 wt% NFC at different revolutions. Figure 2-7b shows that there was an increase of 18% in tensile strength when the number of revolutions was increased from 180,000 to 240,000. The authors stated that above 3 wt%, properly dispersion of NFC is one of the key factors to boost the reinforcing capacity of the material for composites manufacturing.

In a similar effort, Campano et al. (2018) studied the mechanical and chemical dispersion of cellulose nanofibrils to improve its reinforcing effect on recycled paper. For the experimental conditions, the amount of CNF was fixed at 1.5 wt%, and c-PAM and CH were selected as retention aids. The authors reported an increase of approximately 9% and approximately 15% in tensile index when the pulping time of the recycled pulp mixed with CNF was increased from 10 min (30,000 revs) to 60 min (180,000 revs) using c-PAM and CH, respectively. A significant decrease in porosity accompanied this increase. According to the authors, porosity is one of the

signs that indicate a homogeneous dispersion and higher retention of the CNF within the fiber network. It was also determined that the temperature used during pulping (referring to pulping as pulp disintegration) does not have any effect on the dispersion of the CNF, as similar results in tensile index were obtained for 20 °C and 50 °C for the same pulping time.

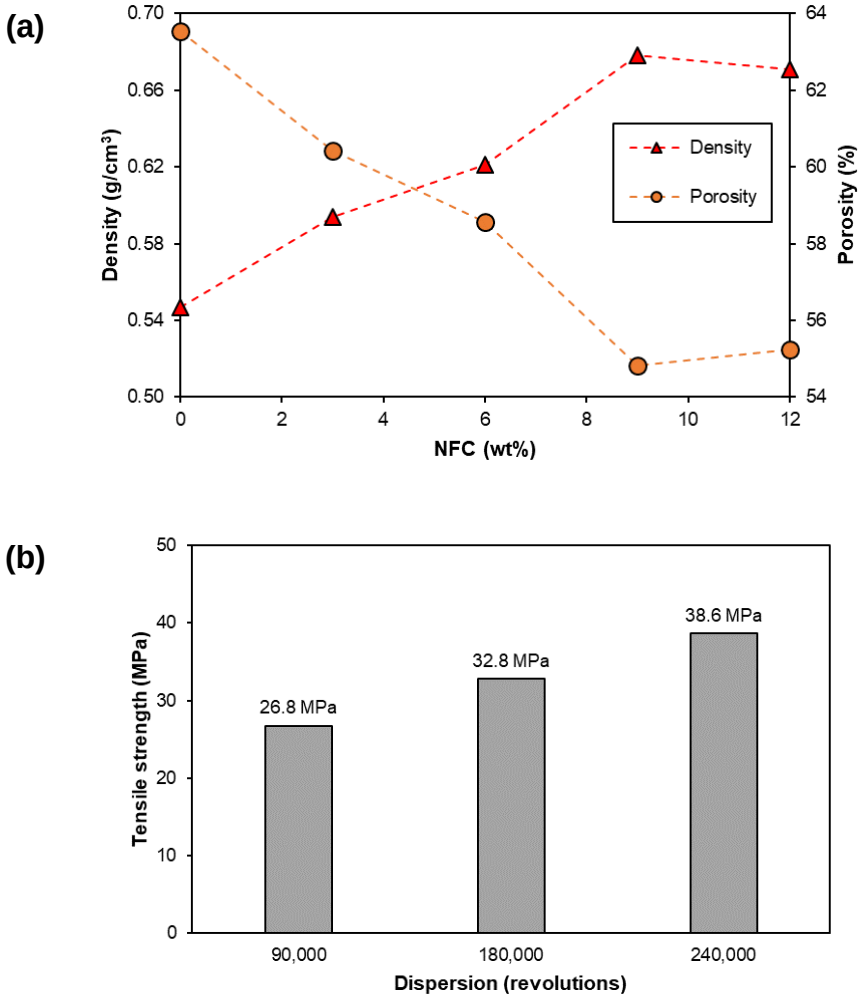

Figure 2-7: Evolution of physical and mechanical properties of unbleached Eucalyptus pulp: (a) reinforced with different contents of NFC dispersed at 180,000 revolutions; (b) reinforced with 3 wt% NFC using a different number of revolutions for dispersion (adapted from Alcalá et al. 2013)

Finally, the combination of dispersing agents in low concentrations (0.003%) with the CNF allowed a reduction in the pulping time. This result was attributed to more effective dispersion of the CNF; however, the increase in the tensile index from shorter pulping times was not as large as the increase obtained with longer pulping times (20.6% versus 30.0%). Ultimately, the dispersion strategy to implement in each process will depend on practical considerations. The mechanical properties of paper sheets reinforced with MNFC depend not only on the combination of intrinsic and extrinsic variables and the furnish composition discussed in the previous sections. The influence of the degree of dispersion of the papermaking furnish also plays a fundamental role before the formation of the paper sheet. Therefore, as mixing of the MNFC with the larger fibers is a required step for fabrication of composites, taking advantage of this process could result in more efficient use of the nanocellulose. Currently, there are different approaches applied in the industry to increase the mechanical properties of paper. Many of them consist of modifying raw materials, which greatly increase the production cost. However, a clear understanding of the effects that mixing has on the distribution of the MNFC into a fiber furnish could allow papermakers to obtain outstanding results by changing the mixing process rather than modifying the raw materials. As an example, the basis weight, which is a critical variable contributing to the mechanical resistance of the paper sheet, could be easily reduced and the losses in paper strength could be compensated with the addition of MNFC under the proper mixing conditions.

2.6 Economic potentials of MNFC as a driver for fiber reduction

2.6.1 What is the paper strength expected by consumers?

There are at least three main influencers on paper strength: (i) individual fiber strength and their arrangement in the sheet, (ii) the intensity of the fiber-fiber bonds, and (iii) aspects of

the feedstock raw material, such as fiber length distribution (Ankerfors et al. 2013). Additionally, as already discussed, the uniformity of formation within the paper sheet also can profoundly affect paper strength. Long fibers generally produce a sheet with a higher tensile strength compared to short fibers (Page 1969), which is because they have more sites to bond with multiple fibers. Paper is stronger in the machine direction than the cross-direction due to fibers preferentially arranging themselves lengthwise in the machine direction. Ultimately, tensile failure of paper occurs because of the interaction between interfiber bonding and fiber failure. Products, such as printing and packaging grades, have well developed fiber-to-fiber bonds, and it is expected that the sheet will fail due to broken fibers. Page's famous 1969 theory proposes that while the sheet is under a load, fiber bonds will start to fail. As the fiber bonds start to fail, there will be fewer bonds in the rupture region to disperse the load, causing individual fibers to take on more load until reaching their rupture strain. Tissue grades have relatively weak fiber-to-fiber bonds, which will cause the sheet to fail due to the breaking of fiber-to-fiber bonds instead of the breaking of individual fibers.

The strength requirements of paper products depend on the grade and final application. For printing and writing grades, tensile strength is needed to feed the sheet through the printers. Similarly, for tissue paper tensile strength is needed to withstand strain and stresses in the tissue machine and converting operation. The challenge with tissue is that most of the things that are done to help improve tensile strength hinder other desirable properties such as bulk and softness. Although a reduction in the tensile strength will improve the bulk and softness of the tissue sheet, if the tensile strength is too low, then the sheet will not support itself on the paper machine (de Assis et al. 2018b). In packaging grades, paperboard strength (usually ring crush or burst) is critical because all containerboards are rated for a certain cargo loading.

The easiest way to produce a stronger sheet of paper is to add more fiber to prepare a unit area of paper sheet (increase in basis weight). End-use customers are not concerned with how much fiber is used to produce their paper; they are mainly concerned with the final paper strength (along with softness and bulk for tissue grades). This can be seen with the use of filler in printing and writing grades. Fillers are significantly cheaper than fiber so companies use as much filler as they possibly can without negatively impacting the paper properties (He et al. 2017). This fulfills the customer's expectation while keeping the cost as low as possible, which translates into a higher profit margin. It has been shown that by introducing MNFC into a papermaking furnish, the strength properties of the paper can be increased. However, customers generally are not willing to pay a premium for an enhanced strength (de Assis et al. 2018a). As an alternative, the authors of this review suggest it is more feasible to change the mindset from using MNFC to improve the strength properties of commercially available papers to using MNFC to produce a lighter-weight version of these papers (keeping all the properties consistent to what is currently on the market) by reducing the overall fiber content. This is in agreement with the trend in papermaking of reducing fiber (Retulainen and Nieminen 1996) and, at the same time, should allow for a more rapid introduction of the MNFC into the industry.

2.6.2 Case study: reducing the grammage of unrefined hardwood chemical fiber sheets

This section intends to demonstrate the potential savings obtained from the grammage reduction driven by the addition of NFC to paper sheets having a target tensile strength. The analysis is based on experimental data presented by Hamann (2011), who studied the effect of grammage reduction for sheets prepared with unrefined hardwood chemical pulp with 10% addition of NFC, as shown in Figure 2-8. In a parallel study, the author tested the effect of

different NFC loads on the tensile strength of 60 g/m^2 sheets. These results, indicated by the colored dots in Figure 2-8, were added to the original chart.

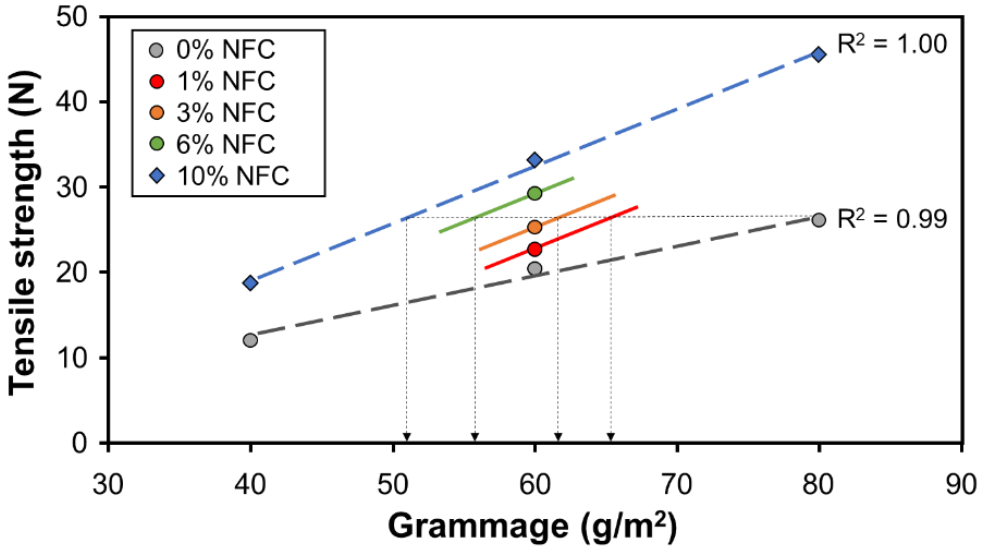

Figure 2-8: Grammage reduction is driven by the addition of NFC. Note that the same tensile strength is reached by using different combinations of grammage and NFC load (adapted from Hamann 2011)

For the analysis, an 80 g/m^2 sheet without NFC, with a tensile strength of 26.2 N, was selected as the base case. The authors found a strong linear correlation between the grammage and the tensile strength with and without NFC (R^2 equals to 1.00 and 0.99, respectively). Therefore, it was assumed that there is not a strong dependence between the rate of change in the tensile strength per grammage unit and the NFC load used. Considering the slope of the dataset with 10% NFC, the tensile strength was extrapolated for each NFC load in the 60 g/m^2 sheet to reach a value of 26.2 N. As a result, it was possible to obtain paper sheets with different grammages and NFC loads exhibiting the same tensile strength value. The results are shown in Figure 2-8.

Figure 2-9 shows potential cost reduction driven by the addition of NFC for both recycled and virgin fibers. The grammage reduction was calculated considering the amount of fiber that is possible to reduce for the different NFC-grammage combinations obtained from Figure 2-8. The cost reduction was assessed as the difference between the US dollars per tonne of dry pulp saved and the US dollars associated with the NFC load required to deliver the target tensile strength value. Two cost references (low and high) were selected to evaluate the sensitivity of the fiber cost on the cost reduction. These values, USD 820 and USD 1,100 per tonne of fiber respectively, were taken from the RISI database and correspond to the lowest and highest cost of northern and southern mixed bleached hardwood kraft (Canadian/US) between December 2016 and April 2018 (Fastmarkets RISI 2017b). The cost per dry tonne of NFC considered was USD 1,493. This value corresponds to an MNFC manufacturing facility that is co-located within a mill that produces northern bleached softwood kraft (NBSK) pulp (Abbati de Assis et al. 2017).

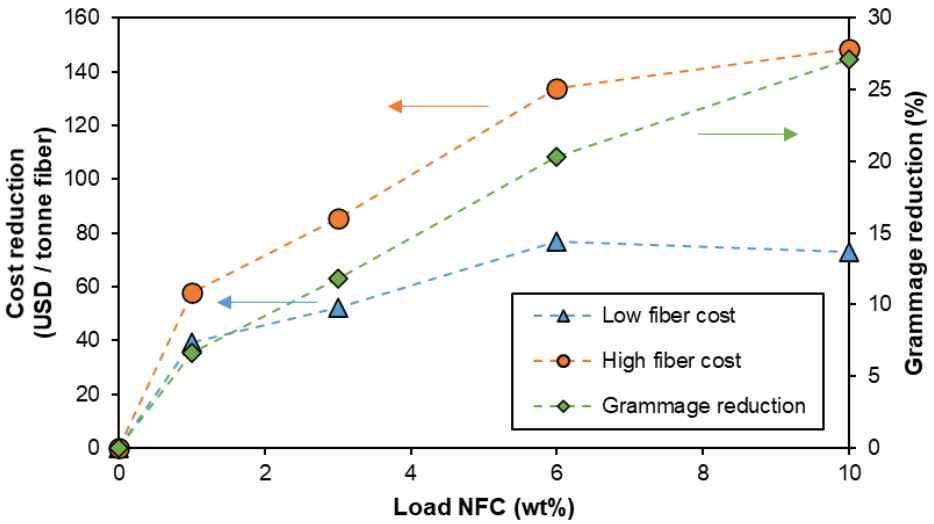

Figure 2-9: Potential cost reduction per tonne of fiber driven by the addition of NFC. The gray dotted line indicates the % of grammage reduction that can be obtained by adding the indicated NFC load. The orange and blue dotted line show how such cost reduction would translate in USD savings per tonne of fiber depending on the fiber cost. Low and high fiber cost are estimated to be USD 820 and USD 1,100 per tonne of fiber respectively. The cost per dry tonne of NFC considered was USD 1,493 based on the study published by Abbati de Assis et al. (2017)

Figure 2-9 shows that loads of NFC as low as 1 wt% already drive cost reduction. The CNF load that maximizes the cost reduction depends on the cost of the fiber used for the furnish preparation. For the low fiber cost, this load is around 6 wt%, whereas for high fiber cost there is no maximum within the range studied. As the cost of the raw material increases, savings due to cost reduction are higher. In this study, cost reduction can be as high as USD 77 and USD 149 per tonne of fiber for low and high fiber cost, respectively. Cheaper fibers, *i.e.*, recycled fiber, will have a more restricted range of operation before the addition of MNFC becomes economically infeasible.

Although the numbers shown in this study seem promising, additional aspects need to be considered before such an operation can be scaled-up. First, this analysis is based only on the

tensile strength. A reduction in the grammage deteriorates almost all paper properties, including those indexed by the basis weight (Retulainen and Nieminen 1996). Thus, an integrated analysis considering the lowest acceptable basis weight according to the paper grade produced needs to be considered. Second, Hamann 2011 reported a 50% retention of NFC, and no retention aid was introduced in the paper furnish to improve this value. If retention is less than 50%, using up to 6 wt% NFC might cause problems in the runnability of the paper machine. On top of a negative impact on dewatering, a potential build-up of NFC in the closed loop of the paper machine could increase the viscosity of the recirculating water, making the operation impractical. At the same time, filling of wet-press felts in the paper machine with unretained NFC may also represent an aspect of potential concern due to its difficult removal by conventional treatments. This highlights the need for carrying out an integrated analysis to study the feasibility of the use of MNFC to reduce the fiber content.

2.6.3 Determining the trade-off between the degree of fibrillation and load when using MNFC as a paper strength additive

From the previous discussion, one can expect there to be a fibrillation threshold (optimum degree of fibrillation) from which any further mechanical treatment does not translate into a significant increase in the mechanical properties of the paper. Moreover, a trade-off between the degree of fibrillation and the nanocellulose load required to achieve a target tensile strength value has been reported in the literature (Delgado-Aguilar et al. 2015; Johnson et al. 2016). From this situation, two possible scenarios can be developed: (i) a small load of MNFC is required at the expense of a high degree of fibrillation (small particle size) or (ii) a small degree of fibrillation (high particle size) is required at the expense of a high load of MNFC. In this sense, when using MNFC as a paper strength additive, the question of what the most profitable

scenario is arises. This highlights the importance of understanding the role of the particle size (micro *versus* nano) and degree of fibrillation in the nanocellulose performance.

2.6.3.1 Case study: increasing in 10% the tensile strength of a hardwood sheet using softwood CNF

This section intends to estimate a feasible combination of the particle size and the load of CNF required to reach a target paper strength. The analysis is based on a techno-economic assessment using experimental data presented by Johnson et al. (2016) that is shown in Table 2-5. In that work, the authors determined the load required to reach a target tensile value of 10% above that of a hardwood base sheet by using CNF having different fines content. As a practical approach, the fines content was correlated with the particle size using SEM, e.g., a CNF slurry at 90% fines has dimensions at the nanoscale. Measurements of the particle size for each fines content are not provided in the study. However, it is inferred that for a low fines content, a material with a width at the microscale predominates and the width moves towards the nanoscale as the fines content increases.

The energy required to reach each specific fines content was used as an input in the manufacturing cost model for CNF proposed by Abbati de Assis et al. (2017). This model is based on process data from a CNF pilot facility at the University of Maine, the same facility where the experimental data used for this analysis were collected. Therefore, the manufacturing cost associated with each fines content was estimated, considering one tonne of dry CNF as the basis. The results are presented in Table 2-5.

Table 2-5: CNF load required to increase the tensile index of a hardwood base sheet by 10%

Fines in CNF (%)	**CNF Load (%)**	**Tensile index[1] (N.m/g)**	**Manufacturing Cost[2] (USD/tonne CNF Dry)**
Hardwood base sheet		54.0	-
50	6.1	59.4	1,326
65	5.0	59.8	1,366
75	3.3	59.4	1,394
85	2.7	59.4	1,425
95	3.1	59.4	1,493

[1] Tensile index values from Johnson et al. (2016)
[2] Cost calculated using manufacturing cost model for CNF proposed by Abbati de Assis et al. 2017)

Figure 2-10 shows the CNF load cost per tonne of finished product depending on the fines content in the CNF used.

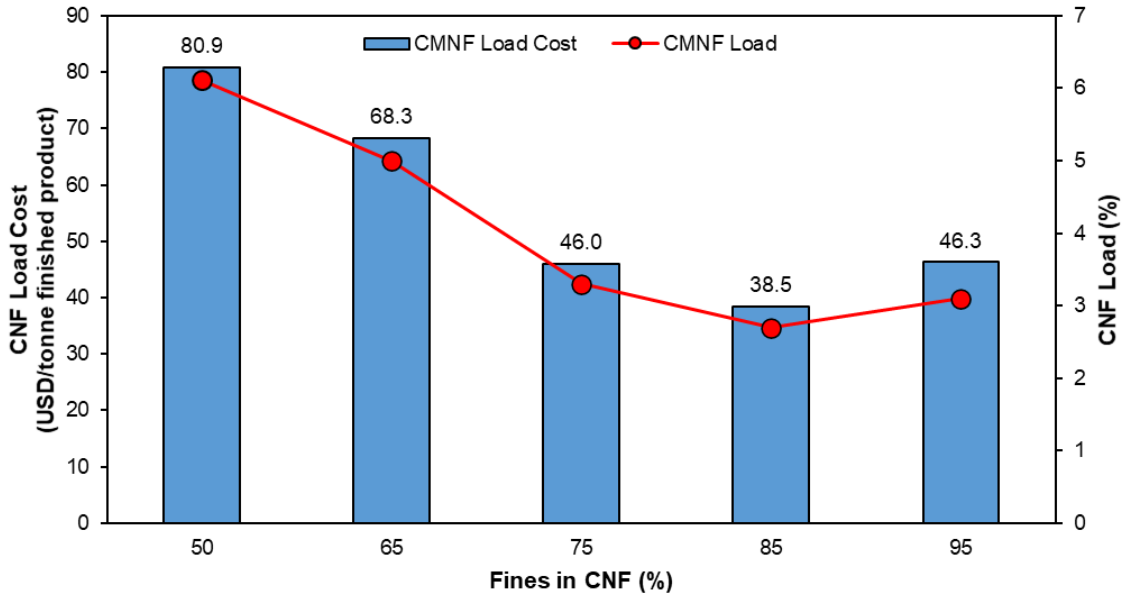

Figure 2-10: Load cost required to achieve a 10% increase in the tensile index of a hardwood base sheet by using softwood CNF with different fines content. As the fines content increases, the CNF load decreases and levels off after a 75% fines content is reached.

As the fines content increases, the CNF load required to increase the tensile index 10% decreases and there is no significant difference in the required load after 75% fines content is reached. These lower concentrations used in conjunction with the more fibrillated CNF (fines content > 75%), offsets the high manufacturing cost. For instance, when going from 50% to 75% fines, the CNF load cost is reduced by approximately 43%. Based on the techno-economic assessment performed, it is possible to state that moving towards the nanoscale is economically justifiable, although, the question arises as to how far one should go.

Starting from 75% fines content, the change of the load cost is less sensitive to the fines content. This is because energy consumption tends to level off as the fines content increases. A drop of 3% in the 95% fines CNF load (from 3.10% down to 3.01%), which would be considered as a favorable scenario, would decrease the load cost approximately 2.3% with respect to the 75% fines CNF load (from USD 46.3 to USD 44.9 per tonne of finished product). This small change might make the producer skeptical about whether it is worthwhile to pursue high levels of fibrillation. Therefore, other variables than just the cost component must be considered in the decision-making process. As discussed elsewhere in this review, there are challenges related to retention, slow dewatering, and drying that need to be to overcome when using CNF as a paper additive which are more likely to justify the use of CNF at a lower fines content.

2.7 Other alternatives for fiber reduction

2.7.1 Dry strength additives

Dry strength additives are commonly used in the paper industry as a way to maintain strength properties with less refining or with lower quality fibers (Hubbe 2007a). Figure 2-11 shows how dry strength additives can be used to reduce the amount of fiber required to produce a specific strength target.

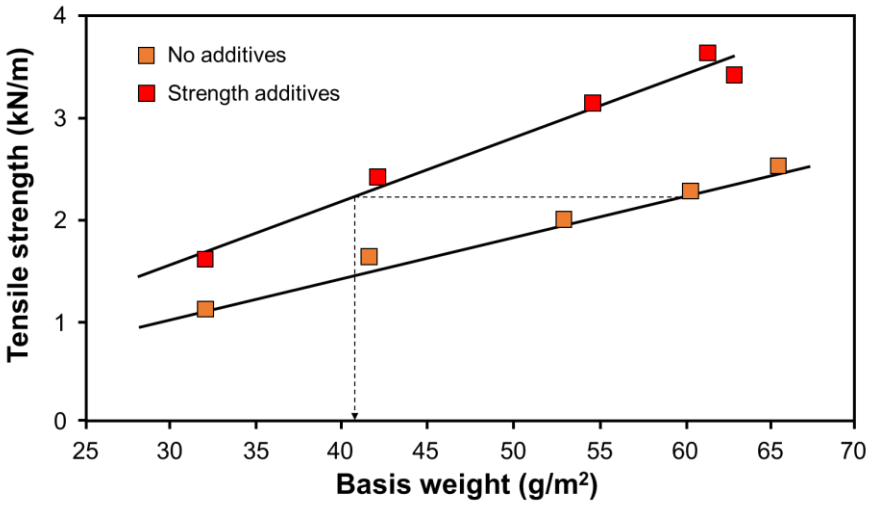

Figure 2-11: The use of 1.2% cationic potato starch and 0.4% carboxymethyl cellulose produced a 42 g/m2 sheet with the same tensile strength as a 60 g/m2 sheet with no additives (adapted from Retulainen and Nieminen 1996)

A general characteristic of dry-strength additives, such as cationic starch, is that strength gains may be cost-effective only up to a modest improvement in properties. Limitations in achievable strength gains are often related to maximum amounts of the polymers that can be absorbed by the fiber surfaces. Many of the paper machine systems that might be considered as candidates for MNFC addition will already be using various dry strength chemical additives at optimized levels, together with optimized levels of refining of the fibers.

A characteristic of using dry strength additives is that the sheet thickness is often reduced compared to the case where no dry strength additives are present; in principle, this might negatively impact properties such as bending stiffness and bulk (Retulainen and Nieminen 1996). The latter are important components of packaging and tissue grades, respectively. However, if the additive makes it possible to maintain strength at a lower degree of refining, then the bulky nature of less-refined fibers might yield the opposite overall effect. Because dry strength additives, with particular reference to cationic starch and various acrylamide-based strength

additives, are likely to remain used in applications where strength might allow basis weight reductions, it is very important that future research work includes evaluations of systems involving various combinations of MNFC and dry-strength chemicals, working together.

2.7.2 Fines-enriched pulp

Fines-enriched pulp is produced using a high intensity, multiple pass refining operation in conjunction with a fractionation process. In laboratory experiments, fines-enriched pulp has been shown to be twice as effective as glue pulp (highly refined kraft pulp used as a plybond enhancer) in terms of increasing multi-ply board strength, but it negatively impacts sheet bulk (Björk et al. 2017). The properties imparted on the sheet by the fines is heavily dependent on the fiber raw material (Fischer et al. 2017). Typically, in a furnish with a high fines content, the fines have been generated by excessively refining the fiber furnish, which breaks off more portions of the fiber layers, and even by fiber cutting in extreme cases. Because the fines Björk et al. (2017) used to enrich the pulp were generated during a separate refining process, this removes the negative impacts on paper properties associated with fiber cutting in the furnish. Despite the negative effects of having too many fines in the sheet, some fines must be present in the sheet to help with fiber-fiber bonding and ultimately the strength of the sheet. Fines-enriched pulp could be an alternative to MNFC; however, fines-enriched pulp produces a weaker, more porous, rougher sheet of paper than in the case of adding MNFC to the furnish (Fischer et al. 2017), which may not be desirable for some applications.

2.8 Concluding remarks

Based on the literature reviewed, the authors have acknowledged the potential to create value in the paper industry by introducing MNFC as a driver for cost reduction, along with the potential challenges associated with said strategy. The high manufacturing costs associated with the increase in fiber prices represent an opportunity for cost savings through the reduction of fiber content in paper products. Standards for paper strength are already established, and customers are not willing to pay a premium to have a super strong product. Therefore, instead of using MNFC as a paper strength additive, the real business opportunity may involve the use of MNFC to reduce the fiber content while delivering the strength commercially required.

The fiber price for the furnish preparation is what determines the optimum amount of MNFC to be used to maximize the cost reduction. For the techno-economic assessment conducted in this review, the tensile strength was the only property considered as a reference. Further research to evaluate the role of MNFC as a driver for fiber reduction in low grammage papers, *e.g.*, tissue and towel, and the impact that this reduction might have on other physical properties, *e.g.*, water absorbency, bulk, and softness, needs to be performed.

Likewise, the use of polyelectrolytes in combination with the MNFC represents an alternative to further increase the cost reduction. For instance, an increase in MNFC retention due to the use of polyelectrolytes could allow a reduction in the load required to achieve a target tensile strength at a given grammage. At the same time, the development of potential polyelectrolyte/MNFC synergies could also be beneficial in the task of reducing fiber.

The use of MNFC as a paper strength additive also requires a feasible combination of the particle size and load in the paper furnish. It was found that lower concentrations of softwood CNF associated with high fines content (high degree of fibrillation) outweigh the higher

manufacturing costs. From an economic point of view, this justifies using nanofibrillated cellulose instead of microfibrillated cellulose; however, operational challenges related to retention, slow dewatering, and drying of the nanocellulose might also need to be considered to select one type or another.

Finally, another important aspect to bring into the discussion is the fiber source used for the MNFC production. Thus far, energy processing cost had been noted as an issue in the manufacturing of MNFC; however, a recent study showed that the fiber source is the major cost driver. The cost of the cellulosic fiber typically represents more than 60% of the total manufacturing cost (Abbati de Assis et al. 2017). Johnson et al. (2016) stated that for high fines content (> 95%) both hardwood and softwood CNF show an equivalent performance when added into a paper furnish. Therefore, the most profitable alternative would consist in using the MNFC manufactured with the pulp fiber with the lower price; however, this might not be true for MNFC with an intermediate fines content. The latter highlights the need to conduct research considering several fiber sources and fines contents in combination with different polyelectrolytes. The authors believe that, on top of the gain in the paper strength, the key point to select the nanoscale and the specific fiber source used for the MNFC production will depend on additional improvements in other physical properties powered by the nano-feature that could potentially add extra value to the paper grade produced.

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3 MICRO- AND NANOFIBRILLATED CELLULOSE FROM VIRGIN AND RECYCLED FIBERS: A COMPARATIVE STUDY OF ITS EFFECTS ON THE PROPERTIES OF HYGIENE TISSUE PAPER[2]

3.1 Abstract

This study aims to understand the effect of micro- and nanofibrillated cellulose (MNFC) on the tensile index, softness, and water absorbency of tissue paper. MNFC was produced from four different fiber sources. The results show that MNFC acts as an effective strength enhancer at the expense of a reduced water absorbency and softness. The impact of the fiber source on MNFC manufacturing cost and the trade-off with performance was also investigated. MNFCs produced from southern bleached hardwood kraft, northern bleached softwood kraft, and deinked pulp exhibited similar performance trends with the MNFC from the deinked pulp having a significantly lower cost. This suggests that MNFCs with similar degrees of fibrillation may be used interchangeably regardless of the fiber source, revealing the possibility to minimize MNFC manufacturing costs based on fiber selection. MNFC produced from bleached Eucalyptus kraft showed the lowest degree of fibrillation and the lowest strength improvements among the MNFCs evaluated.

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3.2 Introduction

The development of nanotechnologies is an emerging field working its way into daily consumer commodities (Wijnhoven et al. 2009). Among cellulosic nanotechnologies there has been a growing interest in the application of micro- and nanofibrillated cellulose (MNFC) in commodity products such as paper, packaging, and packaging films (Abbati de Assis et al. 2017; Sanchez-Salvador et al. 2020; Siró and Plackett 2010). In papermaking applications, adding MNFC to pulp slurries yields paper products with improved mechanical properties (Eriksen et al. 2008; Taipale et al. 2010). In addition to increasing strength, MNFC decreases air permeability by increasing the total bonded area within the fiber network, consequently reducing the porosity of the paper product (Brodin et al. 2014; González et al. 2012). The reduction in air permeability correlates with an increase in sheet density (Sehaqui et al. 2013). The addition of MNFC also reduces the drainage rate of pulp slurries, requiring the implementation of appropriate retention aid programs (Merayo et al. 2017b).

Applications of MNFC in papermaking have focused mainly on printing and writing paper (Eriksen et al. 2008; González et al. 2012) and, to a lesser degree, on packaging materials (Balea et al. 2016; Hietala et al. 2016; Sanchez-Salvador et al. 2020). For such high-density grades, mechanical strength is a critical parameter, which benefits from the MNFC addition (Boufi et al. 2016). Conversely, in tissue papers other physical attributes such as softness, bulk, and water absorbency are more relevant to consumers, depending on the final product application (e.g., bath tissue or paper towels) (de Assis et al. 2018a; Wang et al. 2019b). Meanwhile, strength properties are only required to meet strain and stress conditions associated with manufacturing, converting operations, and consumer end-use (Nanko et al. 2010). Therefore, in previous work we proposed that strength gains obtained from the addition of MNFC could be

strategically used to reduce the fiber content in the tissue paper, without affecting strength performance while diminishing the overall tissue manufacturing cost. However, the anticipated negative impacts on tissue softness and water absorbency need to be quantified (Zambrano et al. 2020b).

The bonding mechanisms of low-density paper materials, such as tissue paper, are significantly different than that of high-density paper grades (Hollmark, 1983). Although MNFC has shown to improve strength in high-density paper, it is hypothesized that low-density tissue papers will be more susceptible to strength improvements due to its inherent loosely bonded structure. To the authors' knowledge, no comprehensive studies have been reported on the bonding mechanism of MNFC in low-density paper, wherein the high degree of bonding necessary for strength is in conflict with the low degree of bonding desired for absorbency and softness (Liu and Hsieh 2000). Hence, the novelty of this research is to elucidate the interactions between MNFC and low-density tissue paper relating to its tensile strength, softness, and water absorbency. The increasing number of patents on the use of MNFC in papermaking, including hygiene tissue applications (Charreau et al. 2020; Zambrano et al. 2020b), highlight the growing interest of manufacturers on the material and thus the significance of this study.

MNFC produced from northern bleached softwood kraft has a minimum product selling price that ranges from USD 1,893/OD tonne to USD 2,440/OD tonne (estimated to achieve a 16% hurdle rate) with the fiber source being a major cost driver (60% of total manufacturing cost) (Abbati de Assis et al. 2017). As such, cost reductions in MNFC manufacturing should consider low-priced fibers. However, before exploring such alternative, it is necessary to understand how different fiber sources might affect the MNFC performance. Therefore, the objective of this work was to perform a comparative study on four different MNFCs prepared

from various virgin (hardwood and softwood) and recycled fibers and evaluate their effect on the properties of tissue paper.

3.3 Experimental

3.3.1 Materials

The selected market pulps cover most fiber grades used in tissue making (de Assis et al. 2020). Dry sheets were sourced from pulp manufacturers in the United States. Southern bleached hardwood kraft (SBHK) and deinked pulp (DIP) were kindly provided by Domtar Corporation (Marlboro Mill, Bennetsville, SC) and Resolute Tissue (Sanford, FL) respectively. The identity of northern bleached softwood kraft (NBSK) and bleached Eucalyptus kraft (BEK) pulp manufacturers is kept confidential. Table 3-1 summarizes the pulp cost, fiber morphology, fines content, and compositional analysis of all fiber sources. Pulp cost data were collected from Fastmarkets RISI, considering the average values from 2019 and January - March 2020 (the latest months available for 2020). Since recycled fibers are typically recovered and used directly on the manufacturing site, two fiber costs were considered for MNFC prepared from this grade: (i) the cost of DIP market pulp, and (ii) the cost of recycled fibers at the headbox level from a recycled tissue manufacturing operation (obtained from personal communication with a major recycled tissue producer). Fiber morphology was determined with a fiber quality analyzer (HiRes FQA, OPTest Equipment Inc., Hawkesbury, ON, Canada), based on the measurement of 5000 fibers with length and width greater than 0.2 mm and 7 μm respectively. Compositional analysis of the market pulps was performed following the NREL procedure for determination of structural carbohydrates and lignin in biomass (Sluiter et al. 2008).

Table 3-1: Characteristics of market pulps used for MNFC production and tissue paper preparation

Pulp type	**Hardwood (virgin)**		**Softwood (virgin)**	**Recycled**
Pulp name	Bleached Eucalyptus kraft	Southern bleached hardwood Kraft	Northern bleached softwood Kraft	Deinked pulp
Pulp tag	BEK	SBHK	NBSK	DIP
Cost[1] (USD/tonne)	772	771	947	643; 300[a]
Fiber length[2] (mm)	0.802	1.101	2.343	1.111
Mean width (μm)	15.6	17.9	25.7	17.9
Fines content[3] (%)	4.62	19.84	4.94	11.63
Cellulose (%)	82.6	76.3	82.6	74.9
Total hemicelluloses (%)	16.1	19.2	14.2	18.1
Total lignin (%)	0.9	0.7	0.9	3.7

[1] Pulp cost data obtained from Fastmarkets RISI; [a] Cost for on-site produced recycled fibers.
[2] Length-weighted mean length.
[3] Length-weighted fines. Fines are defined as particles with length between 0.025 mm and 0.2 mm. Note: the ash content was negligible for all the pulps.

3.3.2 Production of MNFC using ultra-fine friction grinder

MNFC samples were produced from the market pulps shown in Table 3-1. The pulp fibers were diluted with tap water to 3 wt% solids content and disintegrated by shear mixing to form a slurry. Each pulp slurry was mechanically fibrillated in an ultra-fine friction grinder Supermasscolloider (model MKZA6-5, Masuko Sangyo Co., Ltd, Saitama, Japan), equipped with grinding disk stones model MKE6-46 deep ditch. The disk rotation speed was set to 2,500 rpm.

Before loading the slurry, a zero-gap width was fixed at the contact point between the stones and the gap width was reduced stepwise during the operation until -250 μm. A negative gap width indicates that a load is being applied to the fibers between the stones. Below -250 μm, the grinding process becomes unstable due to the likelihood of direct stone collision.

The mechanical fibrillation was carried out in batches. The product collected after each pass through the grinder was continuously fed back into the grinder inlet. MNFC samples were collected at a net energy input from which no significant changes in the fines content was

recorded with further mechanical grinding. Table 3-3 summarizes the gross and net energy input associated with the MNFC production, and fines content in the MNFC samples, which was above 90% for all the cases. The fines content was considered an indicator of the quality of the fibrillated material since an increase in fines content is concomitantly correlated with the decrease in particle size caused by mechanical grinding (Nechyporchuk et al. 2014). The net energy input to the pulp fibers during grinding was calculated with Eq. (4-1):

$$\text{Net energy input} = \text{Gross energy input} - \text{No} - \text{load power} \qquad (4-1)$$

where the gross energy input was obtained from the grinder power meter reading and the grinding time. The no-load power was calculated from the power consumed by the grinder when operating with water.

3.3.3 Characterization of micro- and nanofibrillated cellulose

3.3.3.1 SEM imaging and particle width distribution

Imaging of the fibrillated celluloses was performed using a field-emission scanning electron microscope (FE-SEM, FEI Verios 460L, Hillsboro, OR). The accelerating voltage was operated at a relatively low range (0.5 – 1.0 kV) to ensure good image resolution without causing damage to the fibrils. SEM samples were prepared by placing a drop of diluted MNFC dispersion at a solid content of 0.005 wt% on the SEM stubs and drying for 24 h at room temperature before imaging.

The width of the nanofibrils and nanofibril bundles was measured from SEM images using an image analysis software (ImageJ 1.47v, National Institutes of Health, Bethesda, MD) (Zhang et al. 2012). The particle width was sorted into bins of 50 nm size, and the particle count

within each bin was normalized to the total number of particles measured to obtain the corresponding width frequency. Each image was carefully examined to ensure that individual fibrils were counted only once, and all observable particles were measured to avoid bias in selecting the particles. Between 150 and 230 particles were measured from at least five SEM images per fiber source.

3.3.3.2 Crystallinity

The X-ray diffraction (XRD) pattern for each market pulp and corresponding air-dry MNFC film was determined using a Rigaku SmartLab X-ray Diffractometer (The Woodlands, Texas, USA) with a Cu K_α radiation at 44 kV and 40 mA. The diffracted intensity was detected in the range of $2\theta = 5° – 45°$ at a scanning rate of 1°/min.

The crystallinity index (CI) was estimated from the maximum intensity height of the crystalline peak at 2θ between 22° and 23° (I_{200}) and the minimum intensity height at 2θ between 18° and 19° (I_{am}), according to the Segal method (Segal et al. 1959):

$$CI = \left(\frac{I_{200} - I_{am}}{I_{200}}\right) * 100 \qquad (4-2)$$

3.3.3.3 X-ray photoelectron spectroscopy

The surface chemistry of each market pulp and corresponding MNFC was investigated with X-ray photoelectron spectroscopy (XPS). The MNFC was analyzed as a dispersion (2 wt% solid content) and as an air-dry film. XPS measurements were performed with SPECS Flex-Mod electron spectrometer using non-monochromated Mg Kα radiation at 300 W with a pass energy of 24 eV for survey scans and 20 eV for high-resolution spectra of carbon (C 1s) and oxygen (O 1s) regions. The take-off angle was perpendicular to the sample surface. Degradation

of the specimens under X-ray irradiation was not detected. Calibration was established by referencing C-C to 285.0 eV.

3.3.3.4 Water retention value

Static gravimetric dewatering of MNFC dispersions was measured using the Åbo Akademi Gravimetric Water Retention device (ÅA-GWR) (TAPPI T 701 pm-01 2001). A volume of 10 mL dispersion with 0.2 wt% solid content was poured into the cylindrical vessel placed above a non-hygroscopic polycarbonate membrane (Nuclepore™ Track-Etched 5 µm-membrane, Whatman®) backed by four absorbent blotter papers, which were enough to avoid saturation (Lahtinen et al. 2014). The vessel was sealed and pressurized at 50 kPa for 90 s (Kumar et al. 2017). Blotter paper was weighed before and after the test to estimate the liquid mass dewatered from the sample. The average of two measurements is reported.

3.3.3.5 Zeta potential

The zeta potential of the MNFCs was determined from electrophoretic light scattering using a Zetasizer Nano ZS instrument (Malvern, UK). Experiments were carried out in a disposable folded capillary cell (DTS 1070, Malvern, UK) loaded with 1 mL of dispersion with no added salt. A solids content of 0.01 wt% was used with the purpose of decreasing overlapping of the electric double layer on the cellulose particles (Han et al. 2013). Measurements were performed in triplicates after the samples were equilibrated at 25°C for 120 s.

3.3.3.6 UV-vis light transmittance

Transmittance measurements were performed on MNFC dispersions with 0.01 wt% solids content using a Genesys 50 UV-vis spectrophotometer (Thermo Fisher Scientific, USA).

Quartz crystal cuvettes of 1 cm path length were used with milli-Q water as the reference. The samples were homogeneously dispersed with an analog vortex mixer (Thermo Fisher Scientific, USA) for 1 min and then immediately tested to decrease the chances of flocculation or settling. Measurements were performed in triplicates.

3.3.4 Preparation of tissue-making slurry

A tissue-making slurry consisting of 70 wt% SBHK and 30 wt% NBSK was used to make 30 g/m^2 handsheets. The market pulps were used as received (with no mechanical refining). Each MNFC was added to the slurry at two loads: 1 wt% and 2 wt% based on OD fiber. MNFC and papermaking fibers were mixed together at 3000 rpm during 5 min and 1.2 wt% solids content using a pulp disintegrator (Testing Machines, Inc., Amityville, NY). After disintegration, the MNFC-pulp slurry was diluted to 0.3 wt% solids content using tap water. A high-density sheet (referred to as refined control) was also prepared from 70 wt% unrefined SBHK and 30 wt% refined NBSK to compare the addition of MNFC versus mechanical refining. The NBSK was refined using a PFI-mill (N°312, The Norwegian Pulp and Paper Research Institute, Oslo, Norway) according to TAPPI T 248 sp-00 (2000) . The refining intensity, controlled by the number of revolutions, was adjusted to match the bulk of the sheet containing the MNFC that yielded the highest strength improvement.

Freeness of the slurry was determined according to the Canadian standard method (TAPPI T 227 om-99 1999). Freeness provides a measure of the drainage rate of the slurry based on gravitational dewatering through a screen with 97 perforations per cm^2. The slurry was set to 20°C and then poured into the freeness tester, which consists of a drainage chamber and a rate measuring funnel having a bottom orifice and a side orifice. The volume of liquid exiting through the side orifice corresponds to the freeness.

3.3.5 Production of handsheets

The procedure for forming handsheets corresponds to a modified version of TAPPI T 205 sp-02 (2006). In the proposed method, wet pressing of the paper web is minimized to preserve bulk, as densification yields poor softness and poor water absorbency of the paper sheet. After formation and couching, handsheets are dried using a cylindrical dryer (Formax 12", Adirondack Machine Co., Gleans Fall, NY) instead of pressed and ring-dried. The operating conditions for the cylindrical dryer were set at 110°C, 1 rpm, and 5 min residence time. Handsheets obtained from this method were not creped.

3.3.6 Handsheet testing

Handsheets were conditioned for 24 h under a standard atmosphere set at 50% relative humidity and 23°C before testing (ISO 187 1990). Basis weight was determined according to ISO 12625-6 (2005). Thickness and bulk (inverse of apparent bulk density) were determined according to ISO 12625-3 (2005). Thickness was measured by applying a static load of 2 kPa on the handsheet sample (digital micrometer, model 49-56, Buchel B.V., Veenendaal, Holland). Tensile strength was determined according to ISO 12625-4 (2005) using a Instron® (model 4443, Canton, MA). Water absorbency was determined according to ISO 12625-8 (2016).

Softness was assessed with a Tissue Softness Analyzer (Emtec Electronic GmbH, Leipzig, Germany). The assessment is based on the analysis of the sound spectrum generated by the combined vibration of a tissue sample and six lamellas that rotate horizontally on the tissue surface causing friction. The vibration is related to both the surface and internal structure of the tissue paper. The frequency peak centered around 6500 Hz, identified as TS7 (TSA softness) provides an indication of the tissue softness. Lower intensity of vibrations will generate a lower TS7 peak height, which is associated with a softer product (Wang et al. 2019b).

The values reported for basis weight and bulk were obtained from an average of 20 measurements performed on different handsheet samples. For all other properties, the results reported are the average of a minimum of seven measurements. The porosity of the handsheets was calculated by following Eq. (4-3):

$$Porosity\ (\%) = \left(1 - \frac{\rho_{sheet}}{\rho_{cellulose}}\right) \qquad (4-3)$$

where the ρ_{sheet} is the apparent bulk density of the handsheet and $\rho_{cellulose}$ is the density of cellulose, assumed to be 1.6 g/cm^3 (Alcalá et al. 2013).

3.3.6.1 SEM imaging of handsheets

Imaging of the surface and cross section of the handsheets was performed using a variable pressure scanning electron microscope (VPSEM Hitachi S3200N, Hitachi High Technologies America, Schaumburg, IL). The samples were sputter-coated with a thin layer of gold-palladium (~35 nm). The accelerating voltage was operated at 10 kV. The cross-section images were produced by cryofracture to avoid collapsing of the fiber network structure.

3.3.7 MNFC manufacturing cost

The manufacturing cost for MNFCs was estimated using the MNFC cost model developed by Abbati de Assis et al., (2017) and the pulp cost data shown in Table 3-1. The financial assessment assumed the MNFC manufacturing facility to be co-located within the pulp mill. The energy input for the model corresponded to the gross energy consumption from the ultra-fine friction grinder (Table 3-3) scaled up to the equivalent energy that would be required by an industrial scale disk refiner. The production of MNFC from NBSK at 90% fines (by

number) was used as the reference (2,500 kWh/OD tonne). It was therefore assumed that as for NBSK (Abbati de Assis et al. 2017), a gross fibrillation energy of 2,500 kWh/OD tonne in a disk refiner would produce fibrillated samples at 90% fines for the different fiber sources.

3.4 Results and discussion

3.4.1 Characterization of MNFCs and effect of fiber source on fibrillation efficiency

The quality of the MNFC fibrillation was qualitatively assessed through SEM images (Figure 3-1). Regardless of the fiber source, the MNFCs exhibited a heterogeneous morphology with similar features: complex, highly entangled, web-like structures composed of individual fibrils, fibril bundles, fine particles, and non-fibrillated fiber fragments. This heterogeneous nature is characteristic of fibrillated cellulose obtained *via* mechanical processing without prior treatment of the fibers (e.g., TEMPO-mediated oxidation or enzymatic treatment) (Chinga-Carrasco 2011b).

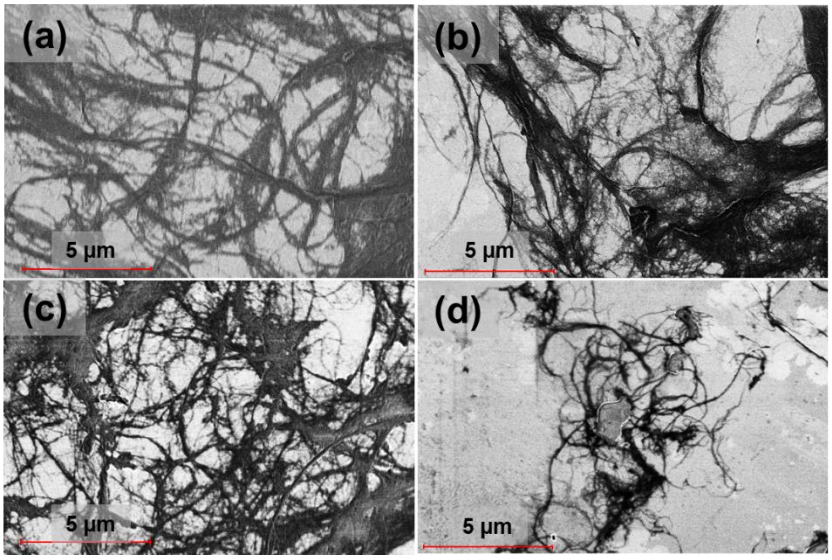


Figure 3-1: SEM images of MNFCs prepared by mechanical fibrillation of (a) BEK, (b) SBHK, (c) NBSK, and (d) DIP fibers (scale bar is equal to 5 µm)

Despite displaying a similar morphology, the level of heterogeneity, (i.e., the degree of fibrillation) varied between MNFCs. Fiber sources responded differently to the mechanical action as shown by the particle width distribution of the final material (Figure 3-2a). The particle width distribution for MNFCs produced from NBSK, SBHK and DIP (NBSK-MNFC, SBHK-MNFC, and DIP-MNFC, respectively) were similar, with more than 70% of the particles below 200 nm. NBSK-MNFC displayed the narrower width distribution, along with the largest number of smaller fibrils ($Fc_{200\ nm}$ = 84%), followed by SBHK-MNFC ($Fc_{200\ nm}$ = 73%) and DIP-MNFC ($Fc_{200\ nm}$ = 70%) (Figure 3-2b). MNFC produced from BEK (BEK-MNFC) showed the widest width distribution with less than 40% of the particles below 200 nm ($Fc_{200\ nm}$ = 37%). These results are consistent with the literature that indicate that when exposed to similar fibrillation energies, softwood fibers undergo more efficient fibrillation than hardwood fibers (He et al. 2018; Park et al. 2018; Spence et al. 2010b; Stelte and Sanadi 2009). The range of particle width obtained for individual nanofibrils (3 – 20 nm) and nanofibrils bundles (20 – 200 nm) is also in agreement with values previously reported, which are known to depend on the fiber source and the shear mechanisms to which fibers are exposed during fibrillation (Jonoobi et al. 2015).

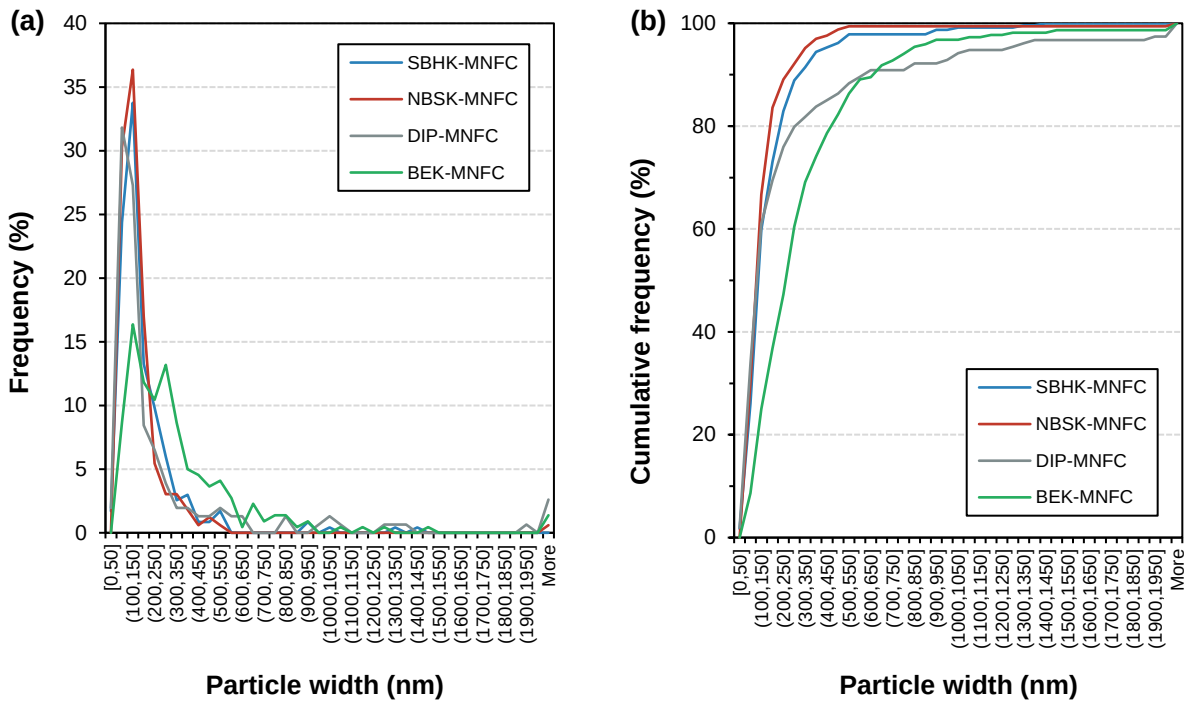


Figure 3-2: Particle width distribution for MNFCs sorted into bins of 50 nm size. The length-weighted mean width of the fibrils was 146 nm, 182 nm, 225 nm and 309 nm for MNFCs from NBSK, SBHK, DIP and BEK respectively.

XPS analysis, which included low-resolution and high-resolution surface scans, was performed on the market pulps and different MNFCs. Results from the analysis are shown in Table 3-2. The low-resolution survey spectra provided information on the elemental composition of the surface (Figures A-1 and A-2 in the Appendix A), revealing the predominant presence of carbon and oxygen. Deconvolution of high-resolution carbon C1 spectra (Figures A-4 and A-5) provided local information on the relative abundance of the carbon atoms in different molecular environments and their respective binding energies.

Peeling away the microfibril structure from the fiber cell wall produced significant changes in the surface chemical composition originally found in the macroscopic fiber, leading to a higher exposure of carbohydrates on the fibrils surface. Accordingly, an increase in carbons C2 (C–O) and C4 (O=C–O) was obtained for the MNFC dispersions compared to their

respective market pulps. This corresponded to a decrease in the carbon C1 (C–C or C–H) content, associated with a reduction in surface coverage by lignin and extractives, which have a strong tendency to precipitate on the fiber surface during kraft pulping (Kontturi 2005).

Overall, the oxygen to carbon (O/C) ratio measured for the MNFC dispersions was higher compared to their respective macroscopic fibers (Table 3-2). The O/C ratio of NBSK and BEK-MNFCs is near to the theoretical value of pure cellulose (O/C ratio = 0.83), which indicates that both MNFCs are exceptionally pure, consisting mainly of carbohydrates on the surface. The slightly higher O/C ratio of the NBSK-MNFC may be attributable to the presence of xylan with a theoretical O/C ratio of 1.0, whereas the lower O/C ratios of SBHK and DIP-MNFCs may result from the presence of aliphatic components initially found in the market pulps (Kontturi 2005).

Although the redistribution of the surface chemical composition had been reported for cellulose fiber exposed to refining (Fardim and Durán 2003; Gharehkhani et al. 2015; Mou et al. 2013), this phenomenon and its extent had not been shown for MNFC. In previous studies, XPS analysis would be performed on air-dry MNFC films, which have a strong tendency to deposit air-born contaminants driven by the high surface free energy of the fibrils. This passivation layer of carbonaceous surface impurities, along with possible traces of non-cellulosic components remaining from the natural fiber, would result in high C–C carbon peaks and reduced O/C ratios in the MNFCs (Andresen et al. 2007; Johansson et al. 2011; Littunen et al. 2011; Uschanov et al. 2011). This issue was also encountered in this work when XPS analysis was performed on air-dry MNFC films (Table A-1); however, the problem was minimized by performing the analysis directly on the MNFC dispersions.

Table 3-2: Surface functional group composition and O/C ratio of market pulps and corresponding MNFC

	% C1 (C–C, C–H)	**%C2 (C–O, C–OH)**	**%C3 (C=O, O–C–O)**	**%C4 (O–C=O)**	
Binding energy (eV)	285	286.4	287.9	289.2	O/C
NBSK market pulp	21	56	22	1	0.75
NBSK-MNFC	17	66	16	2	0.86
SBHK market pulp	33	40	26	0	0.66
SBHK-MNFC	28	57	12	3	0.75
DIP market pulp	31	52	17	0.3	0.71
DIP-MNFC	24	44	16	3	0.74
BEK market pulp	34	52	14	0.4	0.63
BEK-MNFC	18	61	21	0.4	0.81

The MNFC samples were characterized to understand the response of the different fibers to mechanical fibrillation (see Table 3-3). Overall, the MNFCs showed reduced crystallinity compared to their market pulps. The normalized XRD patterns of market pulps and corresponding MNFCs are shown in Figure A-7. The reduction in of crystallinity in the fibrils results from the destruction of cellulose crystals generated by the continuous shearing and compressive forces acting on the fibers during mechanical fibrillation (Nair et al. 2014). The water retention value (WRV) of the MNFCs improved with the quality of the fibrillation, which implies an increase in the number of fibrils and thus in the material's surface area. For instance, NBSK-MNFC had highest degree of fibrillation and showed the highest WRV, whereas BEK-MNFC with the poorest fibrillation resulted in the lowest WRV. These observations are in good agreement with previous works that have reported an increase in WRV with increasing fibrillation (He et al. 2018; Hu et al. 2015). MNFC produced from softwood pulp showed higher WRV (+7%) than MNFC from hardwood pulps. He et al. (2018) also reported a higher WRV for bleached softwood kraft pulp (Radiata pine) (+40%) than hardwood bleached kraft pulp (Acacia), which was ascribed to lower fibrillation of the hardwood fibers.

In addition to the degree of fibrillation, the degree of hydrophilicity, related to the O/C ratio of the material, also correlated with the WRV in the case of NBSK, SBHK and DIP-MNFCs. For instance, NBSK-MNFC with the highest WRV also displayed the highest O/C ratio. However, despite the high O/C ratio exhibited by the BEK-MNFC, the lower WRV suggests that the quality of the fibrillation is the primary driver of the water holding capacity for the MNFCs.

Table 3-3: Characterization of MNFCs

MNFC type	Net energy input (kWh/OD tonne)	Gross energy input (kWh/OD tonne)	Fines content[1] (%)	Water retention value (g/g)	Zeta potential (mV)	Transmittance 400 nm (%)	Transmittance 800 nm (%)	Crystallinity index (%)	
								Market pulp	MNFC
NBSK	6,292	9,584	90	63.7 ± 0.1	-34 ± 2	14.6 ± 0.3	38.7 ± 0.7	89	80
SBHK	6,599	9,622	94	59.5 ± 0.2	-37 ± 2	18.6 ± 0.7	42.9 ± 0.6	87	78
DIP	6,177	8,534	95	57.7 ± 0.7	-32 ± 1	9.4 ± 0.2	29.7 ± 0.4	87	80
BEK	5,591	7,577	91	55.7 ± 0.2	-33 ± 2	5.5 ± 0.1	18.9 ± 0.3	88	81

[1] Length-weighted fines. The value after the ± sign correspond to the standard deviation

The more difficult fibrillation of the hardwood fibers (e.g., SBHK and BEK) over the softwood fiber (e.g., NBSK) has been attributed to their more rigid, complex, and heterogeneous structure. The high Runkel ratio (cell wall thickness divided by lumen radius) of hardwood fibers results in a more rigid structure that needs to be unraveled by extensive mechanical refining to facilitate the liberation of fibrils from the cell wall (He et al. 2018). Softwood fibers rapidly lose their entire structure integrity, turning into a network of micro- and nanofibrils, whereas hardwood fibers tend to resist fibrillation with only the outer layers of the cell wall being fibrillated, even after the application of more severe treatments (Stelte & Sanadi, 2009). Therefore, it is expected for the MNFC made from softwood fibers to exhibit a higher surface area than the MNFC made from hardwood fibers.

The lower crystallinity index, higher WRV and higher light transmittance values obtained for SBHK-MNFC (Table 3-3) compared to BEK and DIP-MNFCs indicate more efficient

fibrillation of SBHK among the hardwood fibers (DIP was predominantly composed of short fibers as shown in Table 3-1). A possible explanation could be related to the higher charge density of the SBHK fibrils, as determined by zeta potential measurements, that might have facilitated fibrillation despite the coarser cell wall characteristic of SBHK fibers (de Assis et al. 2019). Similar observations were made by Fall et al., (2014), who reported a higher nanofibrils yield for Eucalyptus fibers displaying a higher charge density than Acacia fibers.

The higher WRV and higher light transmittance of DIP-MNFC compared to BEK-MNFC also suggest more effective fibrillation of the recycled fibers over the virgin hardwood fibers, despite their more intense hornification effects, which have been regarded as a factor reducing fibrillation efficiency of DIP (Ang et al., (2020). This might be related to the higher fines content in the initial DIP pulp favoring fibrillation (Table 3-1) as it has been suggested that the exposed cross-sections in fines are more easily accessed during mechanical fibrillation (Herrick et al. 1983; Spence et al. 2010b). Another possible cause might be associated with the higher lignin and hemicellulose content found in DIP (Table 3-1) since lignin decreases the amount of crosslinking between cellulose chains facilitating the penetration of water inside the structure (He et al. 2018; Lahtinen et al. 2014), while the amorphous nature of hemicellulose further contributes to swelling of the fibrils (He et al. 2018; Kulasinski et al. 2015). Hemicellulose also inhibits the coalescence of microfibrils, facilitating their release during mechanical deconstruction of the fiber cell wall (Iwamoto et al. 2008).

3.4.2 Freeness of tissue-making slurry

Figure 3-3 depicts the effect of adding MNFC on the freeness of the tissue-making slurry. The addition of MNFC negatively affected freeness, resulting in CSF values that were substantially lower compared to the control slurry. Deterioration in drainage rate with MNFC

addition is a phenomenon thoroughly reported in the literature (Boufi et al. 2016; Brodin et al. 2014; Eriksen et al. 2008). This effect stems from a combination of mechanisms governing the wet web formation process. Plugging of the fiber network porous structure by the freely moving fibrillated particles increases tortuosity and length of the capillaries used for water flow and reduces sheet permeability (Rantanen and Maloney 2013; Taipale et al. 2010). Moreover, the presence of MNFC significantly increases the total surface area in the pulp slurry, which boosts water retention by the formation of hydrogen bonding (Salmi et al. 2009), reducing the solid content of the sheet after wet pressing (He et al. 2017).

The extent of drainage reduction showed a correlation with the degree of MNFC fibrillation and loading in the slurry. These observations are consistent with Johnson et al., (2016), Rantanen & Maloney, (2013) and Taipale et al., (2010), who also reported slower dewatering rates with increasing MNFC dosage and degree of fibrillation. The reduction in freeness was particularly high for NBSK-MNFC, which exhibited the highest degree of fibrillation and WRV, whereas BEK-MNFC with the poorest degree of fibrillation and lowest WRV, resulted in the smallest drop in freeness. He et al., (2017) also associated increasing drainage times with increasing MNFC fibrillation, and overall reductions in MNFC crystallinity. SBHK-MNFC, with an intermediate degree of fibrillation, caused a freeness drop that was between the freeness obtained from the previous MNFCs. As the extent of fibrillation increases, more particles will be available to partially close the fiber network structure, which increases the wet web density, making more difficult the passage of water through the flow channels. This is accentuated by the higher freedom to move that particles with size in the micro- and nanoscale have compared to papermaking fibers. Moreover, the higher WRV associated with a higher extent of fibrillation (Table 3-3), and the ability of MNFCs to form cross-linked networks with

shear thinning behavior (Pääkko et al. 2007) might also have contributed to the decrease in slurry dewatering.

DIP-MNFC showed a response equivalent to that of NBSK-MNFC, even though DIP-MNFC had a poorer degree of fibrillation, as reflected by its lower WRV and light transmittance (Table 3-3). This could be ascribed to more efficient retention of the fibrillated particles with the larger size, causing an effect equivalent to that of the smaller particles, which are less efficiently retained in the wet web during formation. The effects on drainage of the slurry upon the addition of MNFC may result from a trade-off between particle size and retention efficiency. A small particle size will induce a high reduction of drainage; however, there is a limit related to the number of particles that can be efficiently retained in the wet web. Alternatively, more efficient retention in the wet web of larger particles will compensate their larger size, inducing a reduction in drainage comparable to that obtained for the smaller particles. The observations from Johnson et al., (2016) might provide further evidence about this hypothesis, as the authors reported less pronounced reductions in freeness with increasing degree of fibrillation in the MNFC.

Despite the freeness reductions obtained from the MNFC addition, the values were above 500 mL CSF, remaining at suitable levels for machine operations producing virgin tissue grades (Watson and Janssen 2014). The use of cationic polymers could potentially compensate for the freeness reduction, while also improving the retention of MNFC in the paper web during formation (Djafari Petroudy et al. 2014; Merayo et al. 2017b).

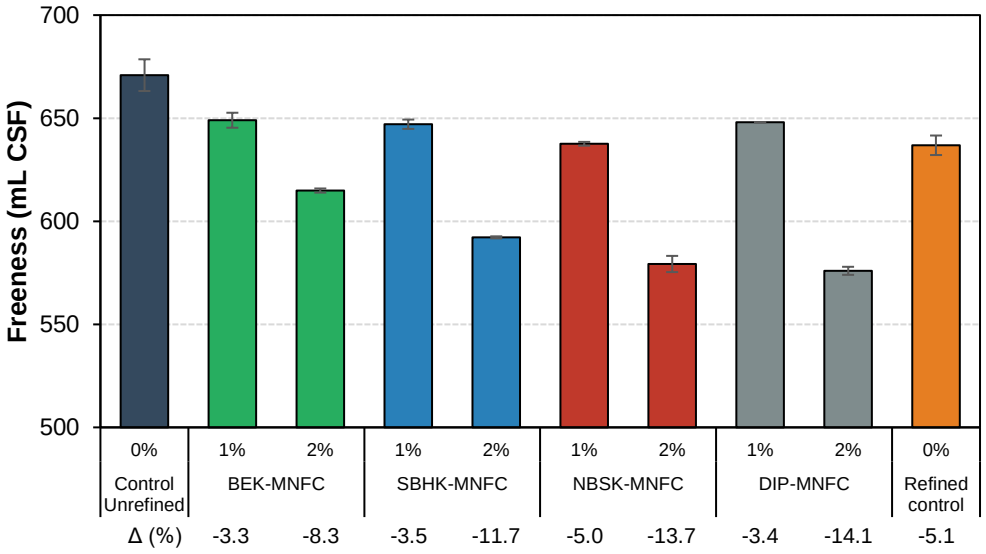


Figure 3-3: Effect of the addition of MNFC on freeness of the tissue-making slurry. The control unrefined is a blank without MNFC. The refined control is a sheet where the NBSK fraction was refined to match the bulk of the sheet containing 2% NBSK-MNFC. Δ is the percent difference in the property with respect to the control unrefined. Error bars indicate standard deviation.

3.4.3 Properties of tissue paper containing MNFC

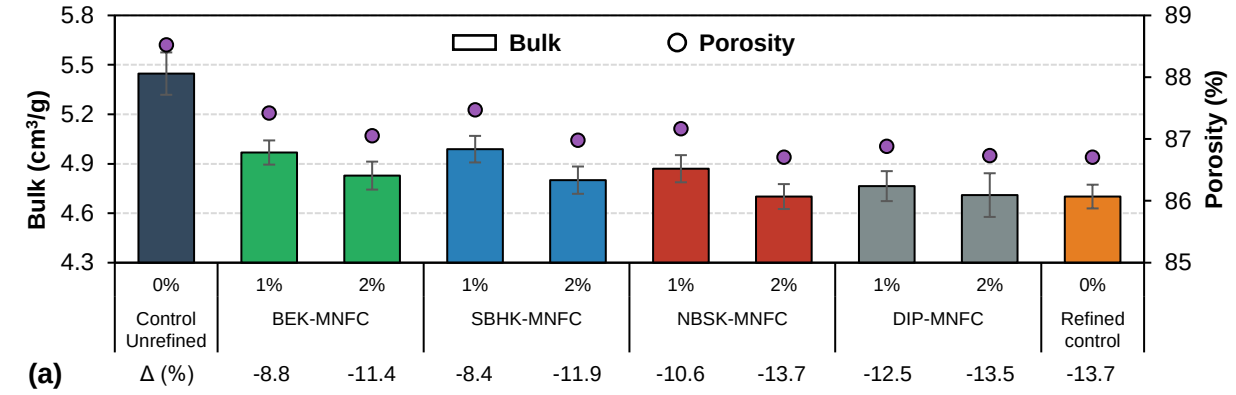
3.4.3.1 Bulk

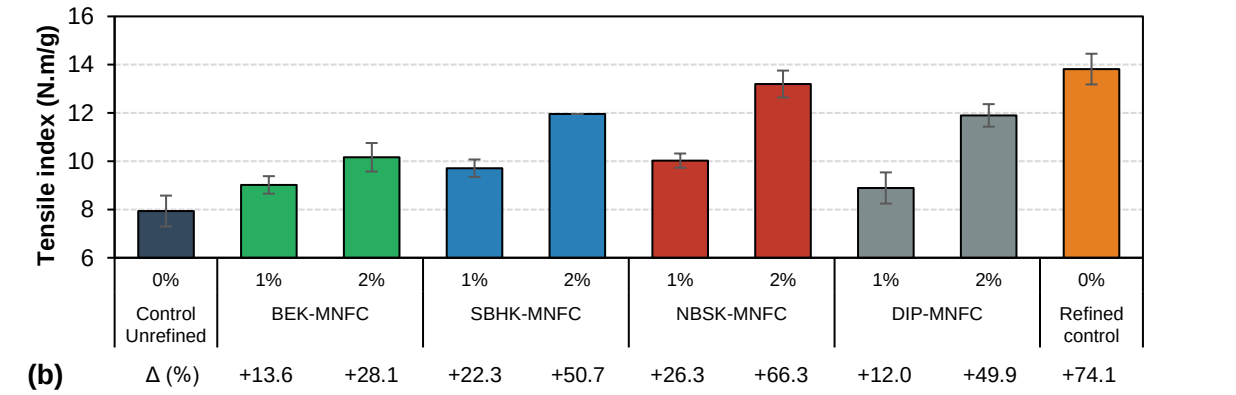
Bulk is an important quality parameter in tissue paper because of its direct relationship with water absorbency and softness (de Assis et al. 2018a; Wang et al. 2019a). Figure 3-4a shows the bulk of tissue paper containing MNFC from the different fiber sources. Overall, the addition of MNFC yielded a tissue paper with lower bulk compared to the control sheet. This could be attributed to the large surface area of the MNFC, which when positioned between fibers increases the number of hydrogen bonds formed during wet pressing, inducing densification of the structure. Further drying of the sheet welds the bonds tightly closed. This effect can be qualitatively observed in both the surface and cross-section of the MNFC-containing sheets (Figure 3-5). In addition, similar to fine particles, MNFC will reduce the radius of the water meniscuses formed during drying of the sheet, which will increase the pressure difference

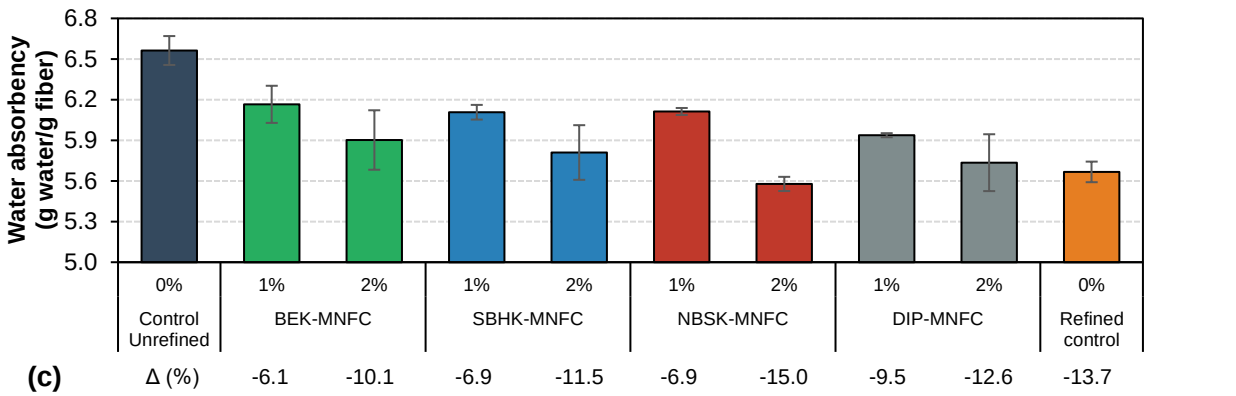
between the water phase and its surroundings, bringing fibers into more intimate contact within the fibrous assembly (Campbell 1947).

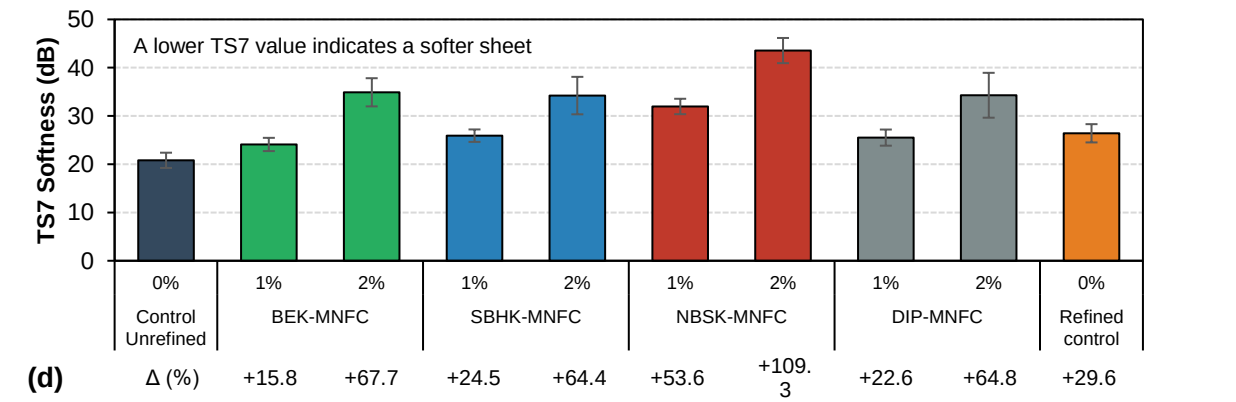
The reduction in bulk increased with the MNFC load. A larger reduction was obtained with a 1 wt% load, followed by a moderate decrease with a 2 wt% load. As the densification progresses, fewer porous sites might remain available to be filled by the fibrillated particles, diminishing the densification with an increasing MNFC load. Minor differences in bulk were observed depending on the type of MNFC. The sheet density upon addition of MNFC have been reported to be larger the smaller the particle size for MNFC produced from a single fiber source (Eriksen et al. 2008). Therefore, similar reductions in bulk, despite the differences in degree of fibrillation, might be derived from a trade-off between retention efficiency and particle size, i.e., a higher retention of MNFC in the sheet due to a higher particle size might compensate the more intense effects inherent to the smaller particles that are less efficiently retained in the web during sheet formation.

Figure 3-4: Effect of the addition of MNFC on (a) bulk, (b) tensile index, (c) water absorbency, and (d) softness. The control unrefined is a blank without MNFC. The refined control is a sheet where the NBSK fraction was refined to match the bulk of the sheet containing 2% NBSK-MNFC. Δ is the percent difference in the property with respect to the control unrefined. Error bars indicate standard deviation.


Bulk
Porosity
Bulk (cm³/g)
Porosity (%)
5.8
5.5
5.2
4.9
4.6
4.3
89
88
87
86
85
0% 1% 2% 1% 2% 1% 2% 1% 2% 0%
Control Unrefined
BEK-MNFC
SBHK-MNFC
NBSK-MNFC
DIP-MNFC
Refined control
(a)
Δ (%) -8.8 -11.4 -8.4 -11.9 -10.6 -13.7 -12.5 -13.5 -13.7


Tensile index (N.m/g)
16
14
12
10
8
6
0% 1% 2% 1% 2% 1% 2% 1% 2% 0%
Control Unrefined
BEK-MNFC
SBHK-MNFC
NBSK-MNFC
DIP-MNFC
Refined control
(b)
Δ (%) +13.6 +28.1 +22.3 +50.7 +26.3 +66.3 +12.0 +49.9 +74.1


Water absorbency (g water/g fiber)
6.8
6.5
6.2
5.9
5.6
5.3
5.0
0% 1% 2% 1% 2% 1% 2% 1% 2% 0%
Control Unrefined
BEK-MNFC
SBHK-MNFC
NBSK-MNFC
DIP-MNFC
Refined control
(c)
Δ (%) -6.1 -10.1 -6.9 -11.5 -6.9 -15.0 -9.5 -12.6 -13.7


A lower TS7 value indicates a softer sheet
TS7 Softness (dB)
50
40
30
20
10
0
0% 1% 2% 1% 2% 1% 2% 1% 2% 0%
Control Unrefined
BEK-MNFC
SBHK-MNFC
NBSK-MNFC
DIP-MNFC
Refined control
(d)
Δ (%) +15.8 +67.7 +24.5 +64.4 +53.6 +109.3 +22.6 +64.8 +29.6

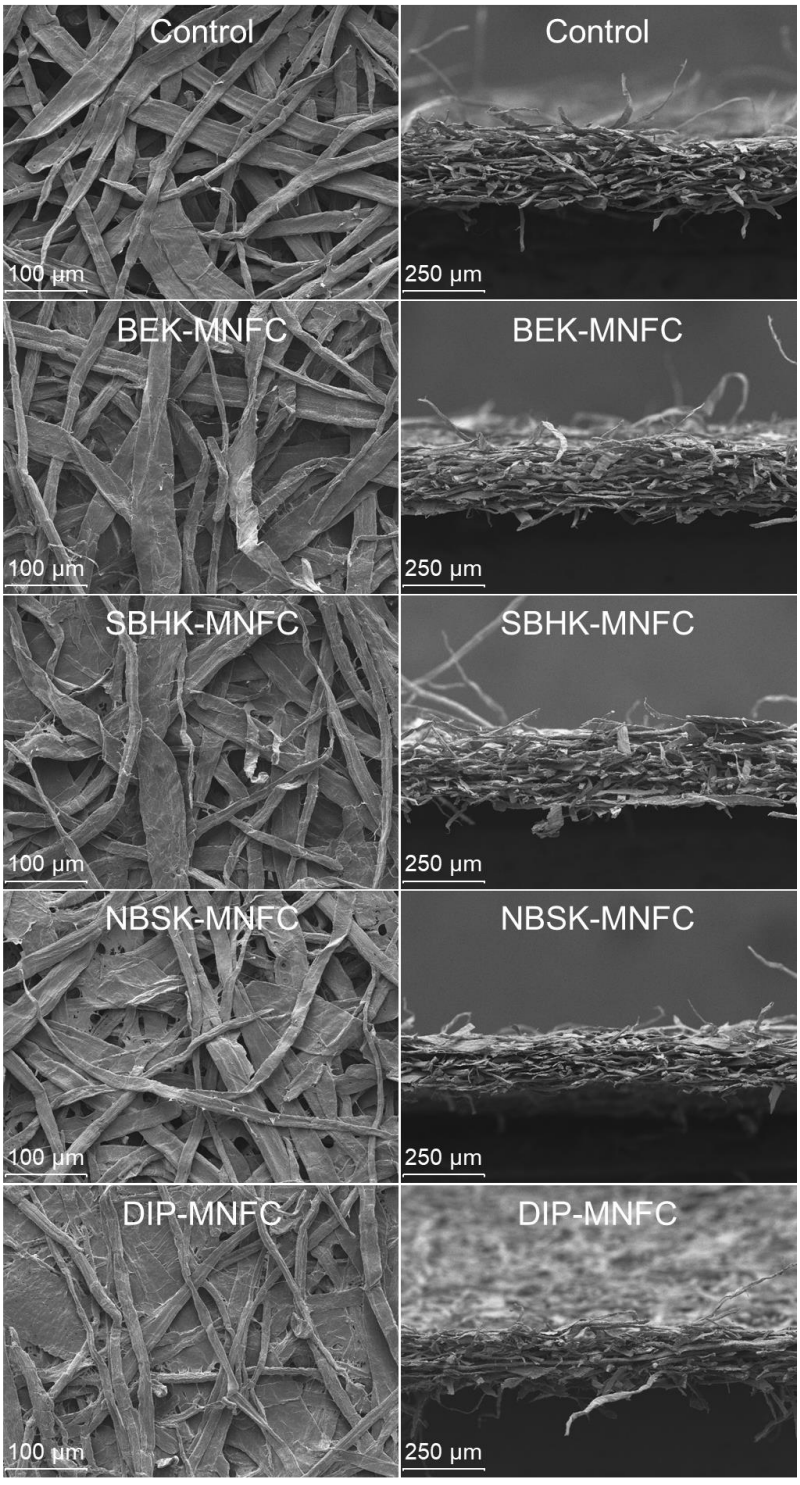


Figure 3-5: SEM images of surface (left) and cross-section (right) of control sheet unrefined and sheets prepared from a slurry containing 2 wt% MNFC

3.4.3.2 Tensile index

Tensile index measurements for each tissue paper are presented in Figure 3-4b. The addition of MNFC to the tissue-making slurry enhanced the tensile index of the tissue paper. Overall, the gain in tensile index increased with the MNFC load. The MNFC performance varied depending on the fiber source with differences in strength improvements becoming more noticeable with the increase in MNFC loading. For MNFCs prepared from virgin fibers, a correlation was observed between the strength gains and the degree of MNFC fibrillation. NBSK-MNFC with the largest degree of fibrillation presented the highest strength improvements (+67% at a 2 wt% load), whereas BEK-MNFC with the poorest degree of fibrillation, showed the lowest (+30% at a 2 wt% load). SBHK-MNFC, with an intermediate degree of fibrillation, showed a performance that was between the two previous MNFCs. Park et al., (2018) also reported a higher tensile strength in sheets containing MNFC from bleached softwood kraft pulp with a higher nanofibril content compared to sheets containing MNFC from bleached hardwood kraft pulp. The reinforcing mechanism of MNFC is based on consolidation of the sheet structure by the increase in the total bonded area (creation of additional fiber-fiber bonds), and the formation of embedded nano-networks along larger fibers that provide the fibrous assembly with points of high resistance (Boufi et al. 2016). It is thus expected that the expansion in surface area that results from the reduction of the fibrils size will increase the MNFC's ability to act as an adhesion promoter, and to form stronger and more stable nano-structures through both mechanical interaction and hydrogen bonding. These factors will result in a more uniform sheet capable of more efficient stress transfer upon loading. In the case of DIP-MNFC, the increase in tensile index was comparable to that of SBHK-MNFC at a 2 wt% load. This could be attributed

to the slightly higher sheet densification induced by the DIP-MNFC (Figure 3-4a), which might compensate for the more fibrillated nature of the SBHK-MNFC.

For MNFC produced from a single fiber source, He et al., (2017) correlated the reduction in the crystallinity of the fibrils with an increase in the degree of fibrillation, and thus in the tensile index of MNFC-reinforced paper. Given the different origin of the fibers used in this study, which resulted in different degrees of fibrillation upon application of mechanical treatment, a general correlation between the reduction in crystallinity and the degree of strength development was not observed; nonetheless, NBSK-MNFC, which exhibited one of the highest reductions in crystallinity, also yielded the highest increase in tensile index.

In addition to the degree of MNFC fibrillation, a higher concentration of C2, C3, and C4 carbons on the surface of the fibrils, involved in the formation of hydrogen bonds between fibers, and a higher O/C ratio, an indicative of the overall fibrils hydrophilicity, may have jointly contributed to the MNFC reinforcing potential. This may explain the improved strength developments of NBSK-MNFC, which in addition to having the smallest fibrils width, also showed the highest concentration of C2 and C3 carbons associated with C–O and C=O/O–C–O bonded carbons (Table 3-2). Similarly, SBHK and DIP-MNFCs, which exhibited comparable fibrils size and O/C ratios, also yielded comparable performance, whereas the inferior performance of BEK-MNFC despite its high O/C ratio may be explained by its predominantly higher fibrils size.

It is important to highlight that the strength gains obtained from the addition of MNFC in tissue paper were remarkably higher when compared to pressed sheets, and were also among the highest reported in the literature (Salas et al. 2019). The loosely bonded structure of tissue papers, resulting from their low basis weight and unpressed nature, will preferentially fail due to

the breakage of hydrogen bonds between fibers rather than breakage of individual fibers. In that sense, the evidence shows that the performance of MNFC is favored in fiber structures where weak fiber-fiber bonding is the primary variable hindering strength properties.

Moreover, the ratio of strength gains to freeness reduction per unit mass of MNFC added to the tissue-making slurry was significantly higher (avg. ratio = 342) compared to the ratio calculated from González et al., (2012) (avg. ratio = 20) and Delgado-Aguilar et al., (2015) (avg. ratio = 126), who produced MNFC-reinforced pressed sheets using slurries with similar freeness (651 mL CSF and 663 mL CSF respectively). This finding also suggests more efficient utilization of the MNFC in low-density structures in spite of the more favored conditions of the aforementioned studies, which employed highly fibrillated TEMPO-oxidized cellulose nanofibrils along with retention aid programs.

When used as tissue strength additives, MNFCs produced from NBSK, SBHK and DIP exhibited differences in the degree of strength development; however, these were minor compared to the significant strength variations between tissue sheets made from these fibers at the macro-scale showed by de Assis et al., (2019). This implies that fiber sourcing is less significant at the micro- and nanoscale regarding strength addition, and thus either fiber could be used for MNFC production. Similar observations can be also derived from Balea et al., (2016) and Merayo et al., (2017), where comparable strength improvements in CNF-reinforced paper were obtained with CNFs produced from TEMPO-oxidized BEK and bleached pine pulps and TEMPO-oxidized BEK and corn stalk organo-solv pulps respectively. The flexibility in fiber sourcing has important repercussions on MNFC manufacturing costs that will be discussed later in this study. It is worth noting that in the case of Balea et al., (2016), the TEMPO-mediated oxidation of the fibers prior to mechanical treatment, which facilitates defibrillation, may have

contributed to reduce the significant differences in performance observed in this study between BEK and NBSK-MNFCs.

3.4.3.3 Water absorbency

Absorbency properties are an important price driver for tissue products designed for wiping and absorbing purposes (de Assis et al. 2018a). Under saturated conditions, the water absorbed by a tissue product will be located within the fiber cell wall, in the inter-fiber spaces, and between plies in the case of multi-ply tissue products. For single-ply products, which correspond to the condition under study, water location is limited to the capillaries between fibers and the micro-, meso, and macropores found within the fiber cell wall (Zambrano et al. 2020a). Figure 3-4c shows the water absorbency of the tissue paper containing MNFC. Overall, the addition of MNFC resulted in tissue sheets with lower water absorbency in relation to the control sheet. This effect increased with the MNFC load in the paper web. The reduction in water absorbency was intimately related to the progressive loss in sheet bulk upon the incorporation of MNFC in the tissue web (water absorbency showed 83% linear correlation with bulk and porosity for all the conditions evaluated, Figure A-8). This densification of the sheet resulted in a reduction in the overall porosity of the fibrous assembly (Figure 3-4a) and thus in a reduction in the pore volume within the structure where most of the liquid is held (Dhiman & Chattopadhyay, 2020). This effect can also be qualitatively visualized from the SEM microphotographs in Figure 3-5, where the MNFC-containing samples displayed a less porous surface morphology with a more compact cross-section. de Assis et al., (2019) also found a reasonably good linear correlation ($R^2 = 0.77$) between the water absorbency and bulk of tissue handsheets made from various types of wood and non-wood pulps. Similarly, Dhiman & Chattopadhyay, (2020) reported a reduction in the absorption capacity of cotton nonwoven fabrics with densification of

the structure, which the authors attributed to a reduction in porosity and average pore size. No significant differences in water absorbency were observed between types of MNFC, which is somewhat expected as the different sheets should theoretically be able to hold similar amounts of water given their similar porosity at a given MNFC load.

Despite the high WRV shown by the MNFC in a wet state (Table 2-1), the experimental data indicates that once the MNFC is incorporated into the fiber network, and it transitions into a dry state, the absorbent features are either lost or outweighed by the physical changes in sheet porosity. It is also possible that the MNFC loading used was not high enough to confer improved absorbency properties to the paper web.

3.4.3.4 Softness

The response in softness to the addition of MNFC is shown in Figure 3-4d. The TS7 value increased with higher MNFC load in the paper web (i.e., a less soft material was obtained). The densification of the sheet caused by the increased MNFC load hinders compressibility and increases the rigidity of the fiber structure (see Figure A-9 in Appendix A), both relating to a reduced overall softness. Another factor that might have also impaired tissue softness could be the reduction in the number of free fiber ends on the sheet surface. The presence of free fiber ends decreases the contact area between the user's hand and the paper surface, thus improving the overall tactile perception. The generation of stronger adhesion forces between fibers by the presence of MNFC may promote better adhesion of fibers on the surface during couching and drying, thereby reducing the number of fibers that stick out from the tissue.

Compared to tensile index, tissue softness was found to be less dependent on the type of MNFC. In the case of BEK, SBHK, and DIP-MNFC, the results suggest that despite differences in degrees of fibrillation, the fiber networks responded similarly to the stresses imparted to the

sheet during the softness test that produces mechanical oscillation of the structure. These observations also suggest that, within a certain fibrillation range, the extent of fibrillation plays a major role when the sheet is subjected to tensile stress, allowing for an increase in tensile strength without negatively impacting tissue softness. Compared to the other MNFCs, the substantial increase in TS7 value obtained with NBSK-MNFC indicates the formation of stronger inter-fiber bonds within the fiber network that result in more intense mechanical oscillations, i.e., higher vibrational energy, relating to poor tissue softness. Therefore, it is also inferred that beyond a certain degree of fibrillation, additional improvements in strength are high enough to start impacting tissue softness negatively.

3.4.4 Comparison of MNFC addition versus selective fiber refining for strength development

In tissue grades produced from virgin fibers, the sheet's strength is typically achieved by selectively refining the softwood fraction. Little to no mechanical refining is applied to the hardwood fraction to preserve the short fibers' bulk and softness (de Assis et al. 2018b).

For the purpose of comparing the MNFC addition versus selective fiber refining as strategies for strength development, a tissue sheet was produced from a tissue-making slurry where only the NBSK fibers were refined (refined control in Figure 3-4). The refining intensity was adjusted to match the sheet's bulk obtained with a 2% load of NBSK-MNFC (the top performer for strength development).

Similar overall effects on the sheet properties and freeness of the slurry were obtained from selective fiber refining, i.e., an increase in tensile index with a reduction in water absorbency, an increase in TS7 softness, and a reduction in freeness. When comparing the two sheets, the tensile index of the sheet reinforced with 2% NBSK-MNFC was only slightly lower

compared to that of the refined control (Δ = 0.60 N.m/g). This highlights the reinforcing potential of the fibrillated material given the small loading used and the resulting effect, almost comparable to bulk refining 30% of the fiber mixture. However, the lower freeness of the slurry with MNFC reflects the challenges related to slow drainage associated with this strategy that were previously discussed.

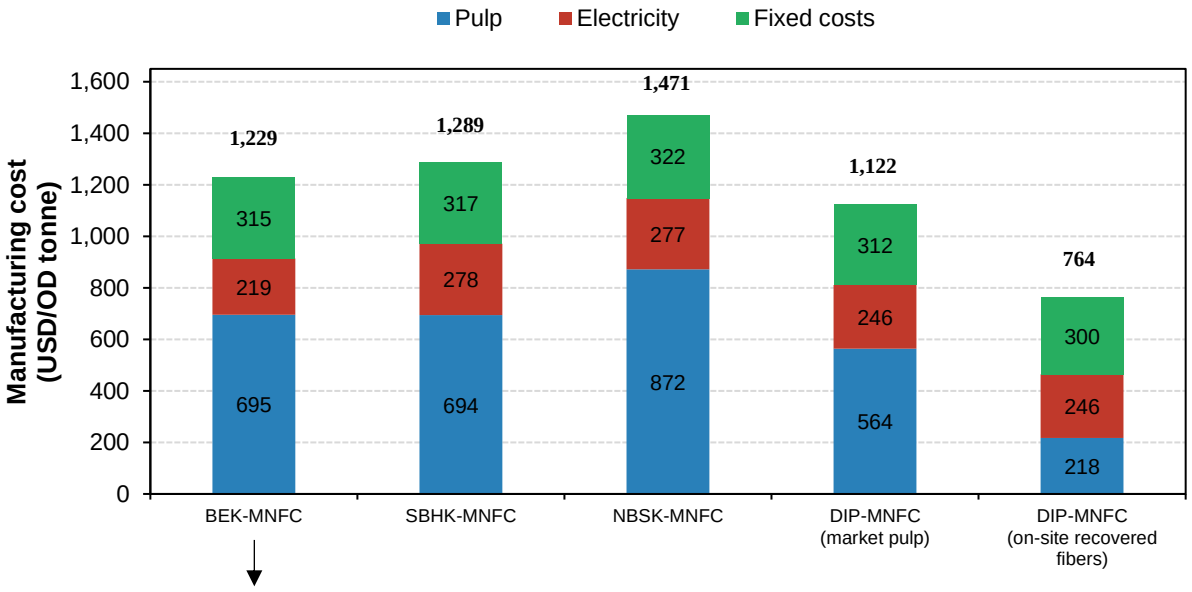
No significant differences were observed in water absorbency, emphasizing its interdependence with the sheet bulk, which was similar for both cases. Conversely, tissue softness showed the most significant difference in terms of properties. The TS7 value of the refined control was remarkably lower compared to that of the MNFC-containing sheet (39% lower). Although both reinforcing strategies are similar in that strength improvements can be related to sheet densification, this observation allows elucidating differences in the sheet strengthening mechanisms. In the case of the MNFC addition, fibrils are homogeneously dispersed throughout the fiber network, acting as a “glue” that uniformly bonds the entire web. This results in a more rigid structure, as reflected by the lower in-plane stiffness of the MNFC-reinforced sheet (Figure A-9), that is able to preserve better the vibrational energy. High vibrational energy has been correlated with a high TS7 peak and poor tissue softness (Wang et al. 2019a), which may explain the higher TS7 value of the MNFC-reinforced sheet. Results from the work by Motamedian, Halilovic, & Kulachenko (2019) are in agreement with this hypothesis, since they found that the presence of 3% fines content reduced by 50% the bending energy of a computer-simulated fiber network, which was attributed to fiber immobilization given the ability of fines to bridge fibers together.

Alternatively, forming a tissue sheet with selectively refined fibers generates a composite structure, where the reinforcing fibers occupy discrete locations within the fiber network. As

such, the paper web will have more discrete inter-fiber bonding, resulting in a structure that is also strong but overall less tightly bound, as the higher inverse stiffness of the refined control indicates (Figure A-9). Compared to MNFC-reinforced paper, which shows a dramatic decrease in air permeability, paper made of refined paper only exhibits slight reductions in air permeability (Su, Mosse, Sharman, Batchelor, & Garnier (2013). This observation also validates the more loosely bonded structure of refined sheets compared to MNFC-containing sheets and may explain the lower TS7 value of the refined control, associated with a more flexible and softer structure.

3.4.5 Relationship between MNFC performance and manufacturing cost

Figure 3-6 shows the MNFC manufacturing cost breakdown for the different fiber sources evaluated, which varied from USD 764/OD tonne to USD 1471/OD tonne. NBSK-MNFC had the highest manufacturing cost attributed to the high cost of NBSK, which accounted for 59% of the total manufacturing cost. BEK and SBHK-MNFC had close manufacturing cost since both fibers had very similar market pulp prices (accounting for 57% and 54% of the manufacturing cost respectively), with the difference being attributed to variations in the gross energy input into the cost model (Table 3-3). DIP-MNFC made from DIP market pulp had the lowest manufacturing cost due to its lower fiber cost, which accounted for 50% of the manufacturing cost. When on-site recovered fibers are used for MNFC manufacturing, the manufacturing cost remarkably decreased with raw materials accounting for 29% of the manufacturing cost. For this scenario, the fibrillation energy represented the largest cost driver, accounting for 32% of the manufacturing cost.



Application cost of MNFC in slurry (USD/OD tonne fiber)

1 wt% MNFC	12.3	12.9	14.7	11.2	7.6
2 wt% MNFC	24.6	25.8	29.4	22.4	15.3

Figure 3-6: Breakdown of MNFC manufacturing cost and application cost in tissue-making slurry. Fixed costs include maintenance, labor, depreciation, overheads, and other costs. Freight and drying costs are subtracted from the pulp cost given the co-location of the MNFC manufacturing facility within the pulp mill.

Since fiber cost is the largest cost driver in MNFC manufacturing, relying on cheaper fiber represents a tempting strategy to lower manufacturing cost, yet this requires understanding the impact of the fiber source on MNFC performance. Therefore, the trade-off between major tissue properties and the MNFC application cost were jointly analyzed.

The trade-off between tensile index and water absorbency is shown in Figure 3-7a. As expected, the enhancements in tensile index are associated with the loss in water absorbency previously discussed. In this context, the MNFC with the best performance will be the one capable of improving tensile index with the minimum impact on water absorbency and at the lowest application cost. SBHK and NBSK-MNFC showed a competitive performance over a

wide range of tensile index values. From a practical perspective, this makes either MNFC a potential candidate for tissue applications and supports the hypothesis previously stated about the micro- and nanoscale offsetting differences in performance observed at the macroscale. NBSK-MNFC has a higher manufacturing cost compared to SBHK-MNFC, which results in an application cost 11% higher. Therefore, the lower cost of SBHK-MNFC gives this MNFC an additional competitive advantage. Factors related to price fluctuations and fiber sourcing must be considered to get a more comprehensive assessment of the benefits of using SBHK over NBSK. The higher application cost of NBSK-MNFC might be also offset with a reduction of the load in the slurry to result in properties within the range obtained from the addition of SBHK-MNFC. At the same time, this might help to decrease the negative impacts observed on slurry drainability (Figure 3-3).

BEK-MNFC did not cover a wide range of tensile index values while yielding water absorbency values below the ones obtained with the other MNFCs produced from virgin fibers. The poor performance along with the high application cost makes BEK-MNFC the less feasible option for tissue applications among the conditions evaluated. DIP-MNFC showed the lowest water absorbency for a given tensile index at a 1 wt% load. However, it also showed a performance that was competitive to that of SBHK-MNFC at a 2 wt% load. Despite having the lowest application cost, the important reduction in freeness caused by DIP-MNFC (Figure 3-3) is an aspect to consider in evaluating its use in tissue manufacturing.

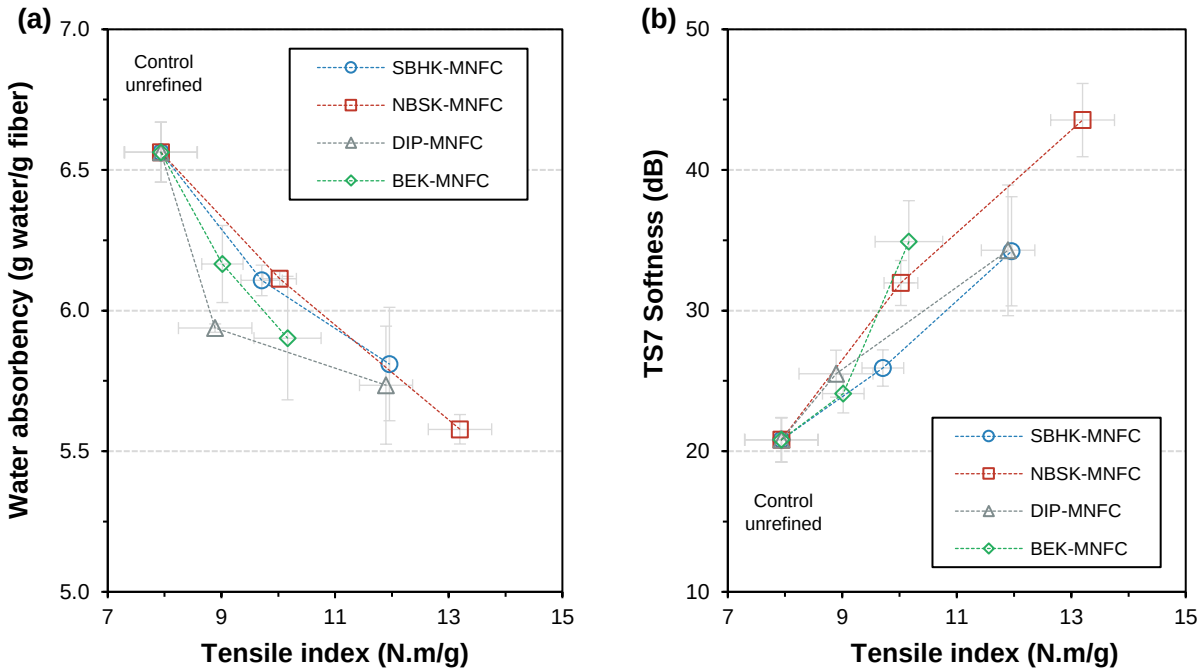


Figure 3-7: Trade-off between tensile index and (a) water absorbency and (b) TS7 softness. A lower TS7 value indicates a softer tissue sheet. Error bars indicate standard deviation.

The trade-off between tensile index and tissue softness is shown in Figure 3-7b. The control sheet had the lowest TS7 value; however, because of its unrefined nature, this sheet might not be able to withstand tissue manufacturing, converting operations, and end-consumer use. In this regard, the MNFC with the best performance is the one that can improve tensile index to a minimal functional value with the minimum impact on softness (lowest TS7 value) and at the lowest application cost. Within a wide range of tensile index values, the addition of SBHK-MNFC produced the lowest TS7 values. This in combination with its good water absorbency and low application cost, makes the MNFC produced from SBHK a good candidate for a strength additive in a tissue paper where a good combination between tensile index, softness and water absorbency is desired.

NBSK-MNFC allowed obtaining a tissue product within a wider range of tensile index at low loading but at higher TS7 values. Thus, for tissue grades that require developing strength with moderate softness and water absorbency, NBSK-MNFC can be a suitable option to consider in case the property enhancements can compensate its high application cost. Finally, DIP-MNFC showed a performance that was comparable to that of SBHK-MNFC. Considering the application cost of DIP-MNFC, which is 13% lower than SBHK-MNFC when made from market pulp and 41% lower when made from on-site recovered fibers, DIP-MNFC has an important cost advantage for utilization in tissue grades where a good balance between tensile index and softness is required with absorbency properties being less critical for an adequate product performance. On the other and, BEK-MNFC showed the poorest performance while causing an abrupt increase in the TS7 value. This reiterates BEK-MNFC as the strength additive with the poorest performance among the MNFCs evaluated.

3.5 Conclusions

This study evaluated the effects of the MNFC addition on the physical and mechanical properties of tissue paper. By adding MNFC into a tissue-making slurry of unrefined fibers, the tensile index of the tissue paper was improved with adverse effects in bulk, water absorbency, and softness. The degree to which the tissue properties were affected increased with MNFC loading and also depended on the fiber source used for MNFC production. MNFC from recycled fibers showed an adequate compromise between tensile index and softness while having the lowest manufacturing cost. MNFC produced from NBSK had the highest degree of fibrillation, yielding the strongest tissue paper at the highest manufacturing cost. MNFC produced from BEK showed the lowest degree of fibrillation, and the poorest performance among the MNFCs evaluated. Comparable property trade-offs between tensile index, water absorbency and softness

were obtained by the addition of MNFCs from NBSK, SBHK and DIP. This suggests that the micro- and nanoscale offsets significant differences in fiber performance present at the macroscale, and that different fiber sources can be used interchangeably, as long as similar degrees of fibrillation are achieved. The selection of the fiber source with the lowest cost can help reduce MNFC manufacturing cost; however, the ease of fibrillation needs to be simultaneously considered as it is fiber dependent and will thus impact the required fibrillation energy.

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4 MANUFACTURING HYGIENE TISSUE PAPER WITH REDUCED FIBER CONTENT AND COMPETITIVE PERFORMANCE: DEVELOPMENT OF THE FIBER REDUCTION TECHNOLOGY[3]

4.1 Abstract

This study describes the conceptualization and demonstration of the fiber reduction (FiRe) technology. The FiRe technology allows to reduce the manufacturing cost of hygiene tissue products by decreasing their fiber content (between 10 to 15%) without impairing product performance or machine runnability. The technology is intended to improve tissue manufacturers' cost position, which has been severely affected by industry challenges related to increasing fiber prices, high market competitiveness, and product commoditization. The technology is based on the combination of papermaking fibers with (i) either extensively refined macro-fibers or micro- and nanofibrillated cellulose and (ii) a commercial cationic polymer. The highly fibrillated cellulose fibers promote significant strength gains in the tissue sheet that are strategically used to reduce the fiber content while maintaining the minimal functional strength and softness required for proper performance and consumer satisfaction. At the same time, the use of a cationic polymer allows counteracting the adverse effects on drainability of the fiber furnish derived from the presence of the highly fibrillated material. This ensures that machine runnability is not affected and that production rates remain at their typical levels.

[3] The material in this chapter was published as a PCT patent application entitled “REDUCED FIBER TISSUE PAPER AND METHODS OF MANUFACTURE” (Authors: Gonzalez, R., Zambrano, F., Jameel, H., Venditti, R. and Lokendra, P. International publication number WO 2020/112955 A1)

4.2 Introduction

Cost reduction is among the top priorities of tissue companies followed by pricing and margin management (Klein 2019). Fiber is the primary cost driver for tissue paper manufacturing. In the North American market, fiber cost represents 45% and 59% of the parent roll cash cost for Away-from-home and At-home tissue products respectively (Rager 2018). In addition to the great importance of fibers to the cost structure of tissue-manufacturing, the fiber supply chain is very sensitive to market effects given the high dependence of the industry on a few fiber sources, the shrinkage in the supply of recycled fibers from high-grade recovered papers, and the high volatility of fiber prices (de Assis 2019).

In this framework, cost reductions based on optimized utilization of fibers is a key area that companies need to pay attention to in order to protect profit margins and stay profitable in a highly competitive environment. Decreasing the amount of fibers typically used in manufacturing is a tempting strategy to drive important cost savings. However, reducing the fiber content in the tissue web with the rest of manufacturing conditions unchanged will decrease the strength of the fiber network. Strength in tissue paper is required to withstand stresses encountered during tissue making, converting operations and use by end-consumers but has little influence on retailing prices. On the other hand, properties such as water absorbency and softness are main price drivers of tissue products. For bath tissue and paper towels, cross-sectional market analysis conducted across the US has shown that consumers will pay higher amounts for softer and more absorbent products (de Assis et al. 2018a; Wang et al. 2019b). Developing strength will render a fiber network of high-density and stiffness, which is opposite to the low-density and flexibility required for improved water absorbency and softness. Thus, manufacturers will try to

achieve a minimum functional strength to provide physical integrity to the product while maximizing softness and water absorbency (Pawlak & Chan, 2019).

In this context, this research presents a technology that allows for a reduction in the fiber content (i.e., basis weight) of tissue products without causing negative impacts on tissue strength and thus product functionality. Basis weight of the tissue product is one of the primary contributors to the strength of the paper web. Therefore, strength losses incurred in by the reduction in fiber content is a critical aspect that the technology addresses as it is desired to reduce the amount of fiber without jeopardizing product performance. This technology, referred to as fiber reduction technology, aims to provide cost-competitiveness to tissue producers through the reduction of fiber manufacturing costs and thus enable tissue companies to respond to current challenges and stay profitable in a highly dynamic business.

4.3 Description of the fiber reduction technology

The fiber reduction technology allows for a reduction in the fiber content of tissue paper between about 1% to 25% based on dry fiber weight. The resulting tissue paper has nominal strength values at a lower fiber content without adverse effects on product performance (e.g., bulk and softness), and freeness of the tissue-making slurry. The fiber reduction technology is a method of tissue manufacture which produces an “excess” of tissue strength, i.e., strength that can be reduced without detriment to the function or desired properties of the tissue paper, and uses some or all of such “excess” strength to compensate for the reduction of the fiber content.

Tissue paper consists of a combination of hardwood and softwood fibers. Hardwood fibers are the primary source of bulk and softness, whereas softwood fibers are the main source of mechanical strength. Strength in the tissue sheet is achieved by refining the softwood fibers, with little to none mechanical refining applied to the hardwood fibers to preserve bulk and

softness in the tissue paper. Under conventional manufacturing conditions (Figure 4-1a), developing strength beyond a minimal functional value is not desired because tissue paper with higher strength will be subjected to problems related to lower softness, bulk, water absorbency and drainage, which will impact tissue quality, cost, productivity and retailing price.

The fiber reduction technology develops tissue strength beyond the minimal functional value, and offsets the excessive strength with a reduction in the fiber content, while retaining the desired tissue strength and product functionality. The fiber reduction redresses negative effects on tissue softness and bulk resulting from the more refined nature of the fibers. This novel tissue manufacturing method relies on state-of-the-art practices, i.e., mechanical refining and wet-end chemistry. In a first manufacturing pathway, a portion of the fiber mixture is subjected to intensive mechanical refining, and a drainage aid is subsequently added to the tissue-making slurry (Figure 4-1b). The intensively fibrillated portion, which may comprise between about 1% to about 60% of the dry fiber weight, is refined to a freeness level unusual in commercial tissue-making operations involving virgin fibers, i.e., between 50 mL CSF to 390 mL CSF. Said portion, which is the main source of mechanical strength in the tissue paper, typically corresponds to the softwood pulp (long fiber fraction). The remaining fraction of the fiber mixture can be partially fibrillated to a freeness level greater than 390 mL CSF, or not treated. This remaining fraction, which is the primary source of softness and bulk, typically corresponds to the hardwood pulp (short fiber fraction). The treatment of the fiber mixture is performed so that the strength of the sheet is primarily developed by refining the long fiber fraction, while the short fiber fraction is protected to preserve bulk and softness in the tissue paper.

Mechanical fibrillation to low freeness values is undesirable in tissue making as it jeopardizes machine speed (slower dewatering), and thus reduces tissue mill productivity

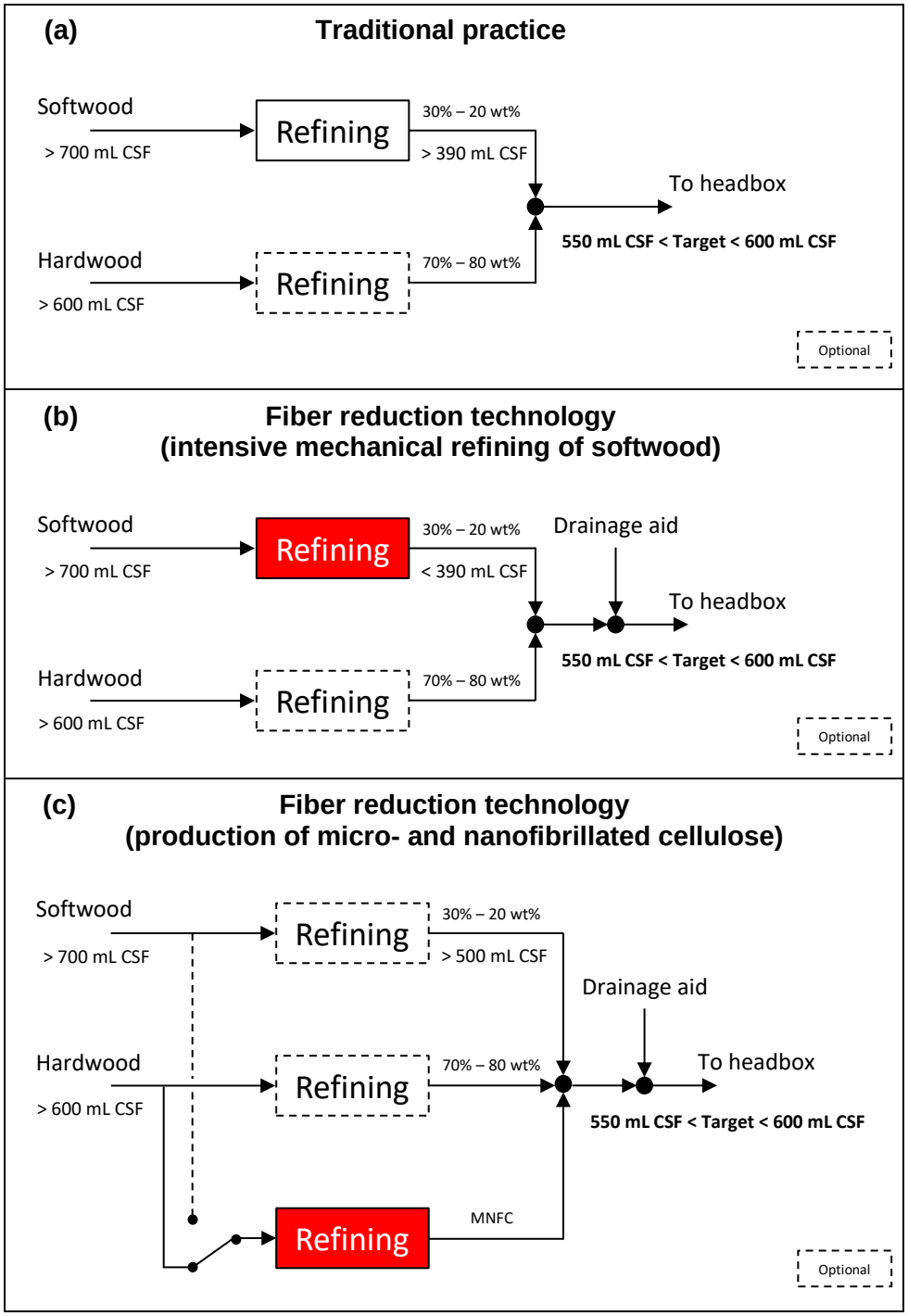
(Watson and Janssen 2014). Moreover, it produces paper webs with unnecessary high strength and limited softness, bulk, and water absorbency, which are advantageous properties for driving high shelf prices (de Assis et al. 2018a; Wang et al. 2019b). Consequently, traditional tissue-making operations avoid refining virgin fibers to freeness values below 420 mL CSF (Watson and Janssen 2014). In applying the fiber reduction technology, the intensive mechanical refining action needed to allow for a reduction in the fiber content will have a negative impact on drainage of the tissue-making slurry. This negative impact on drainage is compensated by the addition of drainage aid, which recovers the freeness of the slurry to levels that are suitable for high machine speeds, while ensuring at the same time, the retention of fine particles that may be generated due to the intensive mechanical action on the cellulose fibers. The dosage of drainage aid is adjusted to maintain the freeness of the tissue-making slurry in a range between 550 mL CSF to 650 mL CSF, depending on the cellulose fiber mixture, and operating conditions of the tissue machine. The incorporation of a drainage aid may also positively contribute to softness and bulk of the tissue paper.

The fiber reduction technology can be also implemented by following a second manufacturing pathway, which can be regarded as an extension of the first one (Figure 4-1c). In this instance, the manufacturing process encompass the use of continued mechanical fibrillation of a portion of the fiber mixture to generate micro- and nanofibrillated cellulose (MNFC) that is then added to the tissue-making slurry in combination with a drainage aid. Cellulose materials at the micro- and nanoscale are well-known for their paper strengthening capacity (Boufi et al. 2016; Osong et al. 2016; Zambrano et al. 2020b). The incorporation of MNFC in a fiber network increases fiber-to-fiber bonding and thus the total bonded are in the paper sheet. Moreover, the self-tendency of MNFC to form nano-networks of outstanding intrinsic strength along larger

fibers provides the macro-structure with points of high resistance. These two factors contribute to an increase in the paper density and an overall improvement in the strength properties (Boufi et al. 2016).

The portion of cellulose fibers that is subjected to the extensive mechanical treatment is typically lower compared to that of the first manufacturing pathway and may comprise between about 0.10% to 10% of the dry fiber weight of tissue paper. The percentage of fiber mixture mechanically treated can be lowered compared to the 1% to about 60% of the method previously described, as a result of significant gains in tissue strength driven by the highly fibrillated cellulosic material. This allows lowering the amount of fibrillated material in the tissue-making slurry to produce the excess strength that is necessary to offset the fiber content reduction in the tissue paper. Upon application of this method, if the target for fiber reduction (strength gain) is achieved solely with the addition of MNFC, the remaining fiber mixture is most advantageously not refined so as to preserve the bulk and softness inherent to the unrefined state of the fibers. Conversely, if the addition of MNFC is not sufficient to attain the target fiber reduction, the remaining fiber mixture, more specifically the long fiber fraction, can be subjected to partial mechanical refining action, e.g., to a freeness value greater than 500 mL CSF, to further develop the strength of the paper web. Another alternative may include increasing the load of MNFC in the tissue-making slurry, improving the quality of the fibrillated material (higher degree of fibrillation) or changing the fiber fraction that is converted to MNFC. In all scenarios, the amount of drainage aid added to the tissue-making slurry needs to be adjusted to maintain the freeness of the slurry at levels that meet tissue machine runnability.

Figure 4-1: Scenarios for tissue manufacturing (a) traditional practice (mechanical refining of softwood pulp to a freeness value above 420 mL CSF, no drainage aid added to the tissue-making slurry); (b) first manufacturing pathway for application of fiber reduction technology (intensive mechanical refining of softwood pulp to a freeness level between 50 mL CSF to 390 mL CSF and addition of drainage aid to the tissue-making slurry); and (c) second manufacturing pathway for application of fiber reduction technology (extensive mechanical fibrillation of a portion of the fiber mixture to produce micro- and nanofibrillated cellulose that is then added to the tissue-making slurry in combination with a drainage aid)


(a)
Traditional practice
Softwood
> 700 mL CSF
Refining
30% – 20 wt%
> 390 mL CSF
To headbox
550 mL CSF < Target < 600 mL CSF
Hardwood
> 600 mL CSF
Refining
70% – 80 wt%
Optional
(b)
Fiber reduction technology
(intensive mechanical refining of softwood)
Softwood
> 700 mL CSF
Refining
30% – 20 wt%
< 390 mL CSF
Drainage aid
To headbox
550 mL CSF < Target < 600 mL CSF
Hardwood
> 600 mL CSF
Refining
70% – 80 wt%
Optional
(c)
Fiber reduction technology
(production of micro- and nanofibrillated cellulose)
Softwood
> 700 mL CSF
Refining
30% – 20 wt%
> 500 mL CSF
Drainage aid
Hardwood
> 600 mL CSF
Refining
70% – 80 wt%
To headbox
550 mL CSF < Target < 600 mL CSF
Refining
MNFC
Optional

4.4 Objectives

The objective of this work is to illustrate the use of the fiber reduction technology to decrease the fiber content of tissue paper by at least 10%. This work will show the technical issues related to intensive mechanical fibrillation of the softwood fraction alone, why such a practice is typically avoided in traditional tissue-making, and the role of the drainage aid to ensure a successful implementation of the technology.

4.5 Experimental

4.5.1 Materials

The market pulps used for tissue paper preparation and MNFC production are shown in Table 4-1. Dry sheets were sourced from pulp manufacturers in the United States. Southern bleached hardwood kraft (SBHK) was kindly provided by Domtar Corporation (Marlboro Mill, Bennetsville, SC). The identity of the northern bleached softwood kraft (NBSK) manufacturer was kept confidential. Table 4-1 also summarizes the pulp cost, fiber morphology, fines content, and compositional analysis of all fiber sources. Pulp cost data were collected from Fastmarkets RISI, considering the average values from 2019 and January - March 2020 (the latest months available for 2020). Fiber morphology was determined with a fiber quality analyzer (HiRes FQA, OPTest Equipment Inc., Hawkesbury, ON, Canada), based on the measurement of 5000 fibers with length and width greater than 0.2 mm and 7 µm respectively. Compositional analysis of the market pulps was performed following the NREL procedure for determination of structural carbohydrates and lignin in biomass (Sluiter et al. 2008). A commercial cationic polyacrylamide (CPAM) was selected as a retention/drainage aid and was kindly supplied by Solenis (Wilmington, DE).

Table 4-1: Characteristics of market pulps used for tissue paper preparation and MNFC production

Pulp name	Southern bleached hardwood Kraft	Northern bleached softwood Kraft
Pulp tag	SBHK	NBSK
Cost[1] (USD/tonne)	771	947
Fiber length[2] (mm)	1.101	2.343
Mean width (μm)	17.9	25.7
Fines content[3] (%)	19.84	4.94
Cellulose (%)	76.3	82.6
Total hemicelluloses (%)	19.2	14.2
Total lignin (%)	0.7	0.9

[1]Pulp cost data obtained from Fastmarkets RISI.
[2]Length-weighted mean length.
[3]Length-weighted fines. Fines are defined as particles with length between 0.025 mm and 0.2 mm. Note: the ash content was negligible for all the pulps.

4.5.2 Preparation of tissue-making slurries according to the fiber reduction technology

4.5.2.1 Fiber reduction via intensive mechanical refining of softwood pulp fraction

A blend of 70 wt% SBHK and 30 wt% NBSK was used to prepare tissue-making slurries of different freeness levels. The freeness of the slurry was adjusted by mechanical refining of the softwood fraction using a PFI-mill (N°312, The Norwegian Pulp and Paper Research Institute, Oslo, Norway) according to TAPPI T 248 sp-00 (2000). The hardwood fraction was used as provided by the manufacturer (with no mechanical refining). Tap water was used for dispersion of the fibers.

A control slurry was prepared by refining the NBSK fraction of the wood pulp mixture to a freeness of 406 mL CSF following scenario (a) in Figure 4-1. The fiber fraction was then mixed with the SBHK unrefined fiber fraction and prepared in a slurry form at 0.3 %wt solids content. This control slurry was used to prepare 30 g/m^2 control handsheets.

For the preparation of tissue handsheets with reduced fiber content, the NBSK fraction of the wood pulp mixture was intensively refined to obtain a freeness of 117 mL CSF, following

scenario (b) in Figure 4-1. This intensively refined fiber fraction was then mixed with the SBHK unrefined fiber fraction and prepared in a slurry form at 0.3 wt% solids content. A CPAM dosage equivalent to 0.052 wt% based on OD fiber was added to the slurry. The CPAM amount was adjusted to match the freeness of the control slurry. The slurry containing intensively refined softwood fibers and CPAM was used to prepare tissue handsheets with a lower fiber content compared to the control sheet, i.e., having a basis weight value between 24 g/m^2 and 30 g/m^2. In addition, handsheets were prepared without the addition of CPAM to illustrate the effect of coupling the reduction in the fiber content with a retention/drainage aid.

4.5.2.2 Fiber reduction via incorporation of micro- and nanofibrillated cellulose

A blend of 70 wt% SBHK and 30 wt% NBSK was used to prepare a control tissue-making slurry at 0.3 wt% solids content. The fibers were used as provided by the manufacturers (with no mechanical refining). Tap water was used for dispersion of the fibers. The control slurry was used to prepare 30 g/m^2 control handsheets.

For the preparation of tissue handsheets with reduced fiber content, SBHK fibers were converted into MNFC according to scenario (c) in Figure 4-1. Mechanical fibrillation was carried out in an ultra-fine friction grinder Supermasscolloider (model MKZA6-5, Masuko Sangyo Co., Ltd, Saitama, Japan) with the fibers in a slurry form having a 3 wt% solids content, using a net fibrillation energy input of 6,599 kWh/OD tonne. The MNFC was added to the control slurry at a load of 2 wt% based on OD fiber in combination with a CPAM dosage of 0.057 wt% based on OD fiber. The CPAM amount was adjusted to match the freeness of the control slurry. The slurry containing MNFC and CPAM was used to prepare tissue handsheets with a lower fiber content compared to the control sheet, i.e., having a basis weight between 24 g/m^2 and 30 g/m^2. In

addition, handsheets were prepared without the addition of CPAM to illustrate the effect of coupling the reduction in the fiber content with a retention/drainage aid.

4.5.3 Preparation of handsheets

The procedure for forming handsheets corresponds to a modified version of TAPPI T 205 sp-02 (2006). In the proposed method, wet pressing of the paper web is minimized to preserve bulk, as densification yields poor softness and poor water absorbency of the paper sheet. After formation and couching, handsheets are dried using a cylindrical dryer (Formax 12", Adirondack Machine Co., Gleans Fall, NY) instead of pressed and ring-dried. The operating conditions for the cylindrical dryer were set at 110°C, 1 rpm, and 5 min residence time. Handsheets obtained from this method were not creped.

4.5.4 Handsheet testing

Handsheets were conditioned for 24 h under a standard atmosphere set at 50% relative humidity and 23°C before testing (ISO 187 1990). Basis weight was determined according to ISO 12625-6 (2005). Thickness and bulk (inverse of apparent bulk density) were determined according to ISO 12625-3 (2005). Thickness was measured by applying a static load of 2 kPa on the handsheet sample (digital micrometer, model 49-56, Buchel B.V., Veenendaal, Holland). Tensile strength was determined according to ISO 12625-4 (2005) using a Instron® (model 4443, Canton, MA). Water absorbency was determined according to ISO 12625-8 (2016).

Softness was assessed with a Tissue Softness Analyzer (Emtec Electronic GmbH, Leipzig, Germany). The assessment is based on the analysis of the sound spectrum generated by the combined vibration of a tissue sample and six lamellas that rotate horizontally on the tissue surface causing friction. The vibration is related to both the surface and internal structure of the

tissue paper. The frequency peak centered around 6500 Hz, identified as TS7 (TSA softness) provides an indication of the tissue softness. Lower intensity of vibrations will generate a lower TS7 peak height, which is associated with a softer product (Wang et al. 2019b).

The values reported for basis weight and bulk were obtained from an average of 20 measurements performed on different handsheet samples. For all other properties, the results reported are the average of a minimum of seven measurements.

4.6 Results and discussion

4.6.1 Tensile strength and reduction in fiber content

The fiber reduction needs to be accomplished without causing negative effects on the strength properties of the sheet. Therefore, the minimum acceptable tensile strength value of the sheet with reduced fiber content should be that of the control sheet.

Figure 4-2a presents the advantages derived from the reduction in the fiber content of tissue sheets using the manufacturing pathway schematically shown in Figure 4-1b. When no CPAM is added to the slurry, intensive mechanical refining of the NBSK fraction to a freeness level of 117 mL CSF increased tensile strength by 15.4% at its maximum value with respect to the control sheet. The freeness of the NBSK fraction is considered low compared with more typical freeness values of above 500 mL CSF used in tissue-making operations (Watson and Janssen 2014). This gain in tensile strength allowed for a fiber reduction in the tissue sheet by as much as 10.8%. Such a reduction in fiber content did not compromise the strength properties of the sheet, which remained either superior or at the same value than in the control sheet.

Although positive results were obtained in terms of reducing the basis weight of the sheet, the freeness value of the slurry decreased by 97 mL CSF units below that of the freeness value of the control slurry. This lower freeness of the slurry could be disadvantageous for

allowing tissue machine performance at high speeds. The addition of CPAM to the slurry, however, helped address the issues related to the low freeness. Thus, the gain in tensile strength allowed reducing the fiber content by as much as 12.1%, while the freeness value was maintained at those of the control slurry. Strength requirements were also met.

Figure 4-2b presents the advantages derived from the reduction in the fiber content of tissue sheets using the manufacturing pathway schematically shown in Figure 4-1c. When no CPAM was added to the slurry, the addition of 2% MNFC increased the tensile strength by 25% at its maximum value with respect to the control sheet. This gain in tensile strength allowed a fiber reduction in the tissue sheet of up to 14.8%. Such a reduction in the fiber content was achieved without compromising strength properties of the sheet, which remained at least at the same value than in the control sheet. For instance, a sheet with 14.8% less fiber content had a similar tensile strength than the control sheet. However, the freeness value of the slurry containing 2% MNFC decreased by about 87 mL CSF units below that of the freeness value of the control slurry. When CPAM was added to the slurry, the freeness value increased to a level approximately the same as found in the control slurry (Δ = 27 mL CSF units). Advantageous results were obtained in terms of ability to reduce the fiber content. Handsheets made from this slurry had about 14.1% less fiber content with respect to the control at a similar strength value. CPAM dosage can be adjusted to match the exact freeness of the control slurry.

It should be noted that the results previously presented cannot be used to compare the relative efficiency of each manufacturing pathway because the conditions followed to prepare the control tissue-making slurry were different. Thus, the control sheets had a different set of physical properties to be matched.

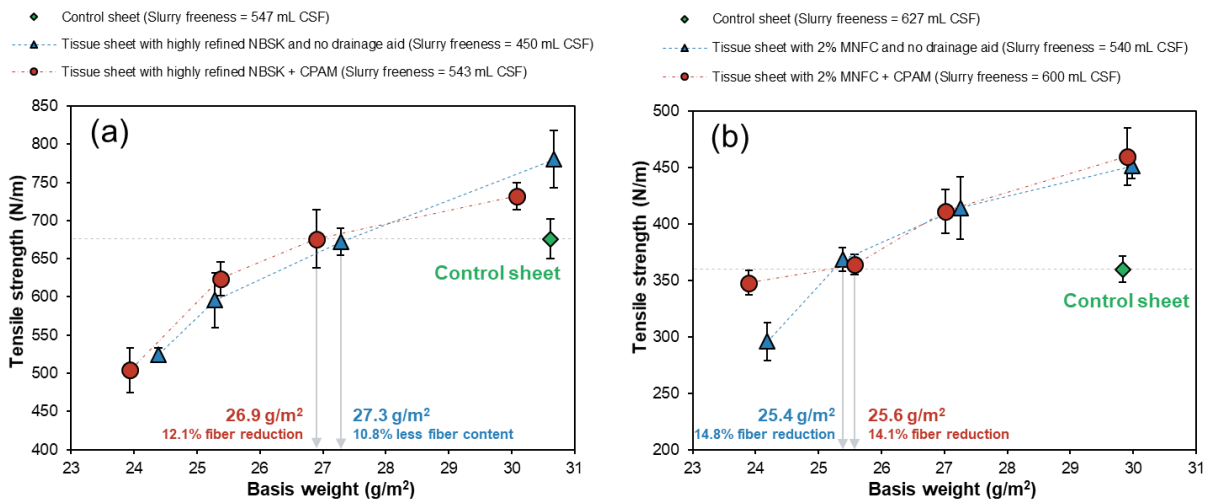


Figure 4-2: Effect of the reduction in the fiber content on tensile strength of tissue paper prepared by (a) intensive mechanical refining of softwood pulp fraction and (b) incorporation of micro- and nanofibrillated cellulose. Error bars indicate standard deviation. The dash-dotted lines indicate the tensile strength of the control sheets.

4.6.2 Tissue bulk

A reduction in the fiber content of the tissue paper should preferably not result in adverse effects on tissue bulk. Figure 4-3 shows the effect on tissue bulk resulting from the manufacturing pathways depicted in Figure 4-1b and 2c. Before the addition of CPAM, the intensive mechanical refining of the softwood portion of the fiber mixture as described in Figure 4-1b reduced bulk of the tissue sheet to values below that of the control sheet (Figure 4-3a). This negative effect was partially counteracted by the reduction in fiber content, which generated an increase in bulk. At the basis weight where the desired tensile strength of the control sheet is achieved, the bulk of the sheet with reduced fiber content was 0.7% below that of the control. The subsequent addition of CPAM to the refined fiber slurry, however, dampened the reduction in bulk observed in first place. A tissue sheet with slightly greater bulk than the control sheet (+3.2%) was obtained at the basis weight where the tensile strength of the control sheet was achieved (but with 12.1% less fiber content).

Similarly, the addition of MNFC to the fiber slurry as described in Figure 4-1c produced a tissue sheet with bulk values that were about 5.9% below that of the control sheet. When the MNFC was combined with CPAM in the slurry, the tissue bulk was maintained at values that were slightly above that of the control sheet within the range of basis weights evaluated (Figure 4-3b). In particular, at the basis weight where the tensile strength of the control sheet was achieved, the bulk of the sheet having a fiber content of about 14.1% less than the control sheet was within 1% of that of the control sheet.

Although the tissue sheets with reduced fiber content were equal to or bulkier than the control sheet, there was always a reduction in the sheet caliper when compared to the control (see Figure 4-4). In all instances, such a reduction in caliper was a consequence inherent to the removal of fibers from the sheet and increased with a higher reduction in the fiber content. The resulting thinner tissue sheets can be advantageous for the manufacture of more compacted tissue rolls with a greater number of sheets per roll while having a performance similar to that of rolls produced from thicker sheets.

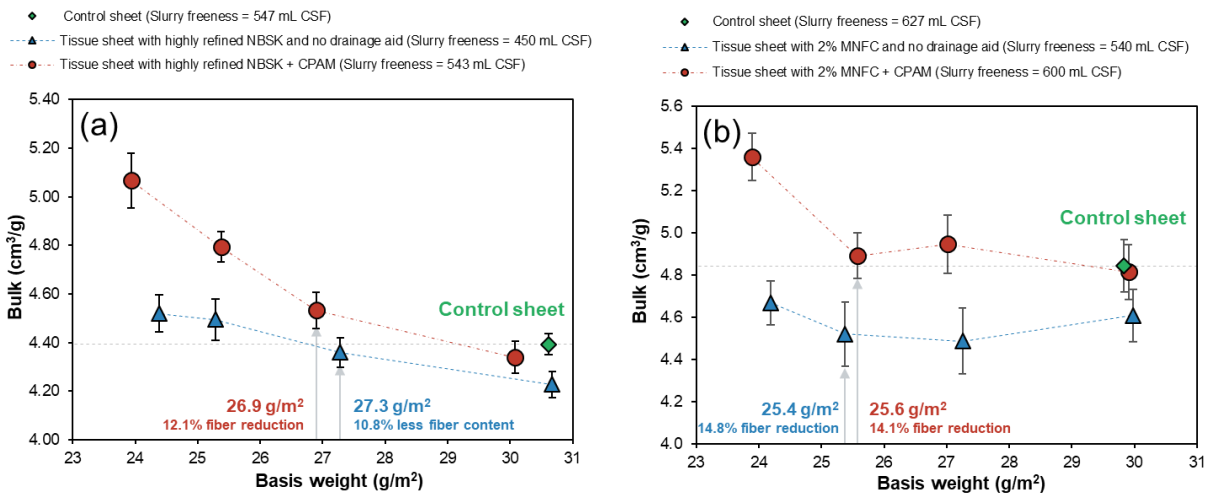


Figure 4-3: Effect of the reduction in the fiber content on bulk of tissue paper prepared by (a) intensive mechanical refining of softwood pulp fraction and (b) incorporation of micro- and nanofibrillated cellulose. Error bars indicate standard deviation. The dash-dotted lines indicate the bulk of the control sheets.

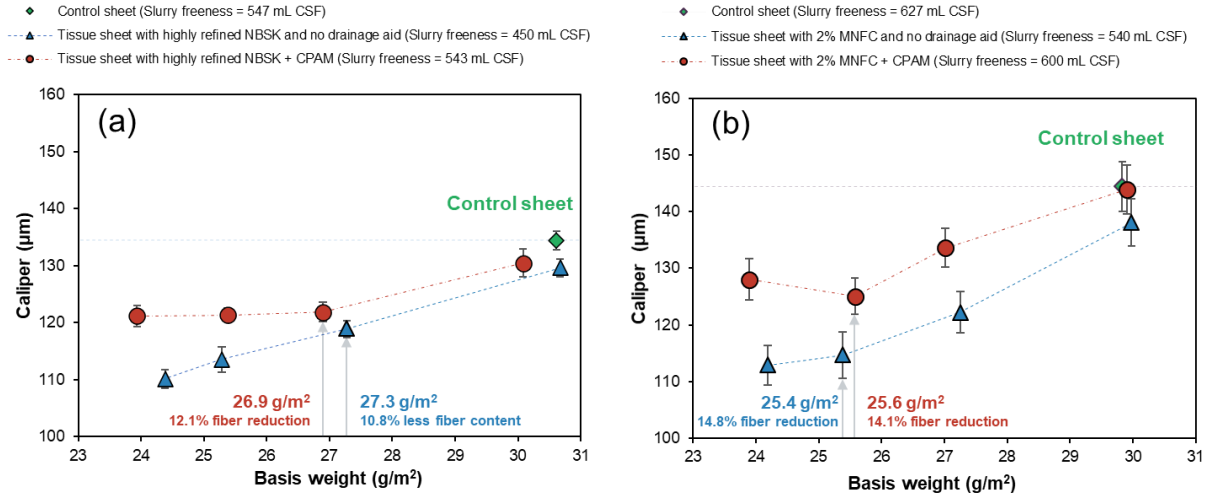


Figure 4-4: Effect of the reduction in the fiber content on caliper of tissue paper prepared by (a) intensive mechanical refining of softwood pulp fraction and (b) incorporation of micro- and nanofibrillated cellulose. Error bars indicate standard deviation. The dash-dotted lines indicate the caliper of the control sheets.

4.6.3 Tissue softness

The reduction in the fiber content needs to be achieved without adversely affecting other desired properties of the sheet, especially tissue softness. In that regard, Figure 4-5 shows the effect on tissue softness resulting from the manufacturing pathways depicted in Figure 4-1b and 2c. The increase in tensile strength obtained from either the intensive mechanical refining of the softwood portion of the fiber mixture or the addition of MNFC yielded a tissue sheet with poor softness (the TS7 values were on average higher compared to the control sheets). A trade-off between softness and tensile strength had been previously reported when MNFC was used as a strength additive in tissue papers (Zambrano et al. 2021).

The reduction in softness was partially counteracted with the reduction in the fiber content of the sheet that in general diminished the T7 values. However, such an effect was not sufficient to attain the softness of the control sheet, specifically at the basis weight where the tensile strength of the control sheet is achieved. The addition of CPAM coupled with the fiber reduction helped further improve softness of the tissue paper. With this combination, reduced fiber content tissue sheets with a softness that was similar to that of the control sheet were obtained. For instance, after CPAM was added to the slurry generated by the manufacturing pathway shown in Figure 4-1b, the softness losses were mitigated with the resulting tissue paper showing improved softness. At the basis weight where the tensile strength value of the control sheet was achieved, the TS7 of the tissue sheet with a reduction in fiber content of 12.1% was 8.2% lower compared to the control sheet (Figure 4-5a). Similarly, after CPAM was added to the slurry generated by the manufacturing pathway shown in Figure 4-1c, a reduction of 14.1% in the fiber content was obtained at a basis weight where the tensile strength of the control sheet was achieved, while the TS7 value was within 2.3% of that of the control sheet (Figure 4-5b).

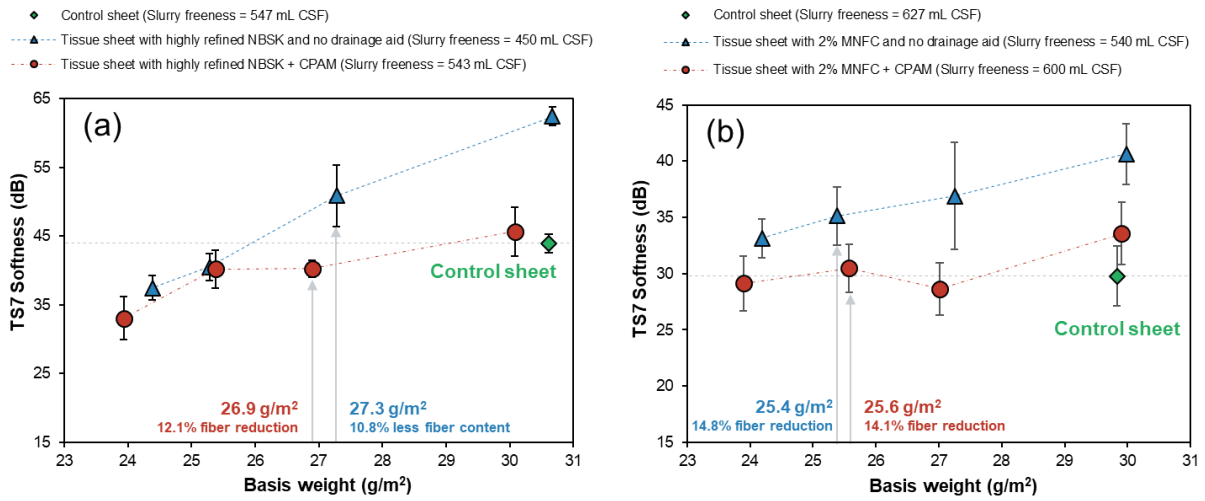


Figure 4-5: Effect of the reduction in the fiber content on softness of tissue paper prepared by (a) intensive mechanical refining of softwood pulp fraction and (b) incorporation of micro- and nanofibrillated cellulose. Error bars indicate standard deviation. The dash-dotted lines indicate the TS7 softness of the control sheets.

4.6.4 Water absorbency

Figure 4-6 shows the effect on water absorbency resulting from the manufacturing pathways depicted in Figure 4-1b and 2 c. The increase in tensile strength induced from the application of both strategies contributed to a densification of the fibrous assembly, and therefore to a reduction in the pore volume necessary for retaining liquids. The reduction in the fiber content further decreased the water absorbency of the tissue sheets in relation to the control sheet. Under saturation conditions, the water absorbed by a tissue sheet is located within the fiber lumen, the fiber cell wall, and in pores between fibers (Zambrano et al. 2020a). Therefore, the results suggest that in spite of the higher pore volume inherent to the bulkier structure driven by the fiber reduction (Figure 4-3), the fiber removal is the primary factor hindering absorbency. As such, the fewer number of fibers available to absorb and retain the liquid within the structure lead to the overall reduction in water absorbency observed.

The addition of CPAM showed opposite effects in relation to its impact on water absorbency (Figure 4-6). When introduced in the sheet containing highly refined softwood fibers, the CPAM slightly increased the absorbency (Figure 4-6a). Contrarily, it caused a reduction in absorbency when present in the sheet containing MNFC (Figure 4-6b). The increase in bulk induced by the CPAM increases the overall porosity of the fibrous assembly and thus the inter-fiber spaces available for holding water inside the structure. Therefore, an increase in absorbency such as the one shown in Figure 4-6a is the trend theoretically expected. The cause behind the reduction in absorbency shown in Figure 4-6b is unclear, and is a subject requiring further elucidation.

Independently of the previous effect, the water absorbency remained at values below than the absorbency of the control sheet within the range of basis weights evaluated. Particularly, at the basis weight where the tensile strength of the control sheet is attained considering the scenario shown in Figure 4-1b for reducing fiber, the water absorbency of the sheet having a reduced fiber content decreased by 9.1% compared to the control sheet (Figure 4-6a). When the scenario depicted in Figure 4-1c was applied for reducing fiber, the water absorbency of the tissue sheet with reduced fiber content decreased by 19% compared to the control sheet, at the basis weight where the target tensile strength was attained (Figure 4-6b).

The negative impact on water absorbency derived from the reduction in the fiber content suggests that the application of the fiber reduction technology may be more suitable in bath tissue grades rather than paper towels, considering that absorbency is a less critical parameter to the overall performance of the bath tissue product.

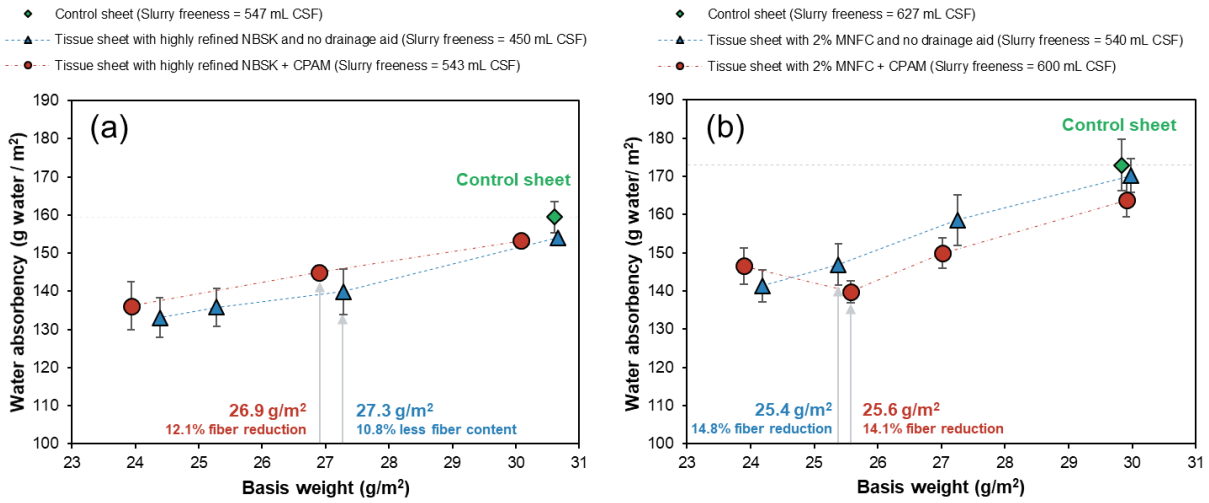


Figure 4-6: Effect of the reduction in the fiber content on water absorbency of tissue paper prepared by (a) intensive mechanical refining of softwood pulp fraction and (b) incorporation of micro- and nanofibrillated cellulose. Error bars indicate standard deviation. The dash-dotted lines indicate the water absorbency of the control sheets.

4.7 Conclusions

This study explored the application of the fiber reduction technology as a cost saving strategy for the hygiene tissue industry. Two methods for reducing the fiber content of tissue papers were demonstrated: (1) intensive mechanical refining of the softwood fraction in the tissue-making slurry to a freeness level between 50 mL CSF and 390 mL CSF; and (2) production and incorporation of micro- and nanofibrillated cellulose into the tissue-making slurry. Both scenarios considered the addition of a drainage aid to the pulp slurry before tissue-making. The methods proposed allowed for a reduction in fiber content greater than 10%. The tissue sheet with reduced fiber content showed similar performance than a control sheet in terms of strength and softness at a reduced caliper. The addition of CPAM as a drainage/retention aid allowed maintaining the freeness of the slurry containing highly refined fibers at a comparable value to the control slurry. The implementation of the fiber reduction technology at a full-industrial scale has the potential to provide important cost advantages to manufacturers through

the reduction of manufacturing costs. The reduction in raw materials and derived reduction in the carbon footprint of the final tissue paper can be also used to the advantage of producers committed to the search of more sustainable processes and products.

4.8 Acknowledgments

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5 FUNDAMENTAL FACTORS AFFECTING ABSORBENCY OF TISSUE PAPERS AND METHODS TO IMPROVE ABSORBENCY[4]

5.1 Abstract

Absorbency is a key performance indicator of paper towels and an important price driver on the shelf. This chapter reviews the fundamental factors affecting the absorbency of tissue papers (e.g., fiber selection, machine technology, wet-end, and creping chemistry) and methods to improve absorbency. A discussion on the practical aspects related to the measurement of the absorbent properties (e.g., absorbency rate and absorption capacity) of tissue and towel is also presented. This chapter also explores aspects related to the end of life of tissue products.

[4] The material in this chapter has been published as:

Zambrano, F., de Assis, T., Zwilling, J., Venditti, R., and Gonzalez, R. (2020). "Absorbency: Even more attractive toward aqueous liquids." Make Paper Products Stand Out - Strategic Use of Wet End Chemical Additives, M. Hubbe and S. Rosencrance, eds., TAPPI Press, 77–109.

5.2 Introduction: Absorbency, the key feature in tissue products

The need for picking up liquids and disposing of them represents one of the most typical situations that consumers encounter while performing household and work duties. Due to their low price and accessibility, tissue products are suitable paper grades to meet the consumer demand for absorbent products (Beuther et al. 2010). Tissue paper is a lightweight paper widely used for hygiene purposes in personal care and professional applications (Boudreau and Barbier 2014). The primary function of tissue paper is to wipe liquids and solids off of a solid surface (Beuther et al. 2010). Ordinary paper materials have an ability to absorb water; the focus of this chapter is on how to increase such absorbency by considering aspects related to fiber selection, machine technology, and chemical additives.

Unlike other paper grades that are heavily pressed before they are dried, manufacturing operations of tissue paper minimize pressing of the wet sheet to render low-density sheets that retain more bulk and surface area per unit volume (typically greater than 0.6 m^2/cm^3) to hold liquids (de Assis et al. 2018b). The term "bulk" denotes the reciprocal of the apparent density of the paper product. The arrangement of hydrophilic fibers in a porous structure gives tissue products the ability to absorb and hold without dripping between five and ten times their weight in liquid (Beuther et al. 2010).

The ability to absorb liquid is a common requirement in creped paper products, such as towels, toilet tissue, and facial tissue, as well as paper diapers (Gigac and Fišerová 2008). Yet the relevance of the absorbency as an indicator of product quality and performance depends to a greater or lesser degree on the specific paper grade. For instance, the order of preferred attributes for consumers to evaluate a premium bath tissue has softness as most important, followed by absorbency, and then strength. Conversely, in the case of premium quality paper towels, the

ranking of features is reorganized to have absorbency in the first position, followed by strength and softness (Poffenberger et al. 2000). It follows that products with superior water absorption capacity can easily stand out from their market competitors, and thus high levels of water absorbency and wet strength are attributes that can drive high shelf prices. Although softness is not an essential property for paper towels, it can also be used by manufacturers as a differentiating attribute to attract more customers (de Assis et al. 2018a).

Absorbency represents a critical property that tissue producers work hard to improve, as often the quality of tissue products is judged on the basis of their ability to wipe up a spill. The global tissue market is a highly competitive sector in the paper industry, and producers tend to keep hermetically the details about manufacturing best practices (Liu and Hsieh 2000). Although it is rare to find public information regarding ongoing research and current manufacturing reality, this has not prevented the global production of tissue from growing at an annual growth rate of 2.6% estimated over the past ten years (de Assis et al. 2018a; Euromonitor International 2017).

The factors that contribute to high water absorbency of tissue products are primarily related to fiber selection, machine technology, and chemistry present in the dry end and wet end of the tissue machine. Improving water absorbency properties requires achieving a fine balance between these parameters. This chapter will describe the factors that affect water absorbency of tissue products along with the phenomena behind the uptake of fluids, as well as issues related to end of life of absorbent tissue products.

5.3 Factor affecting absorbency of tissue products

Bulkiness, softness, and absorbency are the features that will immediately pop into the mind of consumers shopping for hygiene tissue products. Products with the ultimate goal of absorbing liquids are tailored to maximize their absorption capacity. A remarkable example is

the type of chemical pulp known as fluff pulp, which is especially designed for liquid absorption. Fluff pulp has the ability to hold between 10 and 13 times its weight in fluid; thus, it is typically placed in the core of products that require bulk fluid absorption such as diapers and feminine hygiene products (Parham and Hergert 1980).

This section will shed light on the underlying mechanism behind the absorption of fluids in products incorporating cellulosic fibers. This section will also provide an overview of the factors contributing to the absorption phenomenon.

5.3.1 Mechanisms driving the absorption of fluids

There are two phenomena involved in the absorption of fluids by a network of fibers: absorption rate and absorption capacity (Aberson 1969; Parham and Hergert 1980). The absorption rate relates to the velocity of fluid uptake. The absorption capacity accounts for the total amount of liquid that the product can absorb within its bulk.

The absorption rate is primarily controlled by the effective radius of the pores or capillaries within the structure, as well as the contact angle between the surface of the fibers and the absorbing liquid. A sheet or pad of cellulosic fibers consists of a network of interconnected capillaries having different shapes and sizes depending on the bulkiness of the sheet and the dimensions of the fibers. The balance between capillary and viscous forces will also affect the rate of entry of a liquid into such a network (Aberson 1969). The Lucas-Washburn equation, which is shown next, provides a pedagogical approach to understand the factors affecting the absorption rate of loose fiber networks (Eq. 6-1). The equation has been found to be useful for a wide range of porous materials, even though it was originally developed to determine the rate of fully developed laminar liquid flow in vertical cylindrical capillaries (Aberson 1969).

$$\frac{\mathrm{d}h}{\mathrm{d}t} = \frac{r\gamma\cos\theta}{4\eta h} - \frac{r^2 dg}{8\eta} \qquad (6-1)$$

In Eq. 6.1, h is the liquid height in the capillary, *t* is time, η is liquid viscosity, θ is the contact angle of the liquid on the capillary wall, γ is the surface tension of the liquid, *d* is the liquid density, *g* is the acceleration due to gravity, and *r* is the radius capillary. According to the direction of the capillary forces (upward or downward), the second term in the Lucas-Washburn equation will change its sign or will become zero for horizontal capillary movement. The latter simplification gives rise to the following integrated form of the Lucas-Washburn equation (Eq. 6-2). This equation allows calculating *h* for a given time *t*:

$$h = \sqrt{\frac{r\gamma\cos\theta}{2\eta}t} \qquad (6-2)$$

The absorbent flow Q up to a time t can be determined by multiplying h in Eq. 6-2 with the cross-sectional area of the capillary πr^2. From this, it is obtained that Eq. 4-3,

$$Q = Kt^{0.5} \qquad (6-3)$$

where K is a constant of the form Eq. 6-4:

$$K = \pi r^2 \sqrt{\frac{r\gamma\cos\theta}{2\eta}} \qquad (6-4)$$

As can be seen from Eq. 6-3, the absorbent flow is predicted to be proportional to the square root of time. Perfect agreement with data for diverse porous materials is not expected, due to the fact that derivation of Eq. 6-4 involved simplifying assumptions. Notably, one assumes a simple, cylindrical capillary with no structural changes during the absorption and also no changes in the contact angle of the fluid as the absorption progresses (Ko et al. 2016). The phenomenon of water absorption in tissue paper results from the combination of the surface tension and the small pores within the structure, and this is the major reason why the Lucas-Washburn equation has been proposed as a model for studying the absorption in tissue and towel. Further discussion about the validity of the model will be provided later in this chapter.

Absorption capacity depends mainly on the total void volume within the structure and the resistance of the network to structural changes upon the action of compression forces. The absorption capacity is a function of morphological aspects inherent to the fibers that integrate the network such as coarseness, stiffness, and length (Parham and Hergert 1980).

5.3.2 Location of the water in an absorbent tissue sheet

Under saturated conditions, the water absorbed by a tissue product is located within the fiber lumen, the fiber cell wall, in the inter-fiber spaces, and between plies in the case of multi-ply tissue products. Within the cell wall, water is located in micro-, meso-, and macropores. For single-ply products, most of the water is stored in the capillaries between fibers. Multi-ply products provide additional inter-ply spaces to hold and retain substantially greater amounts of water (Figure 5-1) (Kullander et al. 2012; Loebker and Sheehan 2011a).

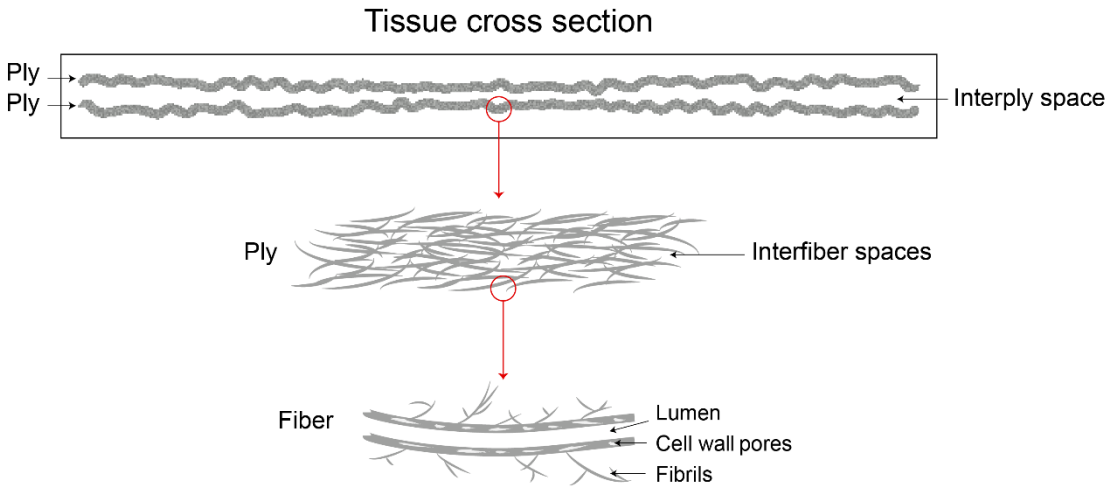

Figure 5-1: Locations of absorbed water in a 2-ply towel

The absorbency capacity gained by adding an extra ply is generally greater than the additional absorbency capacity associated with the individual added ply. Thus, a multiple-ply structure can have an absorbency capacity greater than the sum of the capacities of the individual plies that constitute the total product (Barnholtz 1998; Hermans et al. 2009). In the case of multi-ply products made with plies from different types of paper substrates, the absorption capacity is normally expected to be equal or lower than the arithmetic mean of the absorbency capacities measured for the multi-ply structure formed from each contributing paper substrate (Barnholtz 1998).

The additional space between plies also improves the absorbency rate due to the creation of lamellar flow channels in the large pore structures generated, which reduce the resistance to viscous flow (Hollmark 1984). Two tissue sheets stacked together will absorb water at a rate more than twice compared to a single tissue sheet because of the additional interface (Beuther et al. 2010). Near equilibrium conditions, the absorption rate of 2-ply towels drops to similar values of 1-ply towels (Loebker and Sheehan 2011b).

An important aspect to consider is that the maximum absorbent potential of hygiene tissue products is seldom utilized. The time for absorption is typically limited to a few seconds before disposal. As a result, the in-use capacity turns out to be just a fraction of the theoretical capacity due to the extremely short lifetime of the product upon use (Ko et al. 2016).

Drying and other types of stresses inherent to recycling operations can yield reductions in the amount of water that fibers can hold within their cell walls (Hubbe et al. 2007). The loss of ability of the fibers to swell with water, which is accompanied by a reduction in the flexibility and conformability, has been primarily attributed to the closure of pore spaces in the cell walls, as well as the particular inability of the nanosized pores to reopen upon rewetting of the fibers (Stone and Scallan 1965). Dramatic losses in the water-holding ability are primarily important for well-refined low-yield fibers (De Ruvo and Htun 1983), which are commonly used for manufacturing of recycled tissue and towel. Likewise, fully bleached kraft fibers display much larger losses in water-holding ability after undergoing multiple drying and wetting cycles compared with mechanical fibers (Park et al. 2006). Mechanical fibers are often included in low proportions within tissue and towel furnishes to promote dimensional stability of the products in the wet state.

5.3.3 Structural and chemical properties of absorbent products

After reviewing the mechanisms responsible for the absorption of liquids into a network of fibers, it becomes clear that both structural aspects of the sheet and chemical characteristics of the surface of the fibers will determine the absorbent features of hygiene tissue products and thus their overall performance.

This section elaborates on the features that a product must ideally have to display outstanding absorbent properties. The most important aspects are the bulk of the fiber network

(i.e., the pore size distribution in dry and wet state) and the contact angle between the surface of the fibers and the wetting liquid. The influence of such features on the absorption rate and the absorption capacity will be discussed. Aspects related to how to achieve absorbent structures by controlling different variables of the manufacturing operation will be addressed in a later section.

5.3.3.1 Relationship between bulk and absorbency

As a general rule, tissue products with high bulk are softer and more absorbent (Boudreau et al. 2009). A reasonably good correlation is typically found between the bulk of sheets and the water absorbency ($R^2 = 0.9976$), and absorbency values reach a maximum when pressing of the wet sheet is minimized or avoided. This results from the high porosity that is present within the sheet structure to hold water as the sheet bulks up. A higher porosity is associated with a fiber network with less bonding between fibers (Liu and Hsieh 2000).

The efficiency of the absorption process results from a compromise between the micro-fine pore structure and the large pore structure that coexist in the tissue sheet. The micro-fine pores will induce a large capillary pressure (proportional to 1/radius) that allows absorbing water with a continued force but not quickly, whereas the large pores will absorb water quickly but without a large continued force. Also, the micro-fine pores will be more effective in retaining the absorbed liquid against opposing forces than the large pores; however, the large pores will provide more storage capacity for holding the absorbed water (Beuther et al. 2010; Chatterjee and Nguyen 1985).

An increase in the sheet bulk implies pores becoming wider and thus a consequent increase in the rate of wicking and liquid uptake at first. For absorption taking place upward, a further increase in bulk will make the effect of gravity more pronounced in the wider pores, and thus a slowdown in the absorption rate will occur. On the other hand, a sheet with reduced bulk

will contain a distribution of narrower pores with an absorption rate little affected by gravity when absorbing upward (Aberson 1969).

In summary, changing the bulk of fiber pads prepared with the same fibers will change the pore size distribution and thus, the absorption rate. Also, at an equal pad bulk, sheets made with larger fibers will have fewer fibers per unit weight and therefore, fewer and larger capillaries (Aberson 1969). These effects are quantitatively expressed by the Lucas-Washburn equation (Eq. 6-1).

5.3.3.2 Relationship between air permeability and absorbency

The air permeability has been proposed as an indicator for the absorbency of tissue products. The idea behind this approach is that as the sheet bulk increases, the inter-fiber spaces in the network increase. This structural change causes a decrease in the resistance of air to permeate the sheet, which results in higher air permeability. One should note that air permeability does not provide information about the capillary structure and pore size distribution existing in the interior of the sheet (Liu and Hsieh 2000).

5.3.3.3 Effect of contact angle on capillarity and absorbency rate

The contact angle between the surface of the fibers and the absorbed liquid represents a critical factor in determining the capillary forces of the fiber network and thus its ability to take up fluids. Low contact angles, which imply good wettability of the fiber surfaces by the liquid, are associated with high absorption rates and low leakage rates. The opposite effect is encountered for high contact angles, where low absorption rates are obtained due to poor wettability of the fiber surfaces by the liquid (Parham and Hergert 1980).

Absorbent paper grades are generally manufactured with fully bleached chemical pulps. This type of fibers displays low contact angles with values that may vary over a wide range depending on the raw material and the extent of extractives removal (Parham and Hergert 1980). Higher contact angles are typically found in pulps with undesirable levels of organic extractives. The contact angle can also increase with pulp age, which is primarily caused by migration of extractives from the bulk of the fiber toward the surface during storage. This negative effect can be minimized by controlling the extractives content to levels no greater than 0.1% (Aberson 1969; Parham and Hergert 1980).

An interesting aspect to highlight is that the bulk has a minor effect on the contact angle. This implies that different pore-size distributions in the sheet will have a negligible influence on the determination of the contact angle, and thus the contact angle is an intrinsic feature of the fiber used to manufacture the absorbent product (Aberson 1969).

5.3.4 Tradeoff between properties

Some of the properties of interest in tissue products are in conflict with each other. An increase in tensile strength with other conditions remaining the same will be achieved at the expense of adverse effects on softness and absorbency (Liu and Hsieh 2000). This is because strength requires a tightly bonded fiber network, whereas softness and absorbency involve having a fluffy and loosely bonded structure. Therefore, softness and absorbency must be balanced against strength (Springer and Pires 1988). In practice, tissue producers will try to maximize softness and absorbency by complying with a minimum strength value required to withstand stresses and strains during manufacturing operations and use by end-consumers (de Assis et al. 2018b). In the context of this chapter, Figure 5-2 qualitatively compares the tradeoffs between properties as the water absorbency of the paper products is increased.

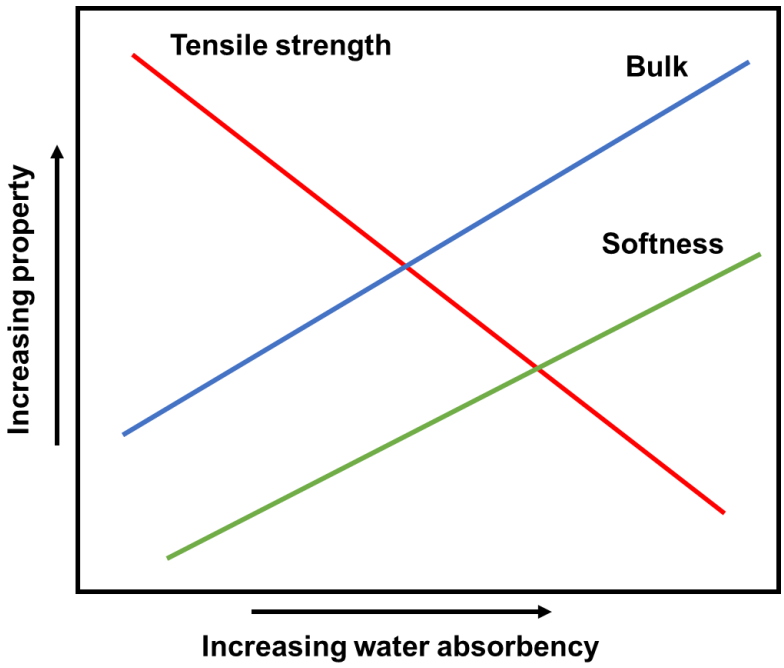

Figure 5-2: Typical tradeoff between properties as the absorbent features of hygiene tissue products are enhanced

5.4 Ways to achieve bulky, porous paper

Absorbency properties of tissue papers mostly depend on the fiber selection, the machine technology, and chemical additives (either dry-end chemistry or wet-end chemistry). The following section will address the issue of how to manipulate these variables to produce tissue products with superior absorbent performance.

5.4.1 Effect of fiber selection

Fiber morphology has a significant impact on bulk and absorbency. Long fibers having high coarseness (softwoods) create fiber webs with larger pores and higher void volume for superior water uptake. On the other hand, short and fine fibers (hardwoods) yield fiber webs with fine pores and lower bulk. One can make an analogy by filling a bucket with sand or stones

(Parham and Hergert 1980). Bigger fibers are also expected to provide more rigidity and stability to the fiber web (Aberson 1969). Fiber mixtures having low content of fines are desirable to make low-density fiber webs. Fines tend to fill the spaces between fibers, causing a reduction in void volume (Axelsson 2001). Depending on the source, fines can have a hydrophobic characteristic that may cause a sizing effect, which will further impede absorbency rate and capacity (Springer and Pires 1988). Fibers having higher degree of curl (gradual fiber curvature), kinks (abrupt change in fiber curvature), and twisting are able to form bulkier and more absorbent fiber webs (Hu and Ko 2006; Trepanier 2017).

The chemical composition of cellulosic fibers is also an important factor for water absorbency. Hemicelluloses are responsible for the high tendency of cellulosic fibers to swell upon contact with water due to their noncrystalline nature and the presence of carboxyl groups (either in the acidic or the carboxylate form depending on the pH) in their structure (Laine et al. 1994). The hemicellulose content in papermaking fibers tends to decrease with increasing recycling cycles (Hubbe et al. 2007; Wistara et al. 1999). It has been reported that the hemicellulose removal has detrimental effects on the wettability of cellulosic materials (Hosseinaei et al. 2011); thus a similar effect is also expected in the case of recycled fibers.

In addition, the presence of lignin will also decrease the wettability of cellulosic fibers, because in its native state this component is much more hydrophobic compared with cellulose and hemicellulose (Hubbe et al. 2015). However, lignin-containing fibers are stiffer and less conformable than fibers from which the lignin has been largely removed. These features give lignin-containing fibers the potential to yield fiber networks with wider pores and increased mechanical stability in the wet state. This tendency could mitigate the negative effect on water absorbency caused by the hydrophobic characteristics of lignin.

Finally, extractives are also detrimental for water absorbency. As noted earlier, a self-sizing mechanism (migration of extractives to fiber surface) can occur during the storage of cellulosic fibers containing extractives. Ultimately, the net effect on the water absorbency of the final product will result from a balance between the hydrophobicity of the fibers and the structural features of the tissue sheet (de Assis et al. 2018b).

Pulping and bleaching processes remove lignin and extractives during the manufacturing of chemical pulps. Consequently, chemical pulps tend to be hydrophilic, having high content of carbohydrates and high porosity. As a result, chemical pulps can swell and promote fast water absorbency. However, chemical pulps are flexible, having a tendency to form dense and strong fiber webs when mechanically refined (de Assis et al. 2018b).

Mechanical pulps can be used in combination with chemical pulps to increase sheet porosity and water absorbency. Mechanical pulps have a higher content of lignin and higher rigidity in the wet state when compared to chemical pulps. The lumen structure of mechanical pulps is more resistant to papermaking operations, thus resulting in formation of bulky fiber webs. However, the high content of fines and lower cell wall porosity, along with the hydrophobic characteristic presented by mechanical pulps (high content of lignin and extractives) can negatively affect absorbency (de Assis et al. 2018b).

Recycled kraft fibers have undergone hornification (loss of ability to swell in water) and present low swellability and wet flexibility. This makes them more stable and stiffer than virgin fibers. Recycled fiber can form fiber webs with good bulk and absorbency. However, the high content of short fibers and fines (organic and inorganic particles) are detrimental to providing superior water absorbency (de Assis et al. 2018b).

Fibers that are resilient to pressure can yield superior bulk in a wet state. Fluff pulps have long, coarse, and stiff fibers that are capable of forming large and stable void volumes (Parham and Hergert 1980). Alkali-extracted fluff pulps have low content of hemicellulose and undergo extensive hornification during the drying process. When rewetted, these hornified fibers will present low swellability and low wet flexibility, which contributes to superior bulk stability and resistance to pressure in the wet state (Lund et al. 2012)

5.4.2 Dimensional stability of absorbent fiber networks

Upon contact with a fluid, the fiber network will experience dimensional changes that will consequently impact the absorbent features of the product. Although a large pore structure provides more storage capacity for fluids, it is also more likely to collapse in the wet state, which decreases the ability to hold the absorbed fluid. It follows that the absorption capacity will start dropping past a certain critical porosity value. For this reason, rigid bleached chemithermomechanical pulp (BCTMP) fibers are used in the production of paper towels as a means to confer higher dimensional stability to the sheet structure upon contact with fluids (Liu and Hsieh 2000).

Absorbent materials undergo compression forces in their environment of usage, which will also directly influence the extent of the dimensional changes. This is especially relevant for fluff pulps found in the core of personal hygienic products, which are continuously exposed to cyclical loads. A fiber network where fiber bonding is well developed will require higher compression forces to disrupt the fiber structure (i.e., it will have a higher resistance to squeezing). The latter implies that the structure will be more prone to maintain its porosity under pressure in a wet state. This also explains why the wet bulk under pressure is a critical parameter for applications involving the use of fluff pulps (Lund et al. 2012). It is important to note that

improving fiber bonding typically causes densification of the structure, which can yield undesired losses in absorption capacity. Table 5-1 provides an example of the effect of applying a compression force on the water-holding capacity of untreated and debonded chemical fluff pulps.

Table 5-1: Effect of compression force on the absorption capacity of fluff pulp pads (adapted from Parham and Hergert 1980)

Pulp Type	**Pulping Process**	**Water-Holding Capacity (g/g)**		**Density (g/cm^3)**
		No Load	**Loaded**	
Hemlock	Sulfite	12.2	5.8	0.071
Debonded hemlock	Sulfite	12.4	5.8	0.072
Southern pine	Kraft	13.1	5.9	0.062
Debonded southern pine	Kraft	13.1	5.7	0.061

The magnitude of the compression force during wet-pressing will also affect the extent to which the water-holding capacity is affected. Higher compression forces will cause a more significant degree of collapse. This has adverse effects on the absorption rate, because small pores in the denser structure will induce a larger viscous drag in the absorbent flow penetrating the structure. Application of zero pressing load will also yield poor absorbency features (Aberson 1969). The maximum absorption rate is obtained when a small load is applied on the structure, which relates to the balance between the micro-fine pore structure and the large pore structure discussed in a previous section.

5.4.3 Effect of machine technology

Tissue products manufactured with different technologies will present distinct behaviors in terms of bulk and water absorbency. While mechanical refining increases fiber web strength, it also promotes sheet densification and reduction of absorbency. Significant reductions in bulk are

expected even at low refining levels (Gigac and Fišerová 2008). Low levels of refining will minimize the production of secondary fines and prevent the formation of denser fiber webs (Axelsson 2001).

The creping process is an important operation for the development of softness and absorbency of tissue paper products. During the creping process, a doctor blade continuously scrapes the fiber web from the Yankee dryer surface (Pan et al. 2018). In this process, a creping chemistry (combination of adhesives and release agents) is typically sprayed on the Yankee surface to promote and control the adhesion between the Yankee surface and the paper web, and also to protect the Yankee surface. In the dry creping process, the fiber web is dried to consistencies around 94%–98% by the steam-heated Yankee surface and hot air flow from the surrounding Yankee hood. After drying, the compressive forces at the doctor blade acting on the paper sheet reduces fiber bonding, promotes delamination of the fiber web, and creates periodic micro- and macrofolds on the fiber web structure (de Assis et al. 2018b).

The creping process increases bulk, absorbency, softness, and stretchability at the expense of lower strength. The development of superior bulk and absorbency is achieved under the explosive creping regime, during which individual fibers tend to significantly separate from each other inside the fiber web. Explosive bulk is favored by high interfacial adhesion, low web cohesion (low fiber bonding), high creping speed, and low creping angle. Higher bulk is also achieved at high creping ratio, meaning that the creped product is much shorter than it was prior to creping (Pan et al. 2018, 2019); however, high creping ratio also yields poorer surface softness due to an increase in creasing and amplitude of the folds in the sheet.

The most common machine technology used for tissue manufacturing is the Light Dry Crepe (LDC). In an LDC tissue machine, the wet web is typically pressed from 15%–25%

consistency to 40%–45% consistency before being transferred to the Yankee dryer. The wet pressing promotes densification of the fiber web and consequent reduction of water absorbency. Therefore, minimum pressing should be applied to maximize bulk and softness and yet achieve the desired strength. Because of its longer nip, a shoe press applies lower pressure than a roll press, which contributes to preserving sheet bulk (de Assis et al. 2018b).

Through-Air Drying (TAD) machines can be used to produce tissue products with superior performance. TAD machines do not have a press section, which results in a final product with higher softness, bulk, and absorbency. Instead of using dryer cans, a perforated TAD cylinder blows hot air to dry the wet fiber web. In the Creped Through-Air Drying (CTAD) machine, the through-air drier dries the wet web until 40%–80% consistency. The final drying and creping are executed in a Yankee dryer. During the TAD process, a TAD fabric is typically used to imprint a knuckle pattern on a fiber web composed of compressed and uncompressed areas. The knuckles are compressed areas that contact the Yankee surface, whereas the pillows are uncompressed areas. The final product has good strength but superior softness and absorbency when compared with LDC products. More recently, structured fabrics have been developed to create continuous lines of high compression to provide superior strength while forming uncompressed pillows for superior bulk and absorbency (de Assis et al. 2018b).

Converting operations also have an impact on tissue bulk and absorbency. Calendering is used to improve surface softness; however, it may negatively impact the caliper, bulk, and absorbency (Gigac and Fišerová 2008). Embossing (engraving of tissue paper by steel or rubber rolls to provide texture) can be used to form tissue paper with multiple plies for superior absorbency. The foot-to-foot embossing configuration is known to create suction pockets

between plies for superior absorbency because the embossing patterns in each ply are aligned to each other (de Assis et al. 2018b).

5.4.4 Effect of wet-end and creping chemistry

Retention aids can be used to enhance bulk. Retention aids induce flocculation of fines and fibers, which forms a fiber web with higher porosity (Springer and Pires 1988). Though typical acrylamide-based retention aids have a hydrophilic character (Hagiopol and Johnston 2011), the typical levels of addition of retention aids are not high enough for there to be an expected chemical effect on wettability.

Higher bulk can also be achieved with debonding agents (Hagiopol and Johnston 2011). Debonding agents are typically applied in tissue paper manufacturing to improve softness by reducing inter-fiber bonding. The reduction of fiber bonding also increases the average distance between adjacent fibers, resulting in higher fiber web porosity. Traditional debonding agents are cationic polymers consisting of quaternary ammonium groups linked to large aliphatic chains that promote the disruption of hydrogen bonding between fibers and consequent improvement in softness and bulk (Conte and Bender 1992; Poffenberger 1996).

The extent of debonding has been shown to depend on such factors as the number of alkyl chains and their content of carbon-carbon double bonds (Conte and Bender 1992). However, the aliphatic chains have a hydrophobic behavior that causes a net reduction in water absorbency (Poffenberger et al. 2000). Other types of debonding agents, such as quaternary ammonium groups linked to a long-chain ester or amide radical of etherified hydroxycarboxylic acids, were reported not to impact absorbency while providing superior softness. Debonding agents consisting of quaternary ammonium groups linked to vegetable oil have been reported to provide good water absorbency (Liu and Hsieh 2000).

The creping chemistry applied to the surface of the Yankee cylinder can also have a critical effect on the bulk of the creped tissue sheet. The final characteristics of the creped product depend on the uniformity of the adhesion between the sheet and the Yankee surface. The complex balance among the interfacial adhesion, fiber web cohesion, and the process inertia is important. Strong adhesion ensures uniform rupture of fiber-to-fiber bonds in the sheet structure when the doctor blade contacts the fiber web. This optimal creping action creates bulk in the sheet and generates a more porous structure to render improved absorbency properties (Boudreau and Barbier 2014). Better bond quality also produces softer tissue (Stitt 2002). Caution is required, as excessive adhesion can lead to web breaks. Excessive adhesion of the fiber web to the Yankee surface may cause the doctor blade to be unable to scrape off the sheet neatly or even slip under the doctor blade. On the other hand, poor or weak adhesion to the Yankee surface may cause localized or complete detachment of the sheet from the metal surface before contacting the doctor blade, which may result in very little to no creping action and thus poor absorbing properties (Boudreau and Germgård 2014).

The fine balance between adhesion and release forces during the creping process will depend on the adhesive chemicals and release oils that are used as a coating layer on the Yankee cylinder surface (Boudreau and Germgård 2014). Common creping adhesives consist of modified polyamidoamine with dialdehyde, modified polyaminoamine epichlorohydrin (PAE) resins, polyvinyl alcohol (PVA), aromatic polyamidoamine, polyamine, or copolymer of the styrene-methacrylic acid (TEA salt) (Boudreau et al. 2009; Hagiopol and Johnston 2011; Rezaei-Arjomand et al. 2013). The ideal adhesive consists of a complex blend of hydrophilic and hydrophobic compounds with ionic or nonionic structure dispersed in water that aims to fit different furnishes, moisture profiles on the drying surface, web speeds, concentration of wet-end

chemicals, and so forth (Hagiopol and Johnston 2011). A suitable creping adhesive must be capable of rewetting upon contact with the wet web to create a tacky coating surface that can efficiently adhere the sheet to the Yankee dryer surface (Boudreau and Germgård 2014). The highest uniformity and strength of adhesion is achieved when the sheet is pressed to the cylinder while the coating is as sticky as possible (Boudreau et al. 2009). The presence of components naturally present in the tissue sheet, such as hemicellulose and fines, also contributes to increasing the strength of adhesion (Boudreau and Germgård 2014).

Small molecules (referred to as modifiers) can be added to the adhesive formulations to change the glass transition temperature (T_g) of the coating (such as plasticizers), to control chemical reactions (such as scavengers), or to improve water absorption (such as humectants), because cross-linking reactions of the adhesive compounds on the Yankee dryer surface may generate harder and hydrophobic coating films with poor adhesion ability. Aliphatic polyols or polyalkanolamines perform both as plasticizers and humectants (Hagiopol and Johnston 2011). Water may also act as a plasticizer for polymers blends with high T_g values (Furman and Su 2007).

The common industrial practices consider the use of formulations of adhesive polymers and release oils. Typically, these two classes of components exhibit opposite characteristics. Whereas the adhesive fraction is very polar, water soluble, and cationic, the release fraction is nonpolar, insoluble in water, and neutral. Emulsifiers are often required to disperse the hydrophobic release aid in the aqueous adhesive medium. In case cationic emulsifiers are used, these can simultaneously act as potential softeners to add extra value to the release oil emulsions. Possible oil migration from the coating film to the paper can have detrimental effects on the absorbency; therefore, amphiphilic polymers such as alkyl-polyprolylene glycol have also been

used to overcome this issue (incompatibility between amphiphilic release aid and creping adhesives such as PVA or PAE resin has been reported). Another popular class of release agents consist of cationic compounds with a long hydrocarbon tail. Release aids help by decreasing the adhesion and releasing the sheet from the Yankee surface at the doctor blade. As a result, a more uniform coating layer on the surface of the Yankee cylinder can be maintained for longer operation periods before a replacement of the doctor blade is required. The mechanism through which the release aid alters the dynamic surface tension of the adhesive is still being studied (Hagiopol and Johnston 2011).

5.5 Evaluating the absorbent performance of tissue products

Testing the absorbent properties of tissue products aims to answer two questions: (1) how much fluid the product can absorb and (2) how fast the fluid absorption can occur. These questions are inherently related to the concepts of absorption capacity and absorption rate introduced in previous sections. More interesting is to know that the testing conditions may influence the absorbency results. In this context, where tissue producers require objective indicators of the absorbent performance to rank their products among the competition and to use them as quality control, this section provides a discussion of practical aspects related to the measurement of the absorbent properties of tissue and towel.

5.5.1 Instrumentation

The instruments and experimental setups proposed for evaluating the absorbent performance of tissue and towel are based on two types of wicking: radial wicking and linear wicking. Both wicking test types will be discussed below.

Two devices that find their measuring principles in radial wicking are commercially available. These are the ATS (Absorbency Testing System) by Sherwood Instruments and the GATS (Gravimetric Absorbency Testing System) by M/K Systems. Both instruments are automated systems that determine the absorption rate and capacity of absorbent paper products. The measuring principle slightly varies from one device to the other. The ATS uses volumetric measurements, whereas the GATS uses gravimetric measurements for quantifying the absorption properties (Beuther and Veith 2009).

Procter & Gamble also has a Capacity and Rate Tester (CRT), which relies on gravimetric measurements to run in a similar mode to the Sherwood ATS and the M/K GATS. The CRT is a radial orifice wicking instrument, which aims to improve some of the issues reported for the commercial instrumentation in terms of repeatability and reproducibility (Loebker and Sheehan 2011a).

These absorbency testing devices operate based on an early design developed by S. G. Reid (Figure 5-3). Water is supplied to the tissue sheet through a small capillary that allows the liquid to radially diffuse from the center of the sample towards the edges. The time required to transfer the liquid from a fluid reservoir to the sample is recorded (Reid 1967). The wetting follows a two-dimensional radial wicking with little occurring in the Z-direction. This results from the relatively low thickness of hygiene tissue papers, which causes the flow in the X and Y direction to be the driver for the absorbency, with the flow in the Z-direction being typically neglected (Ko et al. 2016).

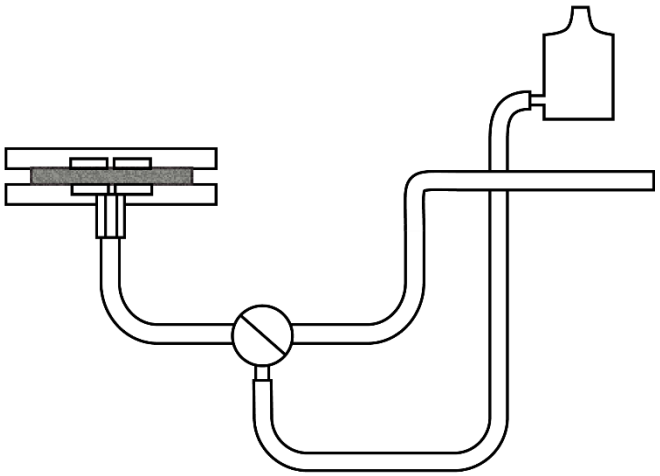

Figure 5-3: Early orifice wicking instrument designed by S.G. Reid for measuring the rate of absorption of water by creped tissue paper (Reid 1967). Modern instrumentation follows the same measuring principle.

In the case of linear wicking, simpler alternatives to carry out absorbency measurements have been proposed. These include, for instance, recording the distance of movement of a waterfront over time when a paper strip is hung vertically over a water trough (Liu and Hsieh 2000). In that configuration, gravity starts playing a more critical role in the absorption phenomenon, as explained by the Lucas-Washburn equation (Eq. 6-1).

More advanced studies have correlated linear wicking measured by X-ray densitometry with radial wicking for absorbent towels. X-ray digital images in combination with image analysis allow studying one-dimensional absorbency flow in the sheet. The greyscale in the images can be converted to an optical density that shows a correlation with the mass of liquid as a function of X, Y, and time (Figure 5-4). Although such measurements provide insightful information about the absorbent phenomenon, they are impractical for day-to-day application (Beuther et al. 2010). This narrows down the practical alternatives to the radial flow absorbency

tests, which are easy to conduct but have shown numerous challenges to providing reliable data, as will be explained later in this section.

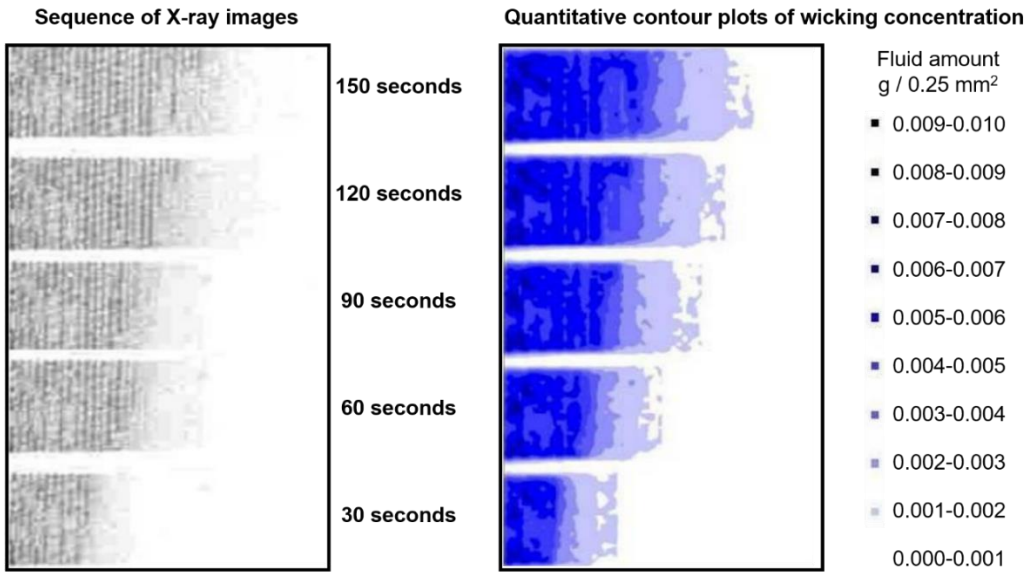

Figure 5-4: X-ray images converted to optical density can be used to study two-dimensional absorbent flow and the mass distribution of liquid in absorbent towels (Beuther et al. 2010)

5.5.2 Measurement of the absorption rate

During absorbency testing, the amount of fluid absorbed by the tissue sample is recorded as a function of time. The fluid uptake, which correlates to the weight gain, is monitored continuously until no further change in the sample weight is observed (i.e., until saturated conditions are achieved). The amount of fluid can be normalized by the sample weight (g/g) or by the sample basis weight ($g/g/m^2$). Normalizing by the basis weight makes the reported values independent of the sample size (Beuther and Veith 2009).

A typical output of an automated absorbency test is shown in Figure 5-5. An additional plot known as the Lucas-Washburn plot can be obtained by plotting the amount of fluid versus the square root of time ($t^{0.5}$). The absorption rate can be calculated from the slope of the curves by applying a linear regression. Products with a higher slope are associated with faster

absorbency rates. Experimental data for commercial tissue products have been shown to correlate fairly well with the Lucas-Washburn theory. Regression analysis between absorbency and $t^{0.5}$ have yielded R^2 values greater than 0.95, which validates the use of the Lucas-Washburn theory as a proxy for estimating the absorption rate of tissue and towel (Ko et al. 2016; Loebker and Sheehan 2011a). Although several authors recommend a $t^{0.5}$ relationship between the mass absorbed and time (Ko et al. 2016; Loebker and Sheehan 2011a; Lundeen 2008), others contend that a linear relationship is more appropriate. As an alternative to this lack of agreement, it has been suggested that using an n^{th}-order polynomial can help to minimize errors, as in reality the relationship between mass absorbed and time follows a complicated logarithmic curve (Beuther et al. 2010).

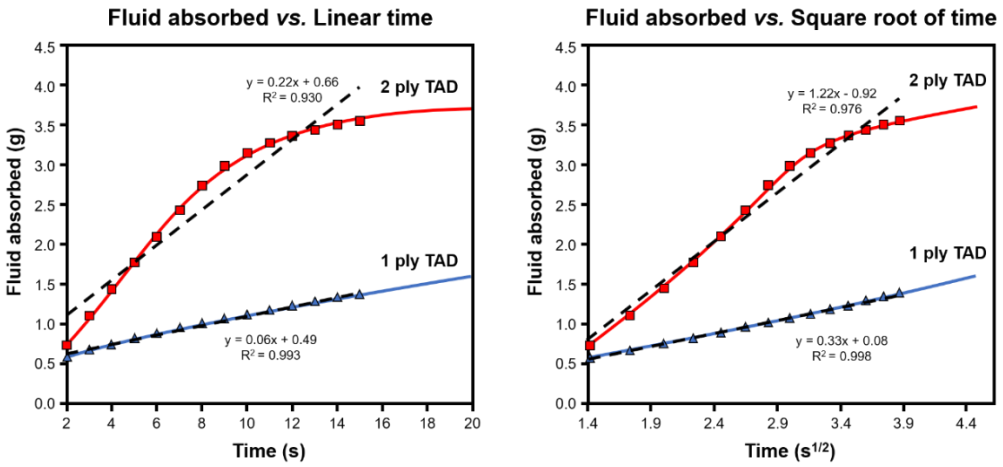

Figure 5-5: Output from absorbency test performed with an automated tester. Data are collected after 2 s to avoid rate fluctuations caused by the initiation surge. The Lucas-Washburn plot (right) is obtained by plotting the fluid uptake versus square root of time. The absorption rate can be calculated from the slopes of the curves. Linear regression of the Lucas-Washburn plot typically yields the greater R^2 and gives more accurate estimations of the absorption rate of tissue and towel (Loebker and Sheehan 2011a).

There has also been discussion about the portion of the curve that should be used for the regression. Some authors recommend to focus on the first portion of the curve and calculate cumulative rates at 2, 5, and 10 s (mass of water taken up from time 0 divided by the amount of time), and average instantaneous rates between 3 and 5 s (Beuther and Veith 2009; Lundeen 2008). Others have considered times past 10 seconds to improve the estimation of the instantaneous absorption rate, especially for fast absorbing samples such as 2-ply TAD (Loebker and Sheehan 2011a). It has also been argued that calculating cumulative rates at 10-s times may reduce differentiation among samples with different absorption rate but similar absorption capacity. The sample with the fastest absorption rate will reach its maximum absorption capacity first, but the time might be long enough for the sample with the slower absorption rate to also reach its absorption capacity (Beuther and Veith 2009). Figure 5-6 shows an example of the situation previously described.

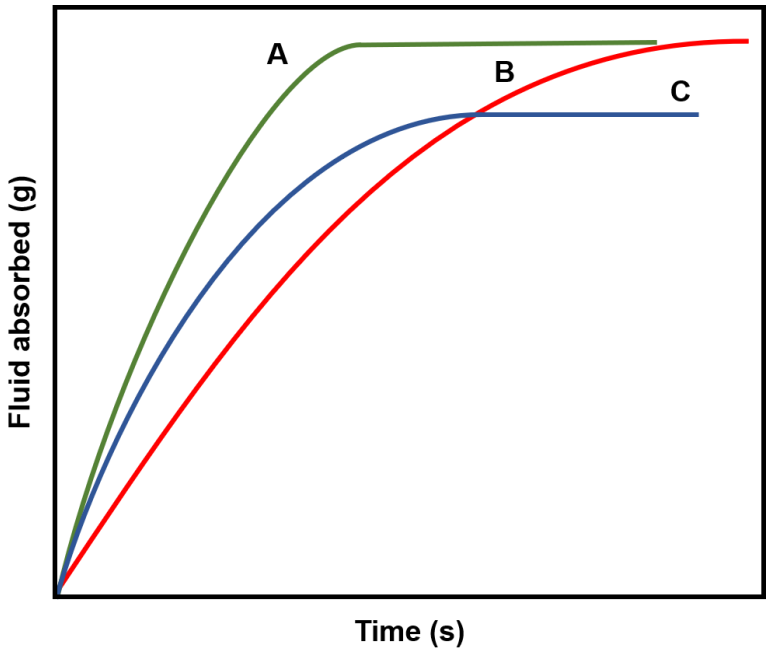

Figure 5-6: Examples of absorbent towels with different absorption rates and capacities. Towels A and B display different absorption rate but similar absorption capacity. Sample C displays intermediate absorption rate and lower absorption capacity.

Despite the high need for determining the absorbent properties of tissue and towel products, there is currently no standard in the paper industry for evaluating the rate of water absorbency (Beuther et al. 2010; Beuther and Veith 2009; Loebker and Sheehan 2011a). Various standards, shown in Table 5-2 have been published over the years; however, they have been withdrawn by the international organizations in charge of developing such methodologies. This has been attributed to poor repeatability and reproducibility as concluded in the TAPPI Interim Report, "Intrinsic absorbency rate and capacity of bibulous paper products" published by the TAPPI Tissue Paper Subcommittee of the Physical Properties Committee in 2008 (Lundeen 2008).

The TAPPI Tissue Paper Subcommittee initiated this study as a response to the concern raised within the industry regarding the several variations of the T561 method (TAPPI T 561 pm-96 "Sorptive rate and capacity of bibulous paper products using gravimetric principles") (Beuther and Veith 2009). Its objective was to develop a methodology for estimating the absorbency rate for tissue and towel. After comparing two proposed absorbency methods using the two commercial absorbency testers (the Sherwood ATS and the M/K GATS) on different tissue products, they concluded that both testers were able to differentiate between samples of different absorbent performance but they were not repeatable and reproducible across laboratories. This situation led to the removal of TAPPI T 561, which remains inactive despite the efforts of M/K Systems to improve the GATS functionality (Beuther and Veith 2009; Loebker and Sheehan 2011a).

Table 5-2: Compilation of standards proposed for measuring the absorbency rate and capacity of hygiene tissue products

Method	**Name**	**Property measured**	**Description**	**Comment**
TAPPI T 432 cm-09	Water absorbency of bibulous papers	Water absorption rate	The test method determines the time required for an unsized and absorbent paper to completely absorb a specified quantity of water (for towel 0.1 mL and for tissue 0.01 mL)	For accurate comparisons of comparable material this method has been substituted by more modern methods as it provides little differentiation between products
ASTM D824-94 (2007)	Standard Test Method for Rate of Absorption of Water by Bibulous Papers	Water absorption rate	The method determines the rate at which an unsized and absorbent paper will absorb water by measuring the time required for the sample to completely absorb a specified quantity of water	Withdrawn in 2010 with no replacement because equivalent TAPPI publication exists (TAPPI T 432 cm-09)
TAPPI T 561 pm-96	Sorptive rate and capacity of bibulous paper products using gravimetric principles	Water absorption rate and capacity	The test method provides a procedure for determining the absorptive capacity and rate simultaneously and dynamically	Provisional method. Currently not available
ASTM D5802-95 (2001)	Standard Test Method for Sorption of Bibulous Paper Products (Sorptive Rate and Capacity Using Gravimetric Principles)	Water absorption rate and capacity	The test method determines the liquid sorption of bibulous papers, paperboard and paper products using gravimetric principles	Withdrawn in 2009 with no replacement due to "insufficient committee interest in reviewing and revising the standard"
ISO 12625-10	Tissue paper and tissue products - Part 10: Determination of demand water absorption rate and capacity, under controlled hydraulic pressure	Water absorption rate and capacity	The test method provides a procedure for radial flow absorbency test	Standard is currently inactive. The method is easy to carry out but there are uncertainties regarding its significance and accuracy
ASTM D4250-92 (2003)	Standard Test Method for Water-Holding Capacity of Bibulous Fibrous Products	Water-holding capacity	The test method determines the water-holding capacity of bibulous papers such as towels, wipes, facial tissues, *etc.*, by using predetermined soaking times and extraction of excess water under predetermined low suction head from a controlled capillary draining action	Withdrawn in 2009 with no replacement due to "insufficient committee interest in reviewing and revising the standard". The method also requires equipment that is not commercially available
ISO 12625-8:2010	Tissue paper and tissue products - Part 8: Water-absorption time and water-absorption capacity, basket-immersion test method	Water-absorption time and water-absorption capacity	The method specifies a basket-immersion test for the determination of water-absorption time and water-absorption capacity of tissue paper and tissue products	Current version. Last reviewed and confirmed in 2016

5.5.3 Measurement of the absorption capacity

The methods developed for measuring the absorption capacity of tissue and towel are "dunk and drain" type tests. They measure the amount of water that a sample can retain after being immersed in water and drained under specific conditions. Results are commonly reported in the literature as water-holding capacity, absorption capacity, or capacity. ASTM D4250-92 ("Standard test method for water-holding capacity of bibulous fibrous products") and ISO 12625-8 ("Tissue paper and tissue products—part 8: water-absorption time and water-absorption capacity, basket-immersion test method"), summarized in Table 5-2, are examples of methods designed to study this property of absorbent products.

It is important to highlight that different absorbent capacities may result from different testing conditions. These differences can include the number of sheets that make up the stack, the inclination angle while draining, and the immersion and draining times (Loebker and Sheehan 2011a). Therefore, even though the absorbent capacity provides an indication of the amount of water that a product can take up in its bulk, it is not an inherent property and only serves as a reference for products evaluated under the same testing conditions. Also, during the test, water abruptly penetrates into the sample from multiple sides, which hinders the study of absorbent flows as well as absorbency rates (Aberson 1969).

A capacity measurement can also be obtained from automated testers (such as the ATS by Sherwood Instruments and the GATS by M/K Systems) by allowing the sample to absorb water until the absorbency rate falls at or below a certain value established by the operator. A value of 9 mg/6 s has been reported in the literature as the termination rate, with the 6-s period being sufficient to prevent premature ends associated with fluctuations in the absorbency rate, especially at the beginning of the test (Loebker and Sheehan 2011a).

5.5.4 In-use absorbency versus intrinsic absorbency

When wiping a spill, the user intuitively tends to position the center of the sheet on top of the spill with or without applying additional pressure. The absorbent action pulls the liquid inside the sheet, which diffuses radially away from the initial point of contact. By holding the sheet against the wet surface, the spill is absorbed much faster compared with a hypothetical situation where the spill is poured onto the sheet (Beuther et al. 2010). This way of wiping a spill brings up two aspects for discussion on how absorbency of tissue should be measured. First, a good absorbency test should be able to evaluate the radial wicking ability of a sheet in contact with a wet surface. Second, the testing method should be designed to simulate the conditions under which the tissue product will absorb fluids.

As discussed before, there is currently no agreement on how to measure absorption rates, as the methods available cannot capture significant differences between samples. Testing conditions and methods to compute the absorbency rate will impact the results to a greater or lesser degree. Variables such as sample size, number of sheets, sidedness of the sheet, vertical head of water supply, and surface properties of the sample holder are likely to interfere with the measured values and generate artifacts that might lead to wrong interpretations when ranking the performance of different products (Beuther and Veith 2009; Loebker and Sheehan 2011a). The absorbency rate is also a function of the direction of flow (machine direction versus cross-direction), with differences becoming more important for highly orthotropic structured tissue (Beuther et al. 2010). Beuther and Veith (2009) provide an insightful discussion about the primary sources of variability encountered when testing absorbency rate of tissue paper, as well as recommendations to address each of them to improve the quality of the data collected from absorbency testing devices.

This dependency of the results on the testing conditions has led to the definition of two types of absorbencies, both being valid measurements but representing different features of the product. On the one hand, there is the intrinsic absorbency, which is inherent to the product and thus independent of external variables. On the other hand, there is the in-use absorbency, which reproduces the absorbency properties obtained under testing conditions that simulate the real-use environment (Ko et al. 2016). Some authors contend that an in-use absorbency is a more meaningful property than an intrinsic one, because "most spills are cleaned up after they hit the table and not before" (Beuther et al. 2010). The addition of a lightweight cover plate to the top of the tissue during testing has been proposed as a modification to evaluate in-use properties with ISO 12625-10 ("Tissue paper and tissue products—part 10: determination of demand water absorption rate and capacity, under controlled hydraulic pressure"), which was originally conceived to measure intrinsic absorbency (Beuther and Veith 2009).

5.6 End of life of tissue products

Tissue products are of high importance to society, but the disposal of such material is of equal importance due to their impact on the environment. Whereas the most commonly applied paper waste treatment is wastewater treatment, less prevalent treatments include recycling, composting, anaerobic and aerobic digestion, incineration, and landfilling (Ghinea et al. 2014). Hygiene tissue products can be categorized as either bath tissue or paper towel, with the two having considerable differences in terms of disposal mechanisms. Bath tissue is typically flushed and transported to a wastewater treatment facility with its organic waste accessory, whereas paper towels are usually transported to solid waste facilities and dealt with in a variety of ways (Schmidt et al. 2007). All food waste, yard waste, contaminated paper, fecal matter, and hair are considered wet waste, whereas noncontaminated materials such as paper products, plastics,

metals, and textiles make up the dry waste (Otten 2017). The management of said products can result in significant economic and environmental repercussions or salutary effects. In short, the end of life of these products may result in the birth of value-added products, such as chemicals or energy, as described later in the section. Some examples of waste recovery options include energy and steam production via incineration, wet oxidation, composting, recycling, soil enhancement, insulation, and fire-resistant materials, among others (Monte et al. 2009).

5.6.1 Bath tissue waste management

Bath tissue is a major category of paper tissue products, with 17.3 million tons produced globally (3 million tons in North America) in 2018 (Euromonitor International 2019). With such an outstanding volume of product generated, it is necessary to strive for responsible management of the subsequent waste produced.

Bath tissue is primarily flushed into the sewage systems, if available geographically, and transported to wastewater treatment facilities along with solid and liquid human waste. Once it has arrived at the wastewater treatment facility, an array of mechanisms is applied to monitor the complete disposal properly. These mechanisms include mechanical breakdown, physical separation, biological treatment, and finally disinfection (Kimberly-Clark 2007).

Mechanical treatment and physical separation of sewage waste act as a screening mechanism to remove larger materials such as rags and plastics that may block the flow of the primary stream of wastewater. This is done through a series of screening of various mesh sizes, starting with a preliminary grinding device, which shreds large materials down to 6–19 mm in size, followed by a coarse 6-mm screening and ending with a fine 1.5–6 mm screening (Kimberly-Clark 2007).

The biological treatment involves using various microorganisms to break down organic substances into carbon dioxide and water under aerobic conditions. The organic substances are sourced from paper products and feces, along with dissolved sugars. The carbon dioxide produced is biogenic, therefore not contributing to harmful greenhouse emissions (Kimberly-Clark 2007). The solids content is thereafter increased to form a sludge, which is then dried into solids. Figure 5-7 describes the breakdown of dry-solids final disposal by European and U.S. standards.

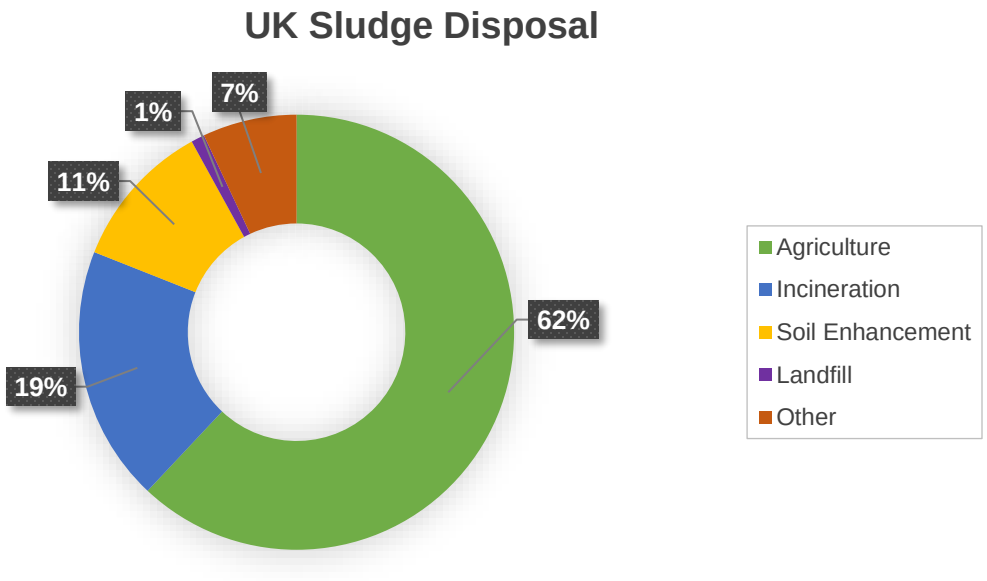

Figure 5-7: Breakdown of sludge disposal from wastewater treatment facilities

5.6.2 Household paper waste management

Household paper waste is a category that can be inclusive of facial tissue, hand towels, kitchen towels, and napkins. Paper towels, being the most widely used household paper product, amounted to 2.6 million tons produced globally (1.1 million tons in North America) in 2018 (Euromonitor International 2019b). These products are primarily sent as solid municipal waste to landfills or are incinerated for energy production (Environmental Protection Agency 2014). This

is a much simpler mechanism of disposal compared with bath tissue, but for good reason. First, residual substances present on the paper products are nearly impossible to remove because of their various compositions (Schiopu and Gavrilescu 2010; Wu 2010). For example, kitchen towels that have been used for cleaning grease off of a counter mixed with facial tissues containing pathogenic mucus cannot be successfully recycled. This is because the theoretical removal of the grease and elimination of pathogens requires very different methods; therefore, extraneous and unrealistic sorting and separating must occur prior to purification of the tissue paper. Second, and less impactful, paper tissue products that are recycled are likely to not be used for further tissue production due to the poor quality of the fibers over numerous recycling occurrences (Ghinea et al. 2014; Ingwersen et al. 2016). That being so, landfilling and incineration are the only practical means of disposal of the products to ensure the safety of consumer health and vitality of recycled paper operations (Schiopu and Gavrilescu 2010).

A consensus can be made that reducing the amount of material ending up in landfills is attractive with respect to meeting societal standards, and various progress is being made to fulfill this goal. For instance, Georgia-Pacific LLC has made an effort to divert 5 tons of paper towels to be recycled into containerboard and other paper products (Georgia-Pacific 2019). One challenge that was necessary to overcome was the removal of wet-strength additive that gives paper towels just that, wet strength. Georgia-Pacific overcame this by altering the chemistry of the wet-strength resin, allowing for easier dissociation from the paper itself.

5.6.3 Biodegradation, landfilling, and incineration

Due to various uses and composition, the fate of paper products may involve either biological treatment, landfilling, or incineration. As described earlier, bath tissue is primarily directly consumed from microorganisms, producing biogenic carbon dioxide (CO_2) and water in

the process. The residual solid waste from wastewater treatment facilities, as well as municipal solid waste such as household paper waste, are either transported to landfills or incinerated at waste treatment centers.

Landfilling is of growing concern because of the massive amounts of greenhouse gases emitted such as CO_2 and methane (CH_4). Methane is significantly more detrimental to the heat sequestration than CO_2 and is a product of anaerobic biodegradation. Composting, involving aerobic digestion of paper products, produces biogenic CO_2, which is of much less concern than CH_4. Biogenic CO_2 is sourced from plant life that removes CO_2 already in the atmosphere. Therefore, the CO_2 produced is a regenerated CO_2 from the atmosphere. Methane, on the other hand, tips the balance due to it having a global warming potential (GWP) 28–36 times that of CO_2 (Environmental Protection Agency 2019).

Biodegradation of landfilled materials follows anaerobic digestion, releasing CH_4 in the process, causing great concern. In the United States, household waste has been reported as having a distribution with 79% going to landfill and 21% being incinerated, whereas the Dutch sent 87% of household waste to be incinerated (Kimberly-Clark 2007). In this context, there is potential to reduce the proportion of waste to be directed toward landfills, limiting the environmental repercussions. Also, efforts to contain these effluent gases is of increasing interest to decrease the environmental repercussions as well.

Incineration is a much more environmentally attractive procedure regarding the waste management of paper products. This involves the combustion of waste and subsequent collection of effluent gases, further used for energy and steam production. If done properly, all effluent gases can be accounted for, and the environmental effect is benign. This method is most commonly applied in European nations (Monte et al. 2009). The selectivity of incineration is not

as pivotal with end-of-life bath tissue sludge, with almost all types of sludge, secondary or biological, being compatible with this process (Monte et al. 2009). Mixed paper, on the other hand, is an attractive source for incineration mechanisms for a variety of reasons. These include easy separation from the waste stream, minimum processing to convert to a condensed form of energy, high heating value, low sulfur content, and low nitrogen oxides, which are a greenhouse gas emission (Gavrilescu 2009). It has been noted that 1 ton of wastepaper can result in 9.8 GJ of thermal energy (Gavrilescu 2009).

5.6.4 Concluding remarks to end-life of tissue products

In conclusion, household paper products and bath tissue wastes are managed quite differently in early stages (Figure 5-8). Due to the homogenous collection of materials present in wastewater, bath tissue is partly converted to CO_2 via biodegradation. Household paper product waste accumulates several foreign substances that limit the recyclability and reprocessing of such products with regard for the consumer's safety. A crossover exists in the fate of these two types of paper waste in that the residual sludge and dry solids from wastewater and solid household paper waste both end up in either landfills, composting, or incineration. From there, they are anaerobically degraded, in the case of a landfill, where methane is produced as a biological by-product; aerobically degraded, in the case of composting, where CO_2 is the biological byproduct; or incinerated to generated steam and flue gases for energy production. Although this is the status quo, methods can be developed for either improved separation for more controlled biodegradation, development of products that are easily recycled, and proper gas collection from landfills and compost piles.

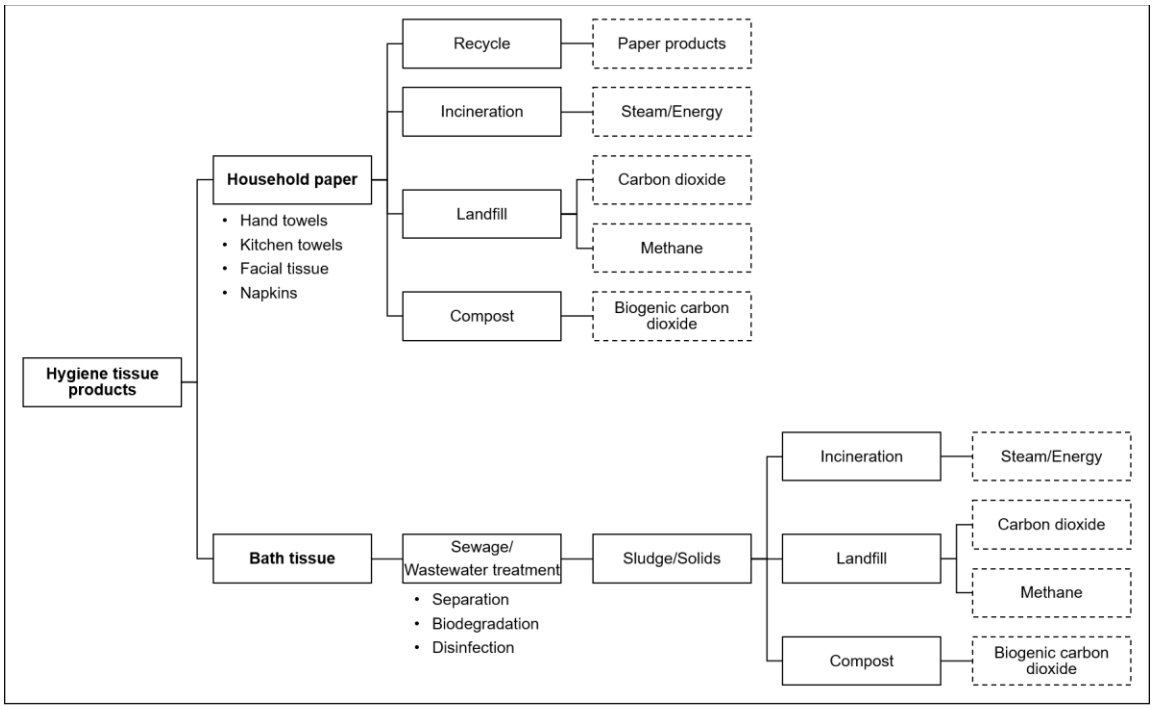

Figure 5-8: Management of hygiene tissue products at end of life

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6 UPCYCLING STRATEGIES FOR OLD CORRUGATED CONTAINERBOARD TO ATTAIN HIGH-PERFORMANCE TISSUE PAPER: A VIABLE ANSWER TO THE PACKAGING WASTE GENERATION DILEMMA[5]

6.1 Abstract

This study evaluated the suitability of old corrugated containerboard (OCC) to be upcycled into a high-quality pulp for tissue paper manufacture. The evolution of the physicochemical properties of OCC fibers and their effect on tissue properties were tracked across each stage of two elemental chlorine free (ECF) bleaching sequences. The properties of bleached OCC were compared to those of deinked pulp (DIP), southern bleached softwood kraft (SBSK), and refined OCC unbleached. Both sequences reduced the kappa number from 89 to <1 and increased brightness from 18.9% to ca. 75% ISO, on average 6.2% ISO units below that of DIP. Overall, bleaching significantly increased tensile index and absorbency rate while having adverse effects on bulk and softness and minor impacts on absorption capacity. The change in properties was correlated to the improvement in fiber bondability and fiber wettability derived from the lignin removal. Compared to DIP, bleached OCC exhibited a higher tensile index, higher freeness, and similar absorption capacity but lower softness. It also showed higher absorption capacity and similar softness than SBSK but lower freeness at a comparable tensile index. The results indicate that upgraded OCC could be used as an alternative fiber to address the forecasted shortage of high-grade recycled papers in recycled tissue grades or replace virgin fibers in producing virgin tissue grades. In addition, it was determined that refined OCC

[5] The material in this chapter has been submitted for publication in Resources, Conservation and Recycling and is currently under peer-review

unbleached could also be suitable for use in tissue grades where high brightness is not an essential product feature.

6.2 Introduction

The recycling of packaging waste, such as old corrugated containers (OCC), has been used for decades to reduce the generation of waste and scrap paper and minimize the manufacturing cost of packaging grades (Chen, Bodirsky, Krueger, Mishra, & Popp, 2020; McKinney, 1994; US EPA, 2014). The production of recycled containerboard in the US has continuously grown in recent years (Waghorne 2019). From 2010 to 2013, the US domestic consumption of OCC remained near 20 million tonnes per year, whereas in 2018, it surpassed 22.5 million tonnes, reaching a historical level of 22.8 million tonnes in 2020 (Fastmarkets RISI 2021a).

Such growth has led to an increasing steady supply of OCC to fulfill the rising demand, along with an excess tonnage allocated for exports (Chang et al. 2019; Fastmarkets RISI 2021b; Kumar et al. 2020). Nevertheless, recent market developments and political decisions, particularly the complete Chinese ban on solid waste imports starting 2021, have dramatically changed the business landscape regarding US exports of recovered paper. The 9.2 million tonnes of US OCC exported in 2015 declined by 18% to 7.6 million tonnes in 2020 (Fastmarkets RISI, 2021b; Institute of Scrap Recycling Industries, 2019; UN, 2020; S. Wong, 2017; Xiao, Dong, Geng, & Brander, 2018). Therefore, despite the higher demand for recycled packaging driven by the COVID-19 pandemic and the efforts to open new markets for US OCC in South Asia, Mexico, and Canada (Fastmarkets RISI 2021a; b), an excess of corrugated packaging derived waste without market allocation is expected in the US in the short term, with the potential to have long term implications (Qu et al. 2019; Tran et al. 2021).

An opposite course of events is encountered for high-grade recovered papers (RCP), which have experienced a shrinking supply over the past decade due to digitalization (FAO 2020; Gregg 2018). This results from the reduction in printing and writing paper consumption, the source of high-grade RCP, which has decreased at a compounded annual growth rate (CAGR) of 4.4% between 2010 and 2019 (Fastmarkets RISI 2021c). The situation has been aggravated by the stay-at-home orders enacted since SARS-CoV-2 spread worldwide in 2020 (Moreland et al. 2020). This anticipated scarcity of high-grade RCP supposes an imminent pressure on tissue paper manufacturers, considering that 33.4% of the tissue paper in the US is made from recovered paper and that the increasing tissue production (CAGR of 1.9% between 2010 and 2019 with an estimated 6% between 2020 and 2021) will continue to demand more raw materials (Fisher International 2021; The Business Research Company 2021). In this context, finding alternative fibers for tissue manufacturing is of the utmost importance in order to secure a steady raw materials supply that can guarantee business stability, while fulfilling the prospect growth.

Historically, OCC has exhibited lower prices than high-grade RCP. Hence, the price differential of OCC (average 150 USD/tonne) to high-grade RCP (average of 221 USD/tonne) between 2010 and 2019 (Fastmarkets RISI 2021c) suggests that there are opportunities for upcycling OCC while remaining cost-competitive. Given the market developments previously described, OCC could be a potential candidate to satisfy the growing demand for high-grade RCP required for tissue paper manufacture. We believe that tissue manufacturers willing to adopt such a strategy will have the ability to implement flexible fiber sourcing programs, enabling cost-competitiveness and protection from future market developments.

Nevertheless, there are challenges related to upcycling OCC into a tissue-making quality and high-performance fiber (i.e., a fiber that resembles a high-grade recycled fiber). In terms of tissue-making properties, the high lignin content makes OCC fibers very stiff and poorly bondable, both factors detrimental to paper's strength (Gulsoy et al. 2013). Besides, lignin gives a brown appearance (low brightness) to the paper product if not removed (alternatively, this feature could be regarded as a possible advantage due to new consumer preferences toward "sustainable" brown tissue products, Wang et al. 2019). OCC is also composed of a mixture of short and long fibers with a lower proportion of the short fiber fraction. A higher proportion of short fibers, such as the one found in high-grade RCP, is preferred since it favors softness (de Assis et al. 2019). In terms of processability, the high variability of the OCC source and OCC's particular nature adds an extra level of complexity to developing any process intended to upgrade OCC into a pulp suitable for tissue-making. OCC is composed of fibers produced from two different pulping processes at very different lignin contents; the corrugated medium (high lignin content) is mainly generated from semi-chemical pulping (ranging from 9–31% softwood and 62–90% hardwood content), whereas the liners (low lignin content) are produced through Kraft pulping (ranging from 48-66% softwood and 31–47% hardwood) (Adamopoulos and Oliver 2006; Zanuttini et al. 2007).

6.2.1 Previous work on upgrading OCC and research objective

Starting in the 1980s several strategies have been used to upgrade OCC pulp into a higher quality pulp. Either the individual application or the combination of pulping, oxygen delignification, alkaline hydrogen peroxide, ozone, elemental chlorine free (ECF) and total chlorine free (TCF) bleaching, have been researched on and reported in the past.

Alkaline hydrogen peroxide (AHP) treatments have been applied for bleaching OCC. Dionne & Hoyos (1995) suggested this strategy as an effective chemical treatment to improve the brightness of OCC pulps. This was also verified by Zanuttini et al. (2009), who in addition to the brightness gains, also reported a 67% increase in tensile index of AHP treated OCC pulp. Medium consistency ozone treatment has also been used to upgrade OCC pulp, resulting in a decrease in Kappa number from 85 to 75 and a 16% increase in tensile index (Zanuttini et al. 2007). Alkaline-sulfite delignification followed by TCF bleaching using QP sequences, allowed for an increase in ISO-brightness of OCC pulp from 47.3% to 57.2% and a reduction in Kappa number from 66.7 to 12.1, without significant adverse effects on pulp strength derived from bleaching. Additional measures such as oxygen delignification have been suggested if a higher brightness degree is required (Latibari 2012).

Direct oxygen delignification of OCC (Kappa = 50 – 100) has proven to be challenging to reach bleachable OCC grades (Kappa = 30), even after applying very high amounts of NaOH (10 – 18%). As an alternative, Kraft pulping followed by oxygen delignification has been proposed as the best method for preparing OCC pulps for bleaching (Danielewicz and Surma-Ślusarska 2011). In this respect, oxygen delignification under alkaline conditions has been applied to Kraft pulped OCC, obtaining a reduction in Kappa number from 32 to 15. Further application of ECF and TCF bleaching allowed reaching an R457 brightness as high as 84% from a starting value of 42% corresponding to the untreated OCC. A three stage sequence comprising two stages of oxygen delignification with an intermediate activation stage using chlorine dioxide, has been also used to generate a bleachable grade OCC (Kappa = 11.4 – 20) (Haywood 1994). Several authors have reported beneficial effects on strength of sheets made from oxygen delignified OCC pulps (Koç et al. 2017; De Ruvo et al. 1986). Fully bleached OCC

pulps of 87 – 90% ISO-brightness have been produced according to a sequence of processes that includes acid washing, Kraft pulping, chelation, oxygen delignification, bleaching (D_0ED_1), and hyperwashing (Danielewicz and Surma-Ślusarska 2015).

Three processes for upgrading OCC, dating from more than 20 years ago, are reported in the patent literature. The treatments include alkaline hydrogen peroxide, oxygen delignification, and peroxymonosulfuric acid respectively, and aim at producing bleachable or fully bleached OCC pulps for white paper or paperboard products (Burton, 1996; Nguyen, 1996; Wong, 2000). Specifically for tissue grades, two patents discuss processes to upgrade OCC pulp for tissue paper manufacture. The first one describes a method for recovering fibers from waste paper, such as OCC, through mild alkaline pulping with oxygen and hydrogen peroxide, followed by rapid fiber decompression and hot washing (Hankins, Prochazka, & Schmitt,1998). This integrated system reduces the Kappa number by at least 50%, bleaches, and cleans the fibers while preserving the integrity of low lignin fibers at a level comparable to that of fibers found in office waste papers. The second patent describes a method for manufacturing tissue paper from OCC treated with a weak alkali condition (NaOH less than 1%) that is claimed as environmentally friendly since bleaching is not performed (Kim, & Baek, 2010). Both patents report on the fiber recovery method without providing details on the quality of the tissue product (e.g., absorbency, softness) made from the upgraded OCC.

In this regard, although a variety of treatments for upgrading OCC have been reported in the aforementioned studies, to the authors' knowledge, there is currently no comprehensive literature that reports on the impact of such treatments on the tissue-making properties of OCC. Unlike other paper grades, tissue papers are strongly driven consumer products that require a delicate balance between properties, typically in conflict with one another, e.g., improved

strength will come at the expense of reduced water absorbency and softness (Zambrano et al. 2021). To fill this gap, the objective of this paper is to systematically study the evolution of the physicochemical properties of OCC fibers and their effect on the resulting tissue properties across different stages of two state-of-the-art ECF bleaching sequences. A detailed discussion on the absorbency mechanism and its relationship with the extent of lignin removal is presented. Moreover, the performance of bleached OCC is compared to that of recycled (deinked pulp) and virgin (southern bleached softwood kraft) market pulps. Recent scholarly literature has started to evaluate the potential of OCC for the production of value-added materials such as lignocellulose nanofibers (Kumar et al. 2020; Yousefhashemi et al. 2019), and dissolving pulp (Jahan et al. 2016). Along these lines, the ultimate goal of this research is to understand the potential of OCC to be upcycled into a high-quality pulp, suitable for tissue paper manufacture, while at the same time providing an alternative to address the current problematic regarding the management of the excess production of packaging waste in the US.

6.3 Experimental

6.3.1 Materials

Old corrugated containerboard (OCC) pulp and deinked pulp (DIP) were kindly provided by Greif Inc. (Gladstone mill, VA) and Resolute Tissue (Sandford, FL). Unrefined OCC pulp was collected from the high-density stock chest. The OCC pulp was centrifuged to approximately 40% consistency. The dewatered OCC pulp was fluffed and stored in a cold room at 2°C for future use.

6.3.2 Bleaching

Bleaching of OCC pulp with the ECF sequences $D_0(EP)D_1P$ and $OD_0(EP)D_1P$ was carried out in accordance with the conditions shown in Table 6-1. Half of the total calculated ClO_2 was charged in each D stage for both sequences. For the $OD_0(EP)D_1P$ sequence, the total ClO_2 charge was estimated based on the kappa number resulting from the O stage. Oxygen delignification was carried out in bomb digesters (cylindrical high-pressure vessels) mounted on a rotating drum and heated by forced convection of air. The rest of stages were carried out in sealed polyethylene bags immersed in a temperature-controlled water bath. Following each bleaching stage, the pulp was filtered through cheesecloth and washed with DI water until obtaining a clarified filtrate. The washed pulp was centrifuged to approximately 30% consistency and fluffed. An undiluted aliquot of the bleaching filtrate was collected for measuring pH and residual bleaching chemicals. Bleaching yields were estimated gravimetrically by dividing the weight of oven-dried (OD) product by the initial weight of OD pulp treated.

Table 6-1: General bleaching conditions

	$D_0(EP)D_1P$				**$OD_0(EP)D_1P$**				
Conditions	**D_0**	**(EP)**	**D_1**	**P**	**O**	**D_0**	**(EP)**	**D_1**	**P**
Consistency, %	10	10	10	10	10	10	10	10	10
Temperature, °C	70	70	70	70	100	70	70	70	70
Time, min	60	60	90	90	60	60	60	90	90
O_2, psi	-	-	-	-	100	-	-	-	-
Kappa factor (KF)	0.3	-	-	-	-	0.3	-	-	-
ClO_2, %	5.0	-	5.0	-	-	3.0	-	3.0	-
H_2O_2, %	-	0.5	-	4.0	-	-	0.5	-	4.0
Caustic factor	-	0.3	-	-	-	-	0.3	-	-
NaOH, %	-	4.0	-	3.0	5.0	-	2.3	-	3.0
Final pH	3.7	11.9	1.9	11.2	9.0	4.2	11.9	2.1	11.9

Reagent doses are expressed as % of dry pulp weight; D: chlorine dioxide stage; (EP): alkaline extraction stage reinforced with hydrogen peroxide; P: peroxide stage; O: oxygen delignification stage

6.3.3 Pulp characterization

The following procedures were applied for pulp characterization: water retention value (WRV) (TAPPI UM 256 2015), kappa number (TAPPI/ANSI T 236 om-13 2013), micro-kappa number for samples with kappa numbers below 10 (TAPPI UM 251 2013), freeness (TAPPI T 227 om-99 1999), zero-span breaking length (TAPPI 231 cm-07 2007), and brightness (ISO 2470-1 2016). Zero-span breaking length was determined using a Pulmac zero-span tester (Middlesex, VT). Pulp brightness was measured using a Technidyne Color-Touch X model CTX-ISO (New Albany, IN). Fiber morphology was determined with a fiber quality analyzer (HiRes FQA, OPTest Equipment Inc., Hawkesbury, ON, Canada). Fiber mass distribution of unbleached OCC pulp was determined using a Bauer-McNett classifier according to TAPPI 233 cm-95 (1995). The fiber surface chemistry was investigated using X-ray photoelectron spectroscopy (XPS) performed with a SPECS Flex-Mod electron spectrometer.

6.3.4 Preparation of handsheets

Handsheets were made from unbleached and unrefined OCC pulp, unrefined OCC pulp following each bleaching stage, unbleached OCC pulp mechanically refined, and unrefined DIP. Unbleached OCC pulp was refined with a PFI-mill (N°312, The Norwegian Pulp and Paper Research Institute, Oslo, Norway) using 1,000, 2,000 and 4,000 revolutions according to TAPPI T 248 sp-00 (2000).

The procedure for forming handsheets corresponds to a modified version of TAPPI T 205 sp-02 (2006). In the proposed method, wet pressing of the paper web is minimized to preserve bulk, as densification yields poor softness and reduces water absorbency of the paper sheet. Briefly, each pulp is prepared in a slurry form at 0.3 %wt consistency using tap water for dilution, the slurry required to target a basis weight of 30 g/m^2 is placed in a standard handsheet

former (Testing Machines Inc., New Castle, DE), and finally the formed sheet is couched and dried using a cylindrical dryer (Formax 12", Adirondack Machine Co., Gleans Fall, NY) instead of pressed and ring-dried. The operating conditions for the cylindrical dryer were set at 110°C, 1 rpm, and 5 min residence time. Handsheets obtained from this method were not creped.

6.3.5 Handsheet testing

Handsheets were conditioned for 24 h under a standard atmosphere set at 50% relative humidity and 23°C before testing (ISO 187 1990). The following procedures were applied for evaluation of physical and mechanical performance of handsheets: basis weight (ISO 12625-6 2005), thickness and bulk (inverse of apparent bulk density) (ISO 12625-3 2005), tensile strength (ISO 12625-4 2005), water absorption capacity (ISO 12625-8 2016), capillary rise (ISO 8787 2018), and roughness (TAPPI/ANSI T 555 om-15 2015). Thickness was measured by applying a static load of 2 kPa on the handsheet sample (digital micrometer, model 49-56, Buchel B.V., Veenendaal, Holland). Sheet swelling was calculated as the ratio between the wet caliper (after the absorbency assay) and the dry caliper (before the absorbency assay), assuming negligible volume expansions in the X and Y directions (de Assis et al. 2019). Tensile strength was determined using an Instron® model 4443 (Canton, MA). Roughness was evaluated using an L&W Parker Print-Surf tester SE 115 (Messmer, Britain). The mean pore size of the handsheets was measured by a capillary flow porometer model CFP-1100AEL (PMI Inc., Ithaca, NY).

Softness and in-plane flexibility were assessed with a Tissue Softness Analyzer (TSA, Emtec Electronic GmbH, Leipzig, Germany). Softness evaluation was performed based on the frequency peak centered around 6500 Hz, identified as TS7 (TSA softness). A lower TS7 peak height is associated with a softer tissue (Wang et al. 2019). The in-plane flexibility (parameter "D" in the TSA assessment), which is oppositely related to flexural rigidity, was used as an

indicator of bulk softness (Gigac and Fišerová 2008). The higher the in-plane flexibility, the higher the bulk softness.

Apparent water contact angles were measured by a sessile drop method using a Phoenix 300 contact angle analyzer (Surface Electro-Optics, Suwon City, Korea). To minimize roughness, swelling and absorptive effects, measurements were performed on the first clear image captured (60 milliseconds after placing the water droplet onto the paper surface). The tangent line-fitting mode was used to estimate the water contact angles from a minimum of five measurements at various locations on the sheet surface. Imaging of the surface and cross-section of the handsheets was performed using a variable pressure scanning electron microscope (VPSEM Hitachi S3200 N, Hitachi High Technologies America, Schaumburg, IL). Samples for cross-section imaging were produced by cryofracture to avoid collapsing of the fiber network structure.

6.3.6 Determination of distribution of water in saturated sheet

The total amount of water absorbed (ABS_{total}) after the absorbency assay will be distributed in the pore volume within the tissue sheet (ABS_{pores}), inside the fiber cell wall due to fiber swelling ($ABS_{swelling}$), and in the spaces between plies (ABS_{plies}) (de Assis et al. 2020). The ABS_{total} (g water/g fiber), ABS_{pores} (g water/g fiber) and $ABS_{swelling}$ (g water/g fiber) can be approximately estimated according to Eqs. 6–1, 6–3:

$$ABS_{total} = ABS_{pores} + ABS_{swelling} + ABS_{plies} \quad (6-1)$$

$$ABS_{pores} = \rho_{water} * \left(\hat{V}_{sheet\ dry} - \hat{V}_{fiber}\right) \quad (6-2)$$

$$ABS_{swelling} = \rho_{water} * \left(\hat{V}_{sheet\ wet} - \hat{V}_{sheet\ dry}\right) \quad (6-3)$$

where ρ_{water} is the density of water (0.998 g/cm^3 at 23°C), $\hat{V}_{sheet\ dry}$ (cm^3/g) and $\hat{V}_{sheet\ wet}$ (cm^3/g) are the bulk of the sheet measured in the dry and wet state respectively, and $\hat{V}_{fiber}$ (cm^3/g) is the specific volume of the fiber, assumed to be similar to the specific volume of cellulose. The density of cellulose was assumed to be 1.5 g/cm^3 (Shen et al. 2010). The ABS_{plies} can be calculated from Eq. 1 by subtracting the ABS_{pores} and $ABS_{swelling}$ from the ABS_{total}. A detailed derivation of these set of equations and associated limitations are presented by de Assis et al. (2020).

6.4 Results and discussion

6.4.1 Initial characterization of unbleached OCC pulp

Table 6-2 shows the fiber morphology of unbleached OCC pulp refined at different PFI-mill revolutions along with bleached Eucalyptus kraft (BEK), northern bleached softwood kraft (NBSK), SBSK, and DIP, which are market pulps commonly used in tissue manufacture. OCC pulp is composed of fibers that are on average longer and wider than BEK and DIP fibers, but shorter and narrower when compared to pure softwood species. This aspect highlights the heterogeneous composition of OCC pulp.

Table 6-2: Average fiber length, fiber width and percent fines for OCC and market pulps used in tissue manufacture

Pulp name	**Old corrugated containerboard**				**Deinked pulp**	**Bleached eucalyptus kraft**[3]	**Northern bleached softwood kraft**[3]	**Southern bleached softwood kraft**[4]
Pulp tag	OCC				DIP	BEK	NBSK	SBSK
Kappa N°	89				Bleached	Bleached	Bleached	Bleached
Brightness, % ISO	18.9 ± 0.3				80.9 ± 0.4	84.0 ± 0.8	85.4 ± 0.6	86
Fiber morphology	0 PFI-revs	1,000 PFI-revs	2,000 PFI-revs	4,000 PFI-revs	As-received	0 PFI-revs	0 PFI-revs	0 PFI-revs
Fiber length[1] (mm)	1.66 ± 0.01	1.48 ± 0.01	1.37 ± 0.02	1.34 ± 0.06	1.07 ± 0.05	0.8	2.34	2.58
Mean width (µm)	22.3 ± 0.2	22.3 ± 0.1	22.8 ± 0.2	23.7 ± 0.4	17.9 ± 0.1	15.6	25.7	28.1
Fines content[2] (%)	13.5 ± 0.3	16.6 ± 0.8	17.5 ± 0.8	17.1 ± 0.9	13.2 ± 0.5	4.6	4.9	5.0

[1]Length-weighted mean length; [2]Length-weighted fines, fines are defined as particles with length between 0.025 mm and 0.2 mm; [3,4]According to Zambrano et al. (2021) and de Assis et al. (2019) respectively

Table 6-3 shows the fiber mass distribution of unbleached OCC pulp with morphology features associated to each mass fraction based on fiber size. The longer fiber fraction (>14 mesh and 14-28 mesh), short fiber fraction (28-48 mesh, 48-100 mesh and 100-200 mesh) and fines account for 55.6%, 23.6% and 20.8% of the OCC pulp by weight, respectively. Compared to other market pulps, the particularly high fines content found in the OCC pulp may represent a challenge related to the upcycling and utilization of this feedstock for tissue manufacturing, as poor solid retention may be encountered during sheet formation. In turn, this can lead to a build-up of fine particles in the water loops of tissue machines that could generate an increase in the charge demand of process waters. An increase in the charge demand may interfere with the action of functional additives added to the tissue-making slurry, such as retention aids, dry and wet-strength resins, and debonders. A fraction of the fines may also be lost during the fiber upcycling process, leading to reductions in the recovery yields.

Table 6-3: Fiber mass distribution of unbleached OCC pulp and morphology of fiber fractions

Fiber fraction	Weight percent (%)	Fiber length (mm)	Width (µm)
Unfractionated	-	1.66 ± 0.01	22.3 ± 0.2
>14 mesh	42.0 ± 2.0	2.62 ± 0.02	26.6 ± 0.2
14-28 mesh	13.5 ± 0.3	1.73 ± 0.03	24.2 ± 0.2
28-48 mesh	13.8 ± 0.8	1.05 ± 0.02	20.2 ± 0.1
48-100 mesh	7.2 ± 0.1	0.69 ± 0.01	18.5 ± 0.1
100-200 mesh	2.5 ± 0.1	0.46 ± 0.01	17.8 ± 0.1
<200 (Fines)	20.8 ± 0.2	-	-

6.4.2 Bleaching with the sequences $D_0(EP)D_1P$ and $OD_0(EP)D_1P$

Table 6-4 shows bleaching results with the sequences $D_0(EP)D_1P$ and $OD_0(EP)D_1P$, carried out under similar kappa and caustic factors, and H_2O_2 charge. Both sequences reduced the kappa number of the unbleached OCC pulp from 89 to <1 and increased the brightness from 18.9% to ca. 75% ISO. The resulting brightness was on average 6.2 % ISO units below that of the benchmark DIP but similar to the brightness reported for DIP market pulp elsewhere (de Assis et al. 2019). Figure 6-1 shows the evolution of pulp brightness across the $OD_0(EP)D_1P$ bleaching sequence. A slight reduction in fiber length, width, and fines content, along with an increase in kink index (an indicator of fiber flexibility), were observed with bleaching progression. Such trend, which has been previously reported for a similar ECF bleaching sequence, has been attributed to softening and shrinkage of the fibers in the axial and radial directions resulting from the subsequent removal of lignin and carbohydrates (Lin et al. 2014). On the other hand, the reduction in fines content is related to particle losses resulting from the several washing stages applied throughout the bleaching sequences.

Table 6-4: Overall bleaching results with the sequences $D_0(EP)D_1P$ and $OD_0(EP)D_1P$

		$D_0(EP)D_1P$				$OD_0(EP)D_1P$				
Pulp and filtrate characteristics	**Unbleached**	**D_0**	**(EP)**	**D_1**	**P**	**O**	**D_0**	**(EP)**	**D_1**	**P**
Kappa N°	89.0	55.1	31.0	6.9	-	53.1	29.2	11.6	4.5	-
Brightness, % ISO	18.9	20.8	28.5	56.8	75.3	24.8	34.5	46.6	60.5	74.1
Fiber morphology										
Fiber length[1] (mm)	1.66	1.56	1.60	1.60	1.54	1.53	1.58	1.55	1.56	1.51
Mean width (µm)	22.3	21.8	22.1	21.6	21.4	21.8	21.6	21.6	21.7	21.3
Mean kink index (1/mm)	1.60	1.77	1.65	1.64	1.66	1.70	1.75	1.63	1.96	1.88
Fines content[2] (%)	13.5	13.9	13.7	12.1	10.9	14.2	12.6	12.3	12.2	11.9
Total yield, %	-	92.0	84.4	78.6	72.5	89.2	84.7	79.4	76.2	71.3
Residual ClO_2, mg/L	-	5.4	-	5.4	-	-	5.4	-	21.6	-
Residual H_2O_2, mg/L	-	-	0.0	-	6.8	-	-	6.8	-	170.0

[1]Length-weighted mean length; [2]Length-weighted fines, fines are defined as particles with length between 0.025 mm and 0.2 mm

The O stage in the $OD_0(EP)D_1P$ sequence reduced the ClO_2 consumption by 41% compared to the $D_0(EP)D_1P$ sequence while generating a similar ISO brightness. In addition, the residuals in the D_1 and P stages of the $OD_0(EP)D_1P$ bleaching filtrates presented larger contents of ClO_2 and H_2O_2 respectively, which suggests that further optimization can help reduce the consumption of bleaching reagents in this sequence, and highlights the advantage derived from the O stage.

It is worth mentioning that the high kappa number of the OCC pulp is far off from what is considered a conventional bleachable grade (kappa number = 12 – 30). Thus, significantly larger amounts of bleaching chemicals are required to reach a high brightness value. Nevertheless, despite the high kappa and caustic factors selected, the overall limited amount of residuals observed in the filtrates indicates almost complete consumption of the bleaching chemicals under the reacting conditions, which is explained by the large quantity of lignin available for reaction across the different bleaching stages. This indicates that there are opportunities for upcycling OCC into a high-value pulp by using low waste processes.

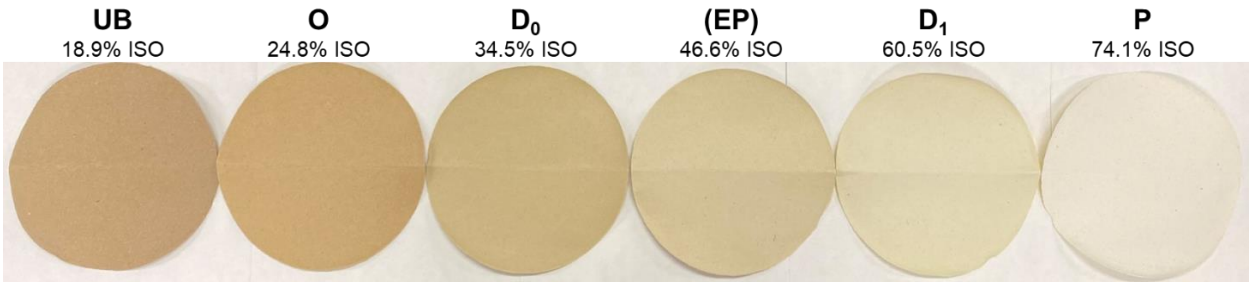

Figure 6-1: Evolution of brightness upon application of $OD_0(EP)D_1P$ bleaching sequence. UB refers to unbleached OCC.

6.4.3 Tissue-making properties of OCC

6.4.3.1 Effect of bleaching on pulp and tissue properties

The effect of bleaching on freeness of the fiber slurry and tissue properties is depicted in Figure 6-2 for the $D_0(EP)D_1P$ and $OD_0(EP)D_1P$ sequences, respectively. Despite the differences obtained in the development of properties across the two bleaching sequences, both bleached OCCs (following the P stage) resulted in tissue sheets with comparable tensile index, absorption capacity, and softness (less than 3% difference), independently of the bleaching strategy applied. Figure 6-3 shows SEM images of the surface and cross-section of sheets made from unbleached and bleached OCC pulps. Table 6-5 shows the evolution of the physicochemical properties of the OCC pulp across each individual bleaching stage.

Bleaching gradually reduced freeness, with the Canadian standard freeness (CSF) values leveling off toward the last stages of the sequence (Figure 6-2a). The reduction in freeness may be primarily attributed to the increase in fiber flexibility and collapsibility caused by the lignin removal. More conformable fibers will form denser wet webs, reducing sheet permeability. In addition, the increase in the fiber's WRV (Table 6-5), which implies a more intimate interaction of water molecules with the fiber cell wall through hydrogen bonding, will also make more difficult the release of water from the wet mat, negatively impacting drainage. Nevertheless,

freeness of bleached OCC remained at levels above the ones reported for deinked pulps (252 – 393 ml CSF), which are widely used in tissue manufacturing operations (de Assis et al. 2019). This has important practical implications, since it suggests that the use of OCC can help improve the drainability of recycled tissue furnishes and thus, the runnability of tissue machines producing recycled tissue grades. Higher drainage rates will be translated into less drying energy, while a better machine runnability will be linked to higher production rates (Gonzalez et al. 2020).

Table 6-5: Evolution of OCC pulp characteristics across the bleaching sequences $D_0(EP)D_1P$ and $OD_0(EP)D_1P$

		$D_0(EP)D_1P$				**$OD_0(EP)D_1P$**				
Pulp characteristics	**Unbleached**	**D_0**	**(EP)**	**D_1**	**P**	**O**	**D_0**	**(EP)**	**D_1**	**P**
O/C ratio	0.51	0.52	0.66	0.74	0.80	0.66	0.64	0.74	0.71	0.79
%C1 (C–C, C–H)	43	42	33	27	18	36	33	27	29	23
%C2 (C–O, C–OH)	48	48	52	58	65	50	56	54	56	57
%C3 (C=O, O–C–O)	6	7	15	14	16	14	11	19	15	20
%C4 (O–C=O)	3	2	0.2	2	0.7	0.1	0.8	0.2	1	0
WRV, g/g	1.41	1.59	2.04	1.77	2.05	1.90	1.87	2.19	1.99	2.20
Zero-span breaking length, km	9.1	9.2	11.5	10.9	9.5	8.8	9.0	10.2	10.0	8.7
Sheet swelling, %	3.2	4.8	13.8	12.7	16.5	20.4	5.6	9.8	22.2	20.3

The standard deviations associated with the WRV, zero-span breaking length and sheet swelling measurements are reported in Table B-1 of the Appendix B

Overall, bleaching yielded denser fiber networks (lower bulk) with a significantly improved tensile index (Figure 6-2b and 6-2c). The reduction in bulk can be qualitatively observed from the reduction in thickness of the sheet made from bleached OCC (Figure 6-3). Following the P stages, bulk decreased by 23%, whereas tensile index increased by 87% compared to the unbleached OCC pulp. The strength improvement results from the increase in fiber conformability and fiber bondability that takes place upon the removal of lignin, which enhances the relative bonded area (RBA) of the treated pulp fiber in comparison with the original pulp fiber (Zanuttini et al. 2007). The inherent fiber strength also increased, as reflected by the

zero-span breaking length (Table 6-5). Therefore, the increase in the strength component associated with the resistance of fibers to breakage is another contributor to the overall strength improvements. It is important to note that the degree of this contribution is less significant compared to that of the resistance of bonds to breakage, considering the low degree of bonding inherent to the tissue sheets (Page 1969). Following the (EP) stages, a slight reduction in tensile index was observed. This reduction may be associated with the decrease in inherent fiber strength (as indicated by the reduction in zero-span breaking length) that occurred toward the latter bleaching stages, likely due to shortening of the cellulosic chains typical after the chemical treatments applied (Haywood 1994).

The increase in tensile index was obtained at the expense of reduced softness, as indicated by the increase in TS7 (Figure 6-2e). Compared to the unbleached OCC, TS7 increased by 130% following the P stages. This may be explained by the structure's densification, which reduces sheet flexibility (Figure 6-2g), an aspect correlated with lower bulk softness (Gigac and Fišerová 2008), and associated with a higher TS7 (Zambrano et al. 2021). On the other hand, roughness, directly correlated with surface softness given the uncreped nature of the sheets evaluated (Hollmark 1976), decreased as the bleaching sequence progressed (Figure 6-2f). The reduction in roughness may be a result of the increase in formation uniformity with bleaching (Figure B-1 in Appendix B), which rendered a more regular surface topography.

Contrary to the important strength development obtained with bleaching, absorption capacity did not show significant changes across both bleaching sequences (except following the D_0 stage) (Figure 6-2d). Only a slight reduction in absorption capacity (8% on average for both bleaching sequences) was observed between unbleached and bleached OCC (following the P stages) compared to the increase in 87% (average for both bleaching sequences) obtained for

tensile index (Figure 6-2c). The details on the underlying absorbency mechanisms including wicking are presented in the following section.

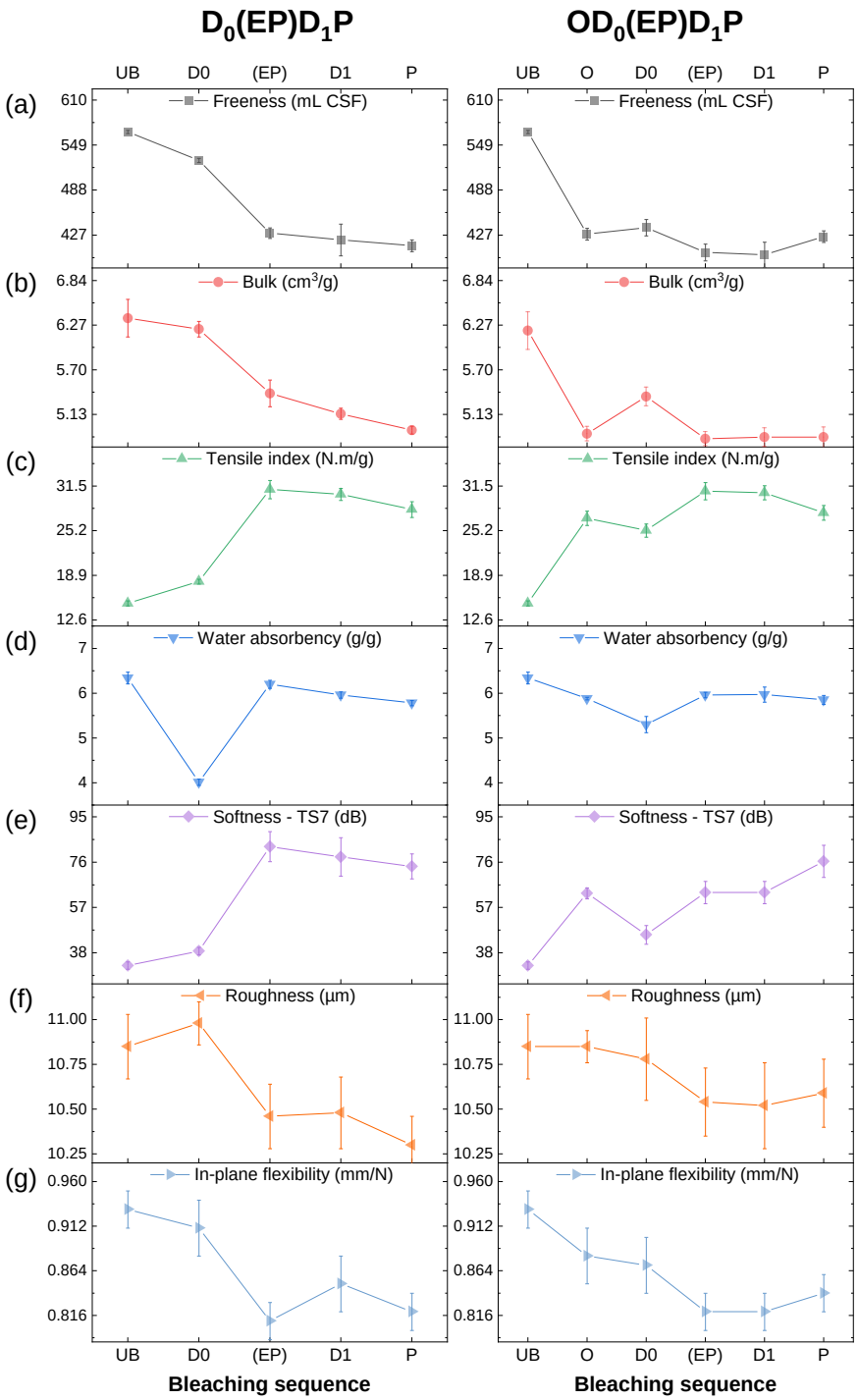

Figure 6-2. Effect of bleaching on freeness and tissue-making properties of OCC pulp. UB refers to unbleached OCC.

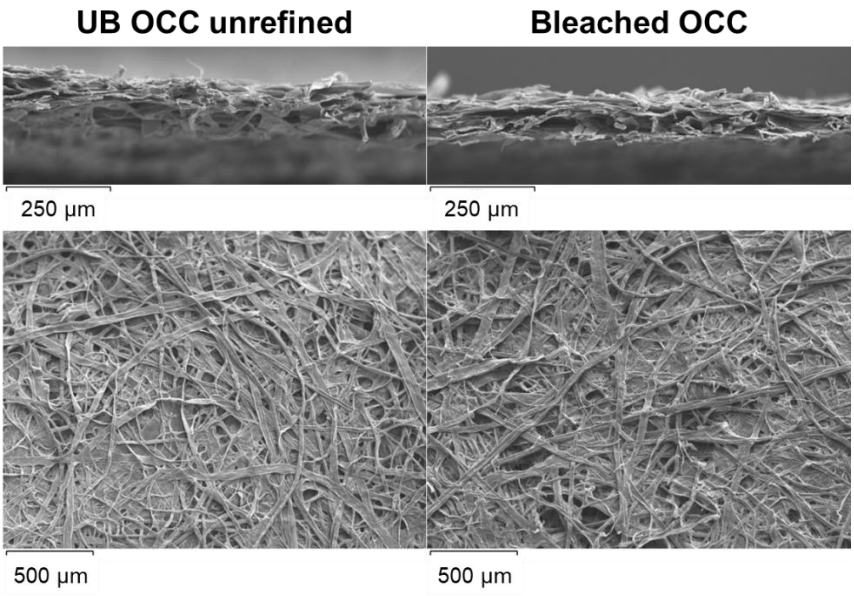

Figure 6-3: SEM images of cross-section and surface of sheets made from unbleached OCC (left) and OCC bleached according to the $OD_0(EP)D_1P$ sequence (right)

6.4.4 Water absorbency mechanism

There are two phenomena involved in the absorption of fluids by a network of fibers: absorption capacity and absorption rate (Aberson 1969; Parham and Hergert 1980). The former accounts for the total amount of liquid that the sheet can absorb within its bulk, whereas the latter relates to the velocity of fluid uptake. This section sheds light on the underlying absorbency mechanism of OCC tissue papers across the bleaching sequences.

6.4.4.1 Water absorption capacity

Under water saturation conditions, the liquid absorbed within a tissue sheet will be distributed between the sheet pore volume, the fiber cell wall and fiber lumen, and between plies (Zambrano et al. 2020). Accordingly, the capacity of the fibrous assembly to absorb water is a function of the structure's pore volume, the ability of the sheet to swell, and the inter-ply spaces in case multiple sheets are stacked together (de Assis et al. 2019).

The slight reduction in absorption capacity that came about after bleaching may not be intuitive under the assumption that the removal of lignin would overall increase the ability of the sheet to swell. Effectively, sheet swelling showed on average a 6-fold increase with bleaching (Table 6-5). Such an increase results from the improvement in fiber hydrophilicity (WRV was regarded as an indicator of fiber hydrophilicity) promoted by the increase in O/C ratio on the fiber surface across the bleaching sequences (Table 6-5). The surface functional group composition shown in Table 6-5 revealed that bleaching led to a decrease in carbon C1 (C−C), associated with a reduction in the fiber surface coverage by lignin. This resulted in an increase in carbons C2 (C−O) and C3 (C=O, O−C−O), which implies a higher surface exposure of hydrophilic moieties, and thus the higher O/C ratio observed.

On the other hand, from a structural standpoint, bleaching resulted in a densification of the fibrous assembly (Figure 6-2b). Such densification implies less void volume available in the sheet to absorb water and thus a reduction in absorption capacity. Several authors have reported strong correlations ($R^2 > 0.75$) between absorption capacity and bulk of tissue sheets (de Assis et al. 2019; Liu and Hsieh 2000; Zambrano et al. 2021), particularly in cases where strength was developed using methods with minor impacts on fiber chemistry (e.g., mechanical refining). In this work, the reduction in absorption capacity (8% on average for both bleaching sequences) did not correspond to the significant reduction in bulk (23% on average for both bleaching sequences).

It follows that the physicochemical features of the sheet impact absorbency in opposite directions as bleaching progresses. While the increase in fiber hydrophilicity favors absorbency due to improved sheet swelling, the reduction in pore volume hinders it. Figure 6-4 depicts the breakdown of the extent to which these two features, in addition to the inter-ply space, contribute

to the sheet absorption capacity. It is observed that the ultimate location of water within the sheet is a function of the lignin content, with the latter governing the absorbency mechanism. At a high lignin content, absorbency primarily stems from the storage of water within the pores of the fiber network since sheet swelling is hindered, whereas at a low lignin content or absence of lignin, it results from a combination of water storage within the sheet pore volume and the fiber cell wall. Overall, the results show that absorbency due to pore volume is the major contributor to absorption capacity; however, at low lignin content, sheet swelling compensates for the reduced sheet porosity, preventing a decrease in absorption capacity. This explains why despite the severe sheet densification, no major differences in absorption capacity were observed between the unbleached and bleached OCC.

In addition to the higher pore volume obtained at a high lignin content, the resistance of the fibrous structure to collapse owing to the high fiber stiffness may be another factor contributing positively to the high absorption capacity observed in the sheet made from unbleached pulp (Liu and Hsieh 2000). Finally, the absorption capacity attributed to inter-ply space did not show significant variations, which is reasonable considering that the number of plies was held constant for the absorbency assay.

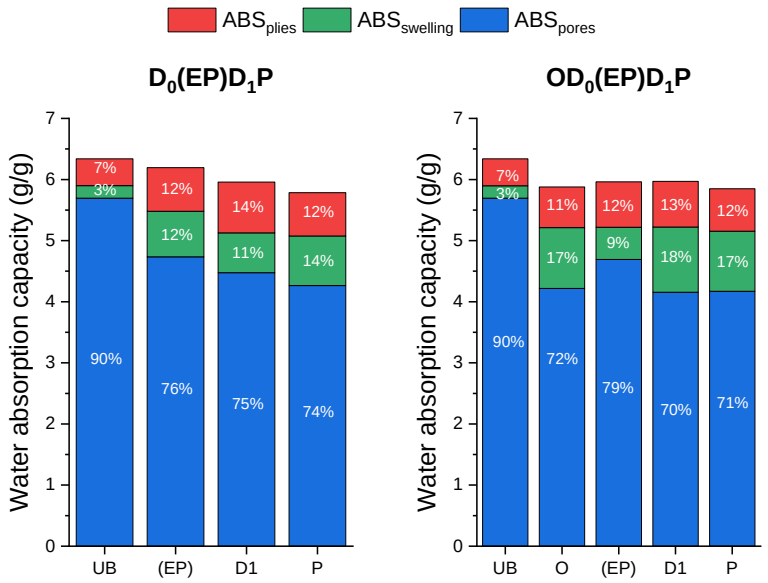

Figure 6-4. Distribution of water in tissue sheet under saturation conditions. The D_0 stages are not shown since the values corresponding to ABS_{plies} resulted negative, suggesting that the sheets did not reach full saturation during the absorbency assay, and therefore, the actual ABS_{pores} is below that of the theoretical value.

6.4.4.2 Wicking and absorption rate

Figure 6-5a shows results for the capillary rise across each of the bleaching stages for both sequences. By plotting the height of the waterfront (h) as a function of the square-root of time ($t^{0.5}$), it was observed that vertical wicking followed the behavior described by the Lucas-Washburn equation (Eqs. 6-4 and 6-5), considering that R^2 were greater than 95% for all the conditions evaluated as shown in Figure 6-5b (with the exception of the D_0 stage in Figure 6-5b.1). These results suggest that the pore size in the tissue sheets is sufficiently small so that the effect of gravity in opposing capillary rise is negligible and Eq. 6-5 is applicable.

$$\frac{dh}{dt} = \frac{r\gamma\cos\theta}{4\eta h} \qquad (6-4)$$

$$h = \sqrt{\frac{r\gamma\cos\theta}{2\eta}} * t^{0.5} \qquad (6-5)$$

where h is the liquid height in the capillary, t is time, η is liquid viscosity, θ is the contact angle of the liquid on the capillary wall, γ is the surface tension of the liquid, and r is the capillary radius.

Despite limitations and simplifying assumptions, the Lucas-Washburn theory has been useful to understand the factors affecting the absorption rate of loose fiber networks and estimate the absorbency rate of commercial tissue products (Ko et al. 2016; Loebker and Sheehan 2011; Zambrano et al. 2020). Hence, the absorption rate was estimated from the slope of the Lucas-Washburn plot *(h* vs. $t^{0.5}$, Figure 6-5b). Unlike absorption capacity, which did not experience major changes from bleaching, the absorption rate showed a dramatic increase (on average 100% following the P stage, Figure 6-6a). Therefore, despite the high absorption capacity inherent to the unbleached OCC pulp, the remarkable increase of absorption rate in the bleached OCC pulp, highlights one major advantage derived from bleaching, in addition to the natural enhancement of brightness.

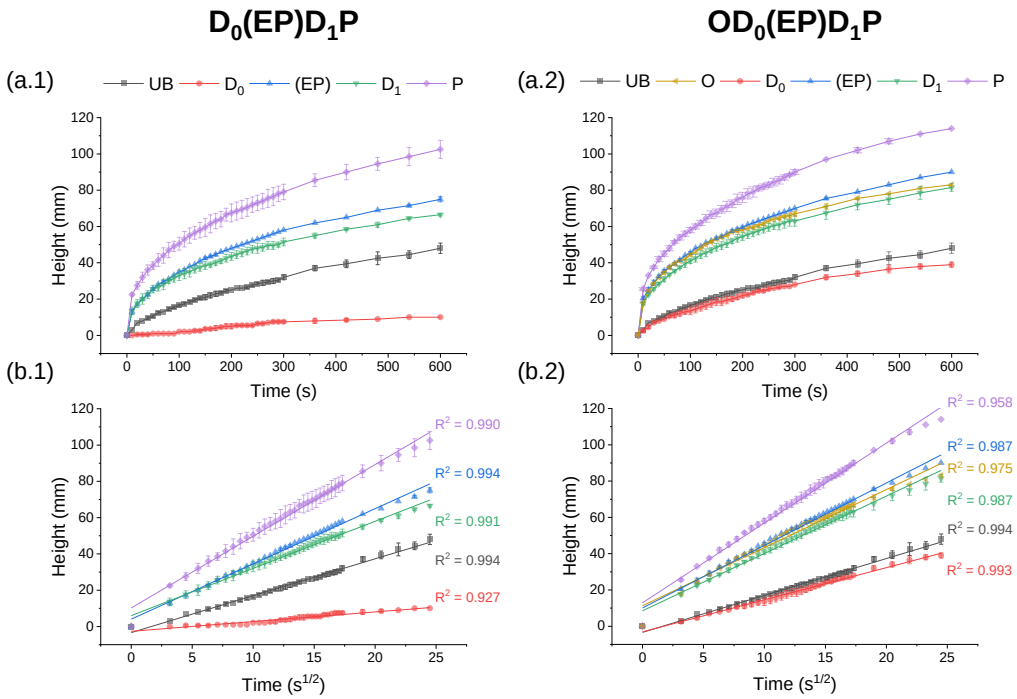

Figure 6-5. (a) Capillary rise for the bleaching sequences $D_0(EP)D_1P$ and $OD_0(EP)D_1P$ and (b) corresponding Lucas-Washburn plots

The absorption rate of a loose fiber network, is primarily controlled by the contact angle between the fiber surface and the absorbing liquid, the effective radius of the pores within the structure, as well as the balance between capillary and viscous forces (Aberson 1969). To gain a better understanding of the mechanisms underlying the wicking of the fibrous assemblies, the apparent contact angle and pore size were measured for the different tissue substrates (Figure 6-6b and 6-6c, respectively). It is useful noting that the term “apparent contact angle” was adopted in accordance with previous literature (Hubbe et al. 2015; Kutnar et al. 2012; Rossi et al. 2012) since the rough, porous, swellable and absorptive nature of the cellulosic substrates makes the measurements difficult to be regarded as ideal or equilibrium quantities (Kamdem and Riedl 1992).

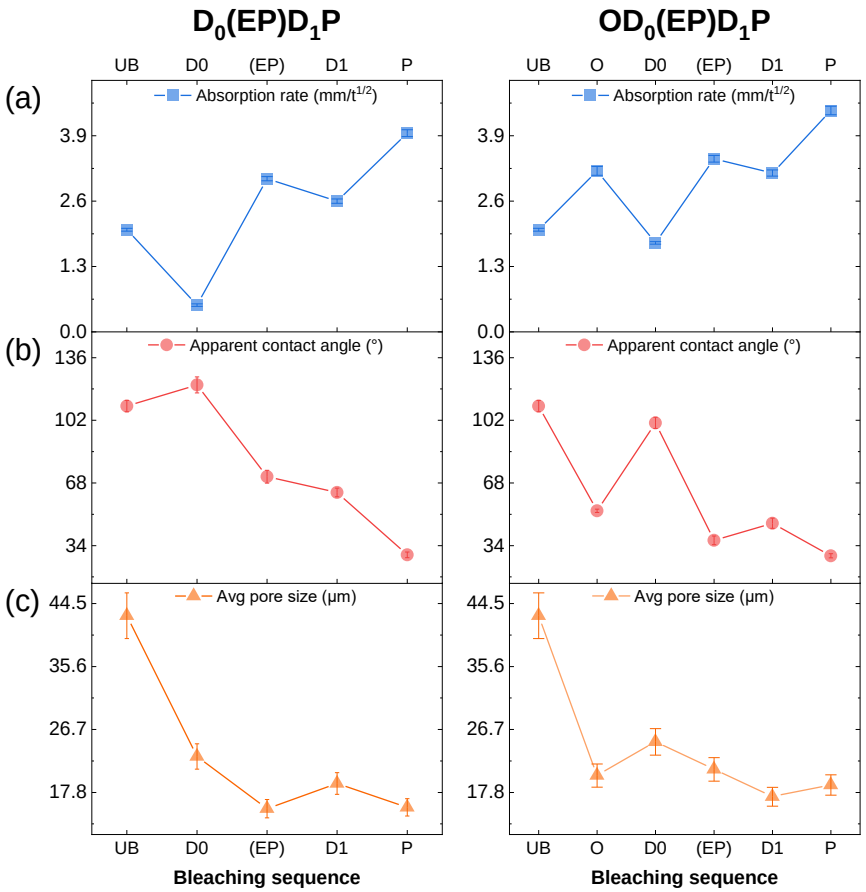

Figure 6-6. Effect of bleaching on (a) absorption rate, (b) apparent contact angle and (c) average pore size of tissue sheets. Error bars indicate standard deviation (a and b) and standard error (c).

The increase in absorption rate may be closely related with the progressive improvement in fiber wettability towards water that occurs with lignin removal and correspondent enrichment of cellulose on the fiber surface. This is evidenced by the high correlation observed between the absorption rate and the apparent contact angle of water on the tissue substrates (Figure 6-7a), which decreases across the bleaching sequence as a result of the increase in the fiber surface O/C ratio (Figure 6-7b). These results are in good agreement with those of Huang et al. (2012), who reported an inverse proportionality between the O/C ratio and the contact angle of water on different wood species. The contact angle values obtained are also in agreement with values

previously reported in the literature, 106° for unbleached Kraft pulp and 30° for bleached Kraft pulp (Ström and Carlsson 1992). Traces of minor components present in the untreated OCC pulp, such as sizing agents, inks, fatty acids, resin acids, and any other extractable substance, may also give rise to the higher contact angles observed during the first bleaching stages (Hubbe et al. 2015).

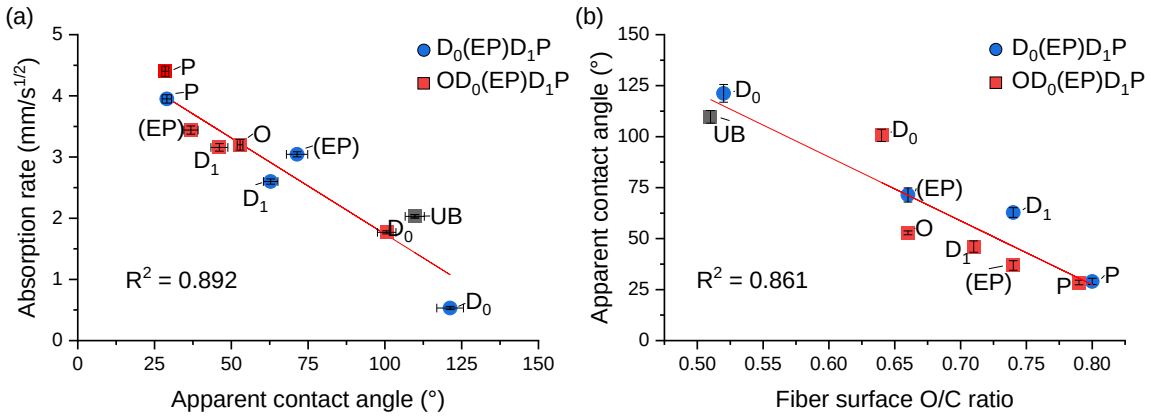

Figure 6-7. Relationship between (a) apparent contact angle and absorption rate and (b) fiber surface O/C ratio and apparent contact angle

The high contact angle following the D_0 stages may also explain the reduction in absorption capacity and rate observed in the tissue sheets (Figure 6-2d and Figure 6-6a, respectively). There are conflicting views in the literature as to what may be causing the increase in contact angle after such stages, which were carried out at low pH and high lignin content. Previous research has indicated that under acidic conditions some impurities can decrease the surface energy of cellulose fibers, increasing the fiber-water contact angle, and thus the hydrophobicity of the surface (Samyn 2013). In contrast, other studies, which have attempted to relate the ionically charged character of cellulose surface to their wettability features, have shown that cellulosic fiber surfaces can yield strong wettability even at very low pH values (Jacob and Berg 1993).

It was also observed that the reduction in apparent contact angle is the effect primarily governing the increase in absorption rate, given that the pore size of the sheet decreases as the structure is densified (Figure 6-6c). A reduction in pore size supposes an increase in the viscous retarding forces (more tortuous flow channels) and thus a slower absorption rate; however, this effect was not observed. Penetration of liquid in paper occurs through channels of highly interconnected capillaries formed by overlapped fibers. When the waterfront encounters a fiber that blocks the wicking channel, the wicking action temporarily stops until the waterfront finds an easier unblocked pathway to continue advancing (Roberts et al. 2003). It is therefore expected that at a high lignin content, fiber blockage has a greater impact on delaying the wicking action due to the poor wettability toward water despite the larger flow channels available for liquid to penetrate. On the contrary, at a low lignin content, wicking through blocking fibers is easier given the lower contact angle and the more porous nature of the fiber cell wall after the lignin removal. This effect will reduce delays in the wicking action attributed to temporary fiber blocking, despite the higher tortuosity of the smaller capillaries that serve as flow channels. It is worthwhile noting that the improvement in formation uniformity (Figure B-1 in Appendix B) may be another variable contributing to the increase in absorption rate with bleaching since better interconnected flow channels could facilitate the movement of liquid through the fiber network.

6.4.5 Trade-off between tissue properties and comparison with market pulps

Tissue papers need to comply with a minimum functional strength adequate to provide smooth machine runnability during papermaking and converting operations, as well as consumer use; however, the development of that target strength will be typically achieved at expense of a negative impact on the rest of tissue properties. In this respect, the following analysis evaluates

the best performing pulps as the ones that maximize freeness, absorption capacity, absorption rate, and softness for a given tensile index value. Figure 6-8 shows the trade-off between tissue properties. The capillary rise and Lucas-Washburn plots for unbleached OCC mechanically refined and DIP are shown in Figure B-2 of the Appendix B. OCC pulp collected after the P stage is henceforth referred to as bleached OCC. For simplicity purposes, only the bleached OCC from the $OD_0(EP)D_1P$ sequence is shown, considering that both bleaching sequences yielded similar tissue properties following the P stages.

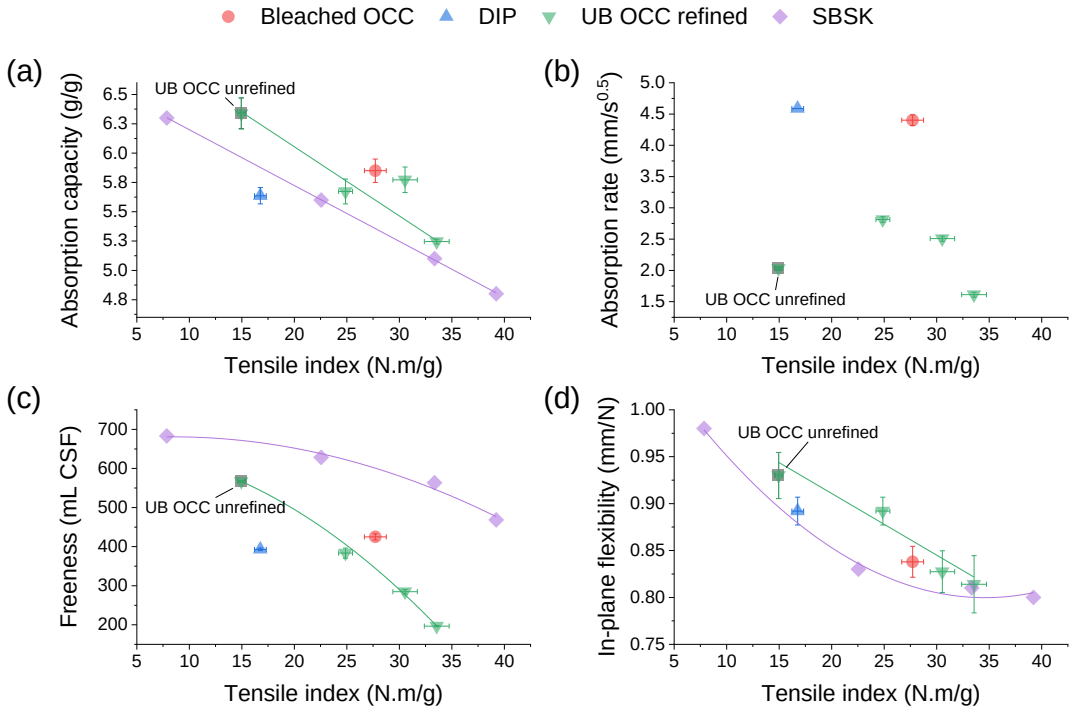

Figure 6-8. Trade-off between tensile index and (a) absorption capacity, (b) absorption rate, (c) freeness, and (d) in-plane flexibility for bleached OCC (unrefined), unbleached (UB) OCC mechanically refined, DIP and SBSK. Only the bleached OCC from the $OD_0(EP)D_1P$ is shown. Data for SBSK according to de Assis et al., (2019), absorption rate was not available from the author.

6.4.5.1 Absorption capacity vs. tensile index

Figure 6-8a shows the trade-off between absorption capacity and tensile index. As previously indicated, bleaching OCC allowed for an increase in tensile index without a significant change in absorption capacity. Compared to DIP, primarily composed of short fibers, bleached OCC exhibited 65% higher tensile index with very similar absorption capacity (both of these sheets showed similar bulk, and thus a similar pore volume available to retain water). This aspect highlights the potential advantages of incorporating upgraded OCC in tissue manufacturing operations struggling to meet nominal strength values given the poor quality of over-recycled secondary fibers.

Compared to SBSK, which was selected as a benchmark of softwood market pulp, bleached OCC displayed a higher absorption capacity for a similar value of tensile index (SBSK yielded a denser structure than bleached OCC). The higher competitive performance of bleached OCC over SBSK highlights another scenario where upgraded OCC pulp can be strategically used as an alternative fiber to more expensive virgin fibers in the manufacture of tissue paper.

Another natural benchmark evaluated was unbleached OCC mechanically refined. As expected, refining increased tensile index, while reducing absorbency. Compared to bleaching as a strategy for developing strength of OCC pulp, refining allowed to produce a tissue sheet having similar absorption capacity at 2,000 PFI-revs than bleached OCC with higher tensile index (+10%) but lower absorption rate (-40% on average). This finding has important practical implications since it shows that refined OCC without bleaching may be a suitable pulp for tissue grades where color is not a key attribute for consumers, and high absorption rates are not required (e.g., professional paper towels). Bleaching, however, has major advantages over refining since it produces pulps with significantly higher absorption rates and drainage for a

given tensile index value (Figure 6-8b) as described below. Hence, there is a trade-off in terms of the benefits from using either unbleached OCC mechanically refined or bleached OCC, which opens a toolbox for possible fiber formulations to balance performance and cost.

6.4.5.2 Freeness vs. tensile index

Figure 6-8c shows the trade-off between tensile index and freeness. As previously discussed, bleaching increases tensile index while reducing freeness of the slurry. In addition to the higher tensile index, bleached OCC also exhibited higher freeness compared to DIP (on average +26 CSF units). Compared to SBSK, bleached OCC showed significantly lower freeness, which can be attributed to the lower number of fines present in the virgin market pulp (Table 6-2). Freely moving fine particles slow the dewatering rate by blocking the drainage channels through which water flows (Hubbe and Heitmann 2007). Finally, when comparing unbleached OCC mechanically refined with bleached OCC at an approximately similar tensile index, it is shown that refining critically impacts freeness of the slurry, resulting in a difference of -144 CSF units. The reduced drainage is mostly related with an increased fines content, caused by the mechanical action (Table 6-2). Therefore, despite the advantages in terms of tissue performance derived from refining, the lower freeness is an aspect for careful consideration. A higher drainage is often preferred as it allows for a higher machine speed and a lower drying energy.

6.4.5.3 In-plane flexibility (bulk softness) vs. tensile index

Figure 6-8d depicts the trade-off between tensile index and in-plane flexibility. Given the limitations of the TS7 for comparing fibers from different sources (de Assis et al. 2020; Prinz et al. 2021), the in-plane flexibility, measured from the TSA, was taken as a proxy for bulk

softness. As previously demonstrated, the increase in tensile index resulting from bleaching OCC jeopardizes softness. Compared to DIP, bleached OCC showed lower bulk softness, which was associated with a higher tensile index. The greater degree of bonding inherent to the higher mechanical strength of bleached OCC, reduces the flexibility and compressibility of the tissue structure, affecting negatively softness (Zambrano et al. 2021). SBSK and bleached OCC showed comparable bulk softness. Finally, bleached OCC and unbleached OCC mechanically refined had a very similar property trade-off; however, it is important to highlight the effect that bleaching has on smoothening the tissue surface (Figure 6-2f).

6.5 Conclusions

This study evaluated bleaching as a strategy to upcycle OCC pulp into a high-quality pulp for tissue paper manufacture. Overall, bleaching significantly increased tensile index, absorbency rate, and brightness while having adverse effects on bulk and softness and minor impacts on absorption capacity. The improved strength resulted from the increase in fiber strength, flexibility, collapsibility, and bondability that takes place upon the removal of lignin, which yields denser tissue sheets, however, at the expense of limited softness, given the higher flexural rigidity of the fiber networks. Although bleaching reduced the pore volume in the sheet, it remarkably improved sheet swelling, which prevented the reduction in absorption capacity inherent to a denser fibrous structure. The increase in fiber wettability derived from the lignin removal, as shown by the decrease in apparent contact angle, was responsible for the major increase in absorption rate.

Compared to market pulps used in tissue paper manufacturing, bleached OCC exhibited a higher tensile index, higher freeness, and similar absorption capacity than DIP but slightly lower brightness and softness. It also showed higher absorption capacity and similar softness than

SBSK but lower freeness at a comparable tensile index. These findings highlight the potential of upgraded OCC to serve as an alternative fiber in the manufacture of recycled tissue grades having difficulties meeting nominal strength values, as well as in the manufacture of virgin tissue grades as an SBSK replacement. More importantly, this research shows how OCC can be upcycled into a high-quality pulp suitable for tissue paper manufacture, which can serve a dual-purpose: alleviate the waste management of OCC in the US, intensified by the increased production of corrugated packaging, and ensure the raw material availability in the face of the shortage of RCP and the rise of at-home tissue demand derived from the COVID-19 pandemic.

For tissue grades in which brightness is not an essential property, mechanical refining can also be used to increase tensile index, obtaining similar absorption capacity and softness than bleached OCC but with significantly lower absorption rate and freeness. Developing strategies to address these issues could open a new window for the production of high-performing unbleached tissue papers. Such products could help to satisfy the growing demand for sustainable tissue that is taking place in the hygiene tissue market while bridging the historic gap reported between sustainability and product performance.

6.6 Acknowledgments

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7 DEVELOPING ALTERNATIVE, HIGH-ABSORBENCY BROWN FIBERS: TISSUE PAPER FROM UPCYCLED CORRUGATED PACKAGING WASTE TO MEET NEW CONSUMER TRENDS

7.1 Abstract

Consumers' rising interest in brown tissue papers, perceived as sustainable, has increased the market share and selling prices of such products despite their limited performance. Meanwhile, the current excess of packaging waste in the US has created an opportunity for using old corrugated containerboard (OCC) as an alternative source of brown pulp; however, OCC exhibits inferior tissue-making characteristics relative to bleached fibers. Herein, we studied the feasibility of total-chlorine-free treatments, namely oxygen delignification, alkaline hydrogen peroxide, and ozonation, to improve the tissue-making quality of OCC pulp. The processes evaluated reduced the lignin content (kappa number from 89 to values as low as 55) and generated brightness gains as high as 8.8% ISO units. The strength of the tissue sheets also improved due to the delignification and increase in fiber swelling promoted by the oxidative treatments. Chemically treated OCC resulted in sheets with higher water absorption capacity and absorption rate and fiber slurries with higher freeness compared to sheets and slurries from mechanically refined OCC, respectively. Therefore, we demonstrate the application of treatments with low environmental impact to upcycle OCC into a high-quality brown pulp suitable for manufacturing high-performance tissue paper.

7.2 Introduction

China's severe restrictions imposed recently on the US paper waste and recycling grades imports, mainly affecting old corrugated containerboard (OCC) and mixed paper waste, have led to profound changes in the US paper industry and recycling supply chains (Qu et al. 2019; Ren et al. 2020; Tran et al. 2021; Zambrano et al. 2021a). Although the increase in e-commerce, accelerated by the COVID-19 pandemic, has generated a rising production of corrugated packaging in the US (+4% from 2019 to 2020 equivalent to 1.3 million tons) (Ebner 2021; Escursell et al. 2021; Fastmarkets RISI 2021; Filho et al. 2021), the packaging recycling rate has declined by 3.3% between 2020 and 2019, translating into ca. 3 million tons without market allocation (American Forest & Paper Association 2021). This waste will most likely end up in landfills or be incinerated, in case repurposing alternatives to obtain value-added paper products are not implemented (Cremiato et al. 2018; Das et al. 2021; Hantoko et al. 2021; Nanda and Berruti 2020). This was explained in detail in our previous work (Zambrano et al. 2021a), where we presented a process for upcycling packaging waste, specifically OCC, to obtain high-performance tissue paper in an attempt to provide a solution to the current waste generation problem. The upcycled OCC pulp developed was a fully bleached grade with improved strength and water absorbency features. Moreover, the case was made that this OCC pulp could also serve as an alternative fiber to alleviate the shrinking supply of secondary fibers from high-grade recovered papers (RCP) used in tissue paper manufacture. The availability of high-grade RCP has been continuously decreasing in recent years owing to the reduction of printing and writing paper consumption (Fastmarkets RISI 2021), which was further intensified by the work-from-home mandates imposed during the COVID-19 pandemic (Fastmarkets RISI 2020; Moore and Cornish 2020). Globally, the use of secondary fibers sourced from high-grade RCP in tissue

furnishes is at a historical minimum level of 35% from its peak of 51% in the year 2000 (Moore and Cornish 2020).

Yet, there is another trend in the tissue paper industry that is increasingly gaining momentum and must be considered in the short term, which relates to the interest in unbleached fibers (de Assis et al. 2018a; Cascades Inc. 2019; Naithani et al. 2020; Pal et al. 2019; Vidal 2015). Based on the fact that bleaching chemicals are not required, the use of brown fibers has been progressively growing in commercial tissue products that claim to have a reduced environmental footprint and thus are labeled as "green", "sustainable", or "eco-friendly" (Adu et al. 2018; de Assis et al. 2018a; Wang et al. 2019). Consumer perception also becomes crucial in this matter since there is a tendency to relate brown papers with sustainability (Vidal 2015; Vlosky et al. 1999). The push for sustainability is a trend common to several industries, including energy, cosmetics, consumer goods, and paper and packaging (Ketelsen et al. 2020). A number of corporations claim to be aligned with the UN Sustainable Development Goals (SDGs) to reach net-zero carbon emissions by 2050 and implement more sustainable practices (Deutch 2020; European Commission 2020; Guterres 2020). This evolution in corporate strategies arises in response to new consumer preferences that include more environmental awareness and willingness to pay a premium for products labeled as eco-friendly (de Assis et al. 2018a; Hensley et al. 2020; Janda 2019).

Based on the current situation, there is an opportunity of using OCC to obtain an alternative brown fiber suitable to produce high-performance unbleached tissue products. The development of this type of fiber is based on the following rationale:

(i) OCC could contribute to improving the sustainability efforts currently undertaken by the tissue industry (de Assis et al. 2018a; Pätäri et al. 2016). This is mainly due to the lower

environmental footprint of unbleached pulps (high lignin content) compared to bleached pulps, which require the use of bleaching chemicals to reach their characteristic high brightness (Danielewicz and Surma-Ślusarska 2011a; Latibari 2012). In addition, the brown color, perceived as sustainable (Barbarossa and De Pelsmacker 2016), could be used as a marketing advantage for manufacturers competing in the eco-friendly product segment or planning to have a share of this market (de Assis et al. 2018a; Blanco et al. 2004; Naithani et al. 2020). Nonetheless, the premium tissue sector composed of bleached products will remain to have the biggest market share.

(i) The incorporation of upcycled OCC into value-added products can be translated into less generation of landfilled or combusted packaging waste, meaning a substantial decrease of CO_2 equivalent emissions (Adu et al. 2018). Additionally, the substitution of virgin fibers by secondary fibers (Zambrano et al. 2021a) can contribute positively towards the material balance on forest growth and recovery of forest lands (Antikainen et al. 2017; Blanco et al. 2004; Li et al. 2021).

However, there are limitations inherent to the use of unbleached OCC for tissue paper applications. Although it has been demonstrated that mechanical refining improves strength, the refined unbleached pulp shows poor absorption rate and drainage when compared to bleached OCC and deinked pulps. Therefore, there is a need to develop suitable treatment methods that could help address these issues (Zambrano et al. 2021a). In this context, the objective of the present work is to produce a high lignin-containing pulp (i.e., brown pulp) with improved absorption rate and drainage from upcycled OCC. To that end, we explore the tissue-making properties of OCC pulp treated with different total chlorine-free strategies, viz., oxygen delignification, alkaline hydrogen peroxide, and ozonation. Considering the fundamental role

that the fiber surface chemistry plays on the water absorption mechanism, our working hypothesis is that these oxidative treatments will improve the fiber wettability towards water, leading to an overall increase in the absorption rate. At the same time, the high rigidity of lignin-containing fibers will ensure high porosity in the resulting fiber networks, which will contribute positively to the absorption capacity of the structure. The outcome will be a brown tissue paper with improved absorbency features obtained from the valorization of packaging waste. Such a product could have the potential to satisfy the growing demand for unbleached tissue papers perceived as eco-friendly (Barbarossa and De Pelsmacker 2016), while reducing the gap in performance of high lignin-containing fibers that has historically hindered the manufacture of high-quality brown tissue papers (de Assis et al. 2018a; Li et al. 2021).

7.3 Experimental

7.3.1 Materials

Unrefined OCC pulp collected from the high-density stock chest was kindly provided by Greif Inc. The pulp was dewatered to approximately 40% consistency by centrifugation, fluffed, and stored in a cold room at 2°C for future use. The fiber mass distribution and corresponding fiber morphology of the OCC pulp are provided in Table C-1 of the Appendix C.

7.3.2 OCC upcycling treatments

Oxygen delignification (O), alkaline hydrogen peroxide (P), and ozone (Z) treatments were explored for upcycling OCC pulp per the conditions shown in Table 7-1. O treatments were carried out in bomb digesters (cylindrical high-pressure vessels) mounted on a rotating drum and heated by forced convection of air. P treatments were performed in sealed polyethylene bags immersed in a temperature-controlled water bath. Z treatments were applied at high consistency

in a rotating spherical reactor at room temperature to pre-acidified pulp (pH = 2 adjusted with sulfuric acid 4N). A gas flow containing 8 wt% O_3 was produced using a laboratory ozone generator (PCI Ozone & Control Systems Inc., West Caldwell, NJ). Different ozone charges were applied by varying the contact time of the gas flow (1 L/min) with the pulp. Unreacted ozone was trapped in a gas absorption bottle containing potassium iodide solution 1 N and measured iodometrically. The ozone consumption on pulp was calculated by the mass difference between the ozone fed into the reactor and the unreacted ozone. Following each treating condition, the pulp was washed with DI water and filtered through cheesecloth until obtaining a clarified filtrate. In the case of the Z-treated pulp, the pH was adjusted to 7.5 with NaOH (1% w/v) after washing. The washed pulp was centrifuged to approximately 30% consistency and fluffed. An undiluted aliquot of the filtrates was collected for measuring pH. Mass yields were estimated gravimetrically by dividing the weight of oven-dried treated pulp by the initial weight of oven-dried untreated pulp. Mechanically refined OCC pulp was also obtained by means of a PFI-mill (N°312, The Norwegian Pulp and Paper Research Institute, Oslo, Norway) using 1,000, 2,000, and 4,000 revolutions according to TAPPI T 248 sp-00 (2000).

Table 7-1: TCF treatment conditions

Conditions	**O_1**	**O_2**	**O_3**	**P_1**	**P_2**	**P_3**	**Z_1**	**Z_2**	**Z_3**	**R_1**	**R_2**	**R_3**
Consistency, %	10	10	10	10	10	10	30	30	30	10	10	10
Temperature, °C	100	100	100	90	90	90	23	23	23	23	23	23
Time, min	60	60	60	90	90	90	5	10	15	-	-	-
O_2, psi	100	100	100	-	-	-	-	-	-	-	-	-
H_2O_2, %	-	-	-	2	4	8	-	-	-	-	-	-
NaOH, %	2	3.5	5	1.5	3	5	-	-	-	-	-	-
O_3, %	-	-	-	-	-	-	1.4	2.9	4.0	-	-	-
Revolutions, PFI-revs	-	-	-	-	-	-	-	-	-	1,000	2,000	4,000
Filtrate pH	8.4	8.6	8.9	9.6	11.2	11.9	2.7	2.7	2.6	-	-	-

The base case is untreated OCC pulp; Reagent charges are expressed as % of dry pulp weight; O: oxygen delignification; P: alkaline hydrogen peroxide; Z: ozone; R: refining

7.3.3 Pulp characterization

The following procedures were applied for pulp characterization: water retention value (WRV) (TAPPI UM 256 2015), kappa number (TAPPI/ANSI T 236 om-13 2013), freeness (TAPPI T 227 om-99 1999), zero-span breaking length (TAPPI 231 cm-07 2007), and brightness (ISO 2470-1 2016). Zero-span breaking length was determined using a Pulmac zero-span tester (Middlesex, VT). Pulp brightness was measured using a Technidyne Color-Touch X model CTX-ISO (New Albany, IN). Fiber morphology was determined using a fiber quality analyzer (HiRes FQA, OPTest Equipment Inc., Hawkesbury, ON, Canada). The fiber surface chemistry was investigated using X-ray photoelectron spectroscopy (XPS) performed with a SPECS Flex-Mod electron spectrometer (Berlin, Germany).

7.3.3.1 Preparation of handsheets

Handsheets were prepared from chemically and mechanically modified OCC pulps treated according to the conditions shown in Table 7-1. The procedure for forming handsheets corresponds to a modified version of TAPPI T 205 sp-02 (2006). In the proposed method, wet pressing of the paper web is minimized to preserve bulk, as densification yields poor softness and reduces water absorbency of the paper sheet. Each pulp is prepared in a slurry form at 0.3 %wt consistency using tap water for dilution, the slurry required to target a basis weight of 30 g/m^2 is placed in a standard handsheet former (Testing Machines Inc., New Castle, DE), and finally the formed sheet is couched and dried using a cylindrical dryer (Formax 12", Adirondack Machine Co., Gleans Fall, NY) instead of pressed and ring-dried. The operating conditions for the cylindrical dryer were set at 110°C, 1 rpm, and 5 min retention time. Handsheets obtained from this method were not creped.

7.3.3.2 Handsheet testing

Handsheets were conditioned for 24 h under a standard atmosphere of 50% relative humidity and 23°C before testing (ISO 187 1990). The following procedures were applied for evaluation of the physical and mechanical performance of handsheets: basis weight (ISO 12625-6 2005), thickness and bulk (inverse of apparent bulk density) (ISO 12625-3 2005), tensile strength (ISO 12625-4 2005), water absorption capacity (ISO 12625-8 2016), and capillary rise (ISO 8787 2018). Thickness was measured by applying a static load of 2 kPa (digital micrometer, model 49-56, Buchel B.V., Veenendaal, Holland). Tensile strength was determined using an Instron® model 4443 (Canton, MA). The mean pore size was measured by a capillary flow porometer model CFP-1100AEL (PMI Inc., Ithaca, NY). Absorption rate was estimated from the slope of the Lucas-Washburn plots (Figure C-1), considering that the R^2 values were greater than 95% for all the conditions evaluated. The Lucas-Washburn plots were built by plotting the height of the waterfront (h) obtained from the capillary rise as a function of the square-root of time ($t^{0.5}$) as described in detail by Zambrano et al. (2021a).

Softness and in-plane flexibility were assessed with a Tissue Softness Analyzer (TSA, Emtec Electronic GmbH, Leipzig, Germany). The softness evaluation was performed based on the frequency peak centered around 6500 Hz, identified as TS7. The in-plane flexibility (parameter "D" in the TSA assessment) was determined as the displacement of the handsheet upon application of a perpendicular force of 100 mN and 600 mN. A lower TS7 peak height and higher in-plane flexibility are associated with softer tissue paper (Wang et al. 2019). The values reported for basis weight and bulk were obtained from an average of 20 measurements performed on different handsheets. For the rest of the properties, the results reported are the average of a minimum of 7 measurements.

Apparent water contact angles were measured by a sessile drop method using a Phoenix 300 contact angle analyzer (Surface Electro-Optics, Suwon City, Korea). To minimize roughness, swelling and absorptive effects, measurements were performed on the first clear image captured (20 milliseconds after placing the water droplet onto the paper surface). The tangent line-fitting mode was used to estimate the water contact angles from a minimum of five measurements at various locations on the sheet surface.

7.4 Results and discussion

7.4.1 Process related aspects: delignification, brightness and yield of pulp

Figure 7-1 shows the relationship between kappa number, brightness, and yield of pulp resulting from the application of the O, P, and Z treatments. In general, all the treatments promoted delignification of the OCC pulp as indicated by the reduction in Kappa number and the increase in pulp brightness. The extent of delignification and brightness improvement were treatment-dependent and intensified with increasing chemical load. O and Z yielded similar levels of delignification (on average 39% at the highest chemical load) under the conditions evaluated, whereas P resulted in lower levels (24% at the highest chemical load). For a similar level of delignification (kappa number), the Z treatment generated the highest brightness improvement, followed by the P and O treatments, respectively. Compared to the initial OCC, the treated OCC pulps showed a lighter brown color, which has been marketed in finished tissue products as beige, mocha, or latte (Cascades Inc. 2019). This improvement in appearance could thus make tissue papers entirely manufactured from OCC more appealing to environmentally conscious consumers (Barbarossa and De Pelsmacker 2016). The pulp yields were proportional to the degree of delignification and remained above 89% for the different treating conditions. These yields were significantly higher than yields reported for multi-stage upgrading sequences

to bleach OCC pulp that are around 70% (Zambrano et al. 2021a). In addition to more streamlined processing, the more efficient utilization of raw materials highlights another advantage from processing OCC in single-stage treatments rather than multi-stage processes.

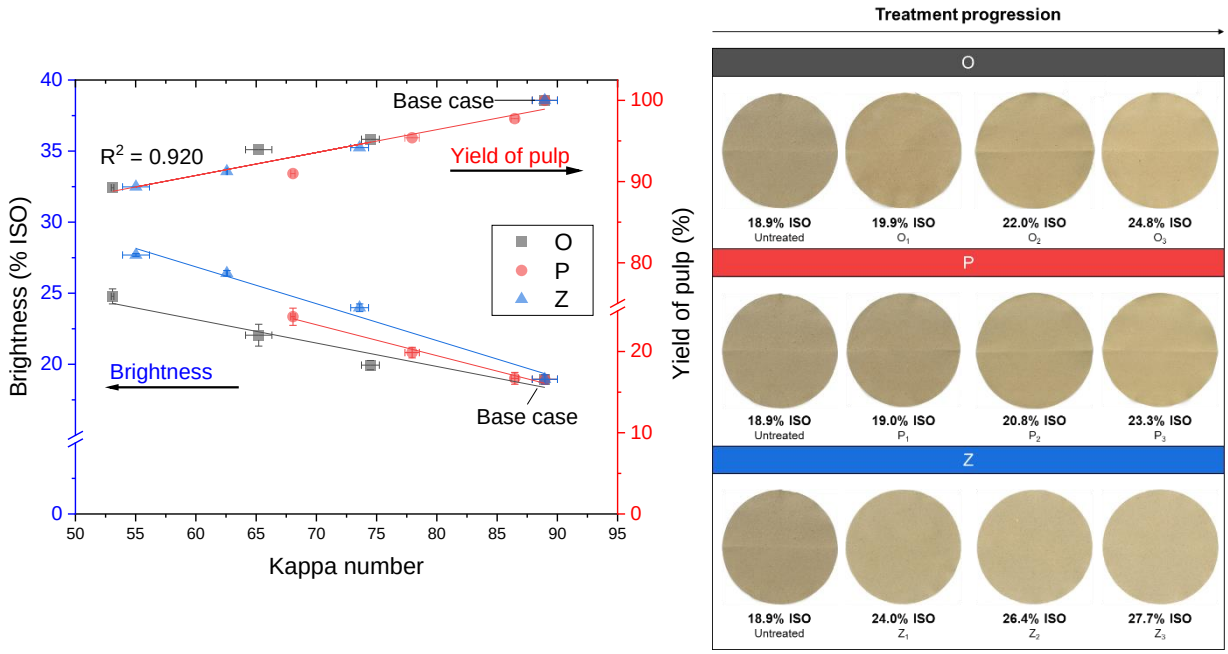


Figure 7-1: Relationship between kappa number, brightness and yield of pulp (left) and evolution in pulp brightness following different treatment conditions (right)

A comparison with previous research on upgrading OCC was performed, as shown in Table 7-2. The properties analyzed were kappa number and brightness. The results obtained in this work are in the range of what has been previously reported, despite the varied nature of OCC and slight differences in treating conditions. Particularly for O and Z treatments, similar delignification rates were achieved compared with Haywood (1994) and Zanuttini et al. (2007). In the case of P treatment, although a higher peroxide load was used, the lower delignification may be related to the likely higher concentration of metals in OCC compared to the virgin liner used by Zanuttini et al. (2009). The negative effect of metals on the performance of the P

treatment is described below. Dionne and Hoyos (1995), who also reported lower brightness gains with increasing metal contamination following P treatments, used a chelation stage and sodium silicate to partly neutralize the catalytic activity of metal ions and increase the brightness gains.

Table 7-2: Comparison of the results obtained in this work with the values reported in the literature on O, Z, and P treatments to upcycle OCC

			Kappa number			**Brightness (% ISO)**		
Treatment	Author	Conditions	Initial	Final	Delignification (%)	Initial	Final	Gain (% ISO units)
O	Haywood (1994)[a]	100 psi O_2 - 4.5% NaOH	92.3	56.0	39	18.3	22.2	3.9
	Danielewicz et al. (2011)	100 psi O_2 - 6% NaOH	103.0	65.0	37	NR	NR	-
	This work	100 psi O_2 - 5% NaOH	89.0	53.1	40	18.9	24.8	5.9
Z	Zanuttini et al. (2007)	0.8% O_3	85.0	75.0	12	NR	NR	-
	Abadie-Maumert et al. (1985)	1.6% O_3	NR	NR	-	16.6	19.1	2.5
	This work	1.4 % O_3	89.0	73.6	17	18.9	24.0	5.1
P	Zanuttini et al. (2009)[b]	1.5% H_2O_2 - 5% NaOH	91.6	72.0	21	NR	NR	-
	Dionne et al. (1994)[c]	1.5% H_2O_2 - 1% NaOH	65.0	NR	-	30.8	36.6	5.8
	This work	4% H_2O_2 - 3% NaOH	89.0	77.9	12	18.9	20.8	1.9

[a] 1% MgSO4 added during treatment; [b] The starting material was industrial liner from virgin unbleached softwood kraft pulp; [c] Pulp pretreated with 0.4% DTPA and 5% sodium silicate added during P to stabilize the alkaline peroxide bleach liquor; NR: not reported

7.4.2 Effect of TCF treatments on fiber chemistry

The relationship between kappa number and fiber surface O/C ratio along with the surface functional group composition of the treated fibers are presented in Figure 7-2a and 7-2b, respectively. Overall, the removal of lignin generated an increase in the surface O/C ratio, which arises from the higher exposure of carbohydrates, oxidation of lignin structures and extractives removal (Hultén and Paulsson 2003; Laine et al. 1999; Risén et al. 2004). This is shown by the higher concentrations of carbons C2 (C−O) and C3 (C=O, O−C−O) and the reduction in carbon C1 (C−C) that indicates a decrease of the surface coverage by lignin and extractives (Figure 7-2b) (Laine et al. 1999). There was also a reduction in carbon C4 (O−C=O), attributed to the removal of carboxylic groups from the fiber surface with the lignin (Lin et al. 2014). Consequently, the fiber hydrophilicity was improved, as demonstrated by the higher WRV

(Esteves et al. 2021) and lower contact angle in the treated OCC pulps in comparison with the untreated pulp (Figure 7-2c and 2d).

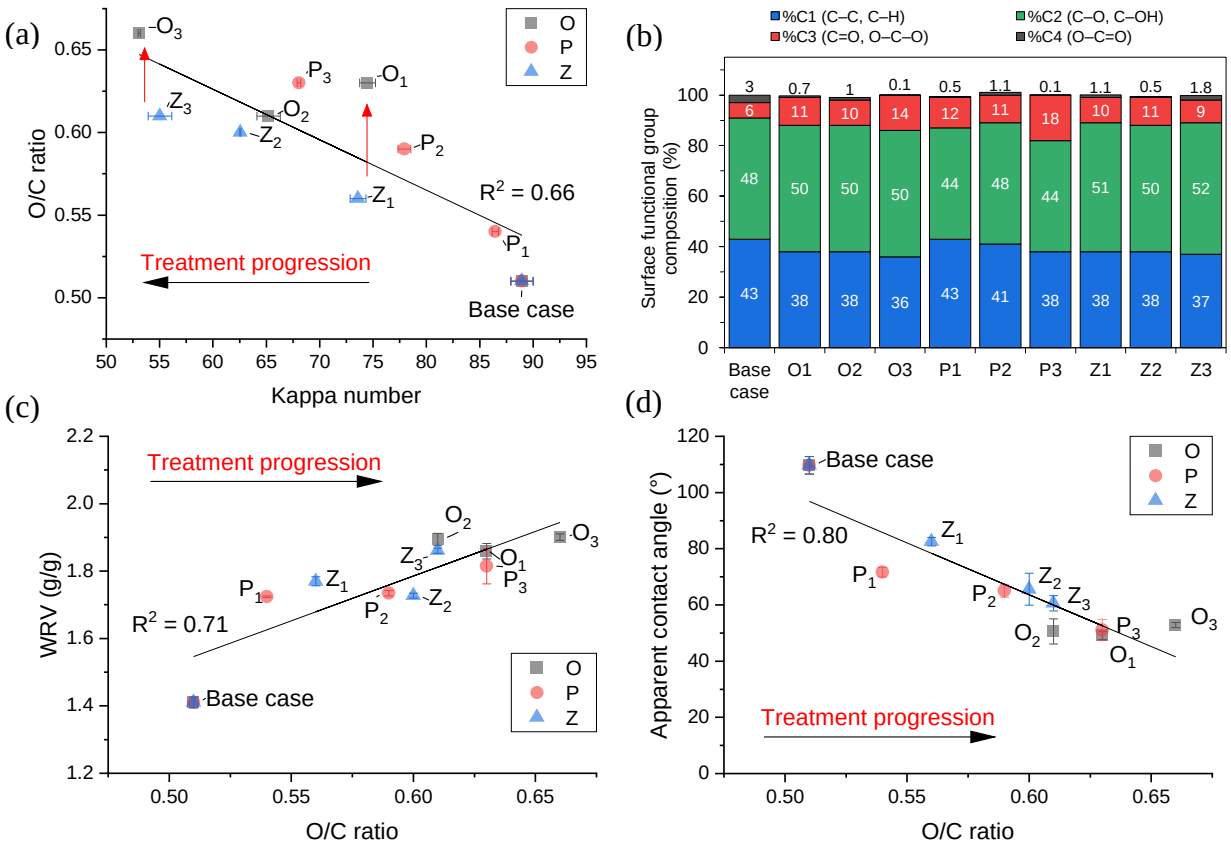


Figure 7-2: (a) Relationship between kappa number and O/C ratio, (b) surface functional group composition of treated pulps, (c) relationship between O/C ratio and water retention value (WRV), and (d) relationship between O/C ratio and apparent water contact angle

Although all the processes increased the O/C ratio, changes in O/C ratio among treatments compared at a similar lignin content suggest differences exist in the residual structures on the fiber surface (red arrows in Figure 7-2a). WRV also showed a poor correlation with kappa number (R^2 = 0.53, Figure C-2a in Appendix C), which indicates that fiber hydrophilicity has a higher dependency on the extent of fiber oxidation than lignin content. Depending on the reactivity with different lignin structures, each treatment generates an array of chemical

functionalities on the fiber. Ozone reacts with all aromatic structures of lignin increasing carboxyl groups (C4) and some carbonyl (or O−C−O, C3) groups, which result in the formation of muconic acid and quinonoid structures. The cleavage of conjugated double bonds in the side chains also generates carbonyl species. Oxygen reacts with structures having free phenolic hydroxyl groups, converting them into carboxylic acids, such as muconic acid structures. Hydrogen peroxide attacks selectively certain functional groups such as carbonyls and some aliphatic double bonds (Gierer 1986). In addition, there are differences in the quantity of surface lignin and surface extractives removed by each TCF treatment (Laine et al. 1999). For the particular case of Z-treated pulps, the overall lower O/C ratio may be related to the formation of oxidized lignin structures that are not readily soluble due to the acid pH of the treatment and the lower effect that ozone has on reducing the surface concentration of extractives (Laine et al. 1999; Pouyet et al. 2014). Further research is needed to better understand the amount of surface lignin and surface extractives that give rise to the differences in surface O/C ratio following the treatments. This task, which is highly complex considering the variety of impurities present in OCC due to the recycling process, was beyond the scope of this work.

In relation to brightness, the generation of carbonyl groups succeeding the application of oxidative treatments is one of the main mechanisms of how some color can persist in the pulp (Gierer 1997; Pipon et al. 2007). The Z treatment resulted in a fiber surface exhibiting a slightly higher concentration of carbon C4 (O−C=O) (Figure 7-2b). This suggests that carbonyl groups present in colored intermediate species known to form during ozonation were further oxidized into carboxyl groups (Pipon et al. 2007), resulting in the higher brightness observed in Z-treated pulps (Figure 7-1). In P processes, the persistence of some chromophores on the fiber surface has been related to the hydroxylation of quinones and the generation of complex chromophores that

make color removal more difficult (Argyropoulos et al. 1995; Pipon et al. 2007). The latter may explain the lower pulp brightness despite the high quantities of peroxide charged. Likewise, oxidation of lignin with reagents of low oxidative potential such as oxygen results in the formation of chromophore species containing carbonyl groups detrimental to brightness (Gierer 1997).

When evaluating the effectiveness of the treatments at lignin removal, the lower delignification from P compared to O and Z (Figure 7-1) may be related to the reduced efficiency of H_2O_2 in the presence of metal ions contained in the pulp (e.g., Fe, Mn, and Cu), which hinder the activity of perhydroxyl ions (HOO^-), the active bleaching species, leading to the catalytic decomposition of HOO^- into oxygen (Dionne and Hoyos 1995). The level of metals in OCC is considerably high (Danielewicz and Surma-Ślusarska 2015; Dionne and Hoyos 1995). Therefore, pretreatment of the pulp with chelating agents (DTPA or EDTA) and sodium silicate has been proposed to partly neutralize the catalytic activity of metal ions and increase the brightness response after peroxide bleaching (Dionne and Hoyos 1995; Xu et al. 1994). Transition metals also lead to a reduction in the efficiency of Z treatments resulting from the ozone decomposition into oxygen (Brolin et al. 1993); however, compared to the P treatment, this effect seems to have had a lower impact considering the higher extent of delignification obtained from the ozonation.

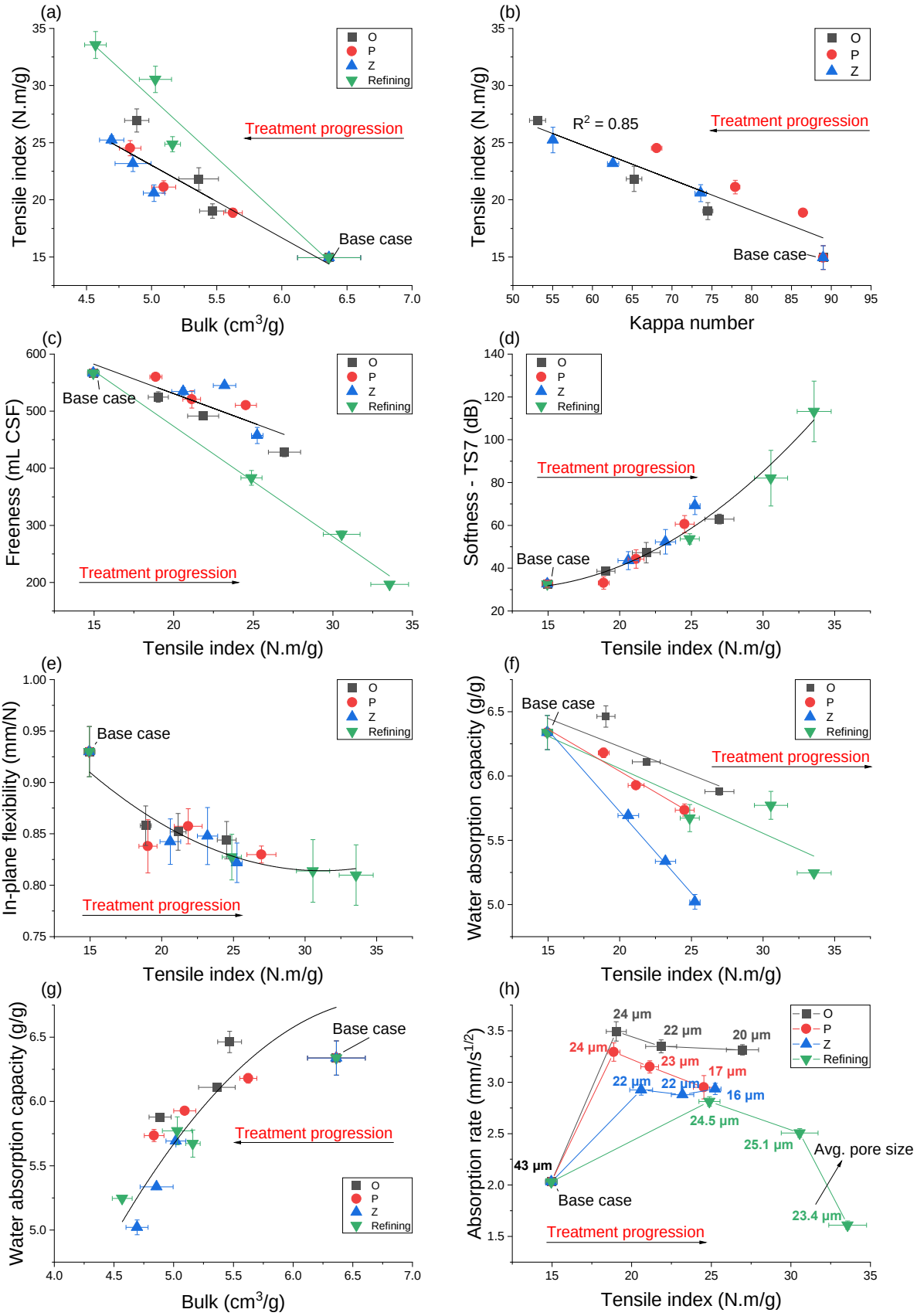
It has also been reported that the catalytic action of transition metal ions substantially promotes the formation of hydroxyl free radicals during O, P, and Z treatments. Such radicals are non-selective species, which attack both lignin structures and carbohydrates. This is critical during bleaching of low lignin-containing pulps (Kappa number < 30) since the cellulose degradation by random chain cleavage reactions leads to a loss of pulp strength (Brolin et al. 1993; Chirat and Lachenal 1997; Dang and Genco 2002). In this work, no significant changes in

pulp strength were observed following the treatments as indicated by the zero-span tensile strength (P-value = 0.089, $\alpha = 0.05$, Figure C-3). Therefore, the results suggest that the high reactivity of hydroxyl free radicals did not have a detrimental effect on pulp strength, implying that selectivity towards lignin is favored when treating high lignin-containing pulps (Kappa number > 50). The latter has important practical implications since it shows that pulp pretreatments intended for improving selectivity (e.g., chelation, acid washing) are unnecessary when upcycling OCC through oxidative treatment methods even though they could have a beneficial impact on reducing the wasteful decomposition of bleaching chemicals.

7.4.3 Tissue-making properties

Tissue papers are multidimensional consumer products with properties that need to be balanced against one another (de Assis et al. 2020). From a process standpoint, a minimum functional strength is required to ensure proper machine runnability during tissue-making, converting operations, and adequate mechanical integrity for the end-user. Such target strength is achieved at the expense of negative impacts on other tissue and slurry properties, e.g., bulkiness, softness, water absorbency, and freeness, also essential for the product's overall performance and machine productivity. Therefore, product development operations strive to develop strength while minimizing the extent of such unfavorable impacts (Gonzalez et al. 2020; Pawlak and Chan 2019). Figure 7-3 shows the tradeoff between tensile index and other tissue properties evaluated for OCC pulps chemically treated. The tissue properties from unbleached OCC pulp mechanically treated are also shown to illustrate the advantages and disadvantages of each upgrading method (chemical vs. mechanical). Figure C-4 shows SEM images of the surface and cross-section of sheets made from chemically and mechanically treated OCC pulps at the highest treatment level.

Figure 7-3: Tradeoff between tissue properties of chemically (O, P, Z) and mechanically (refining) treated OCC pulp. The numbers beside the data points in (h) are the average pore size of the sheets, the standard error for the base case was ± 3.2 μm, the pooled standard error for the rest of measurements was ± 1.8 μm. The lines are guides to the eye.


(a)
Tensile index (N.m/g)
Bulk (cm3/g)
O
P
Z
Refining
Treatment progression
Base case
(b)
Tensile index (N.m/g)
Kappa number
R2 = 0.85
Treatment progression
Base case
(c)
Freeness (mL CSF)
Tensile index (N.m/g)
Base case
Treatment progression
(d)
Softness - TS7 (dB)
Tensile index (N.m/g)
Treatment progression
Base case
(e)
In-plane flexibility (mm/N)
Tensile index (N.m/g)
Base case
Treatment progression
(f)
Water absorption capacity (g/g)
Tensile index (N.m/g)
Base case
Treatment progression
(g)
Water absorption capacity (g/g)
Bulk (cm3/g)
Base case
Treatment progression
(h)
Absorption rate (mm/s1/2)
Tensile index (N.m/g)
24 µm
22 µm
20 µm
24 µm
23 µm
17 µm
22 µm
22 µm
16 µm
24.5 µm
25.1 µm
Avg. pore size
43 µm
Base case
23.4 µm
Treatment progression

7.4.3.1 Tensile strength and bulk

Figure 7-3a shows the tradeoff between bulk and tensile index. All the treatments applied resulted in densification of the paper web, as indicated by the reduction in bulk. Such consolidation in the sheet structure was associated with an increase in tensile index. For chemically treated pulps, the development of strength in the fiber network was correlated with the extent of lignin removal (Figure 7-3b). The reduction in lignin content enables swelling of the fibers, which increases the internal and external fibrillation of the cell wall, leading to better flexibility and conformability, and thus a larger bonded area between fibers and a higher fiber-fiber joint strength (Clark 1969; Esteves et al. 2021; Laine and Stenius 1997a). Although it has been reported that for bleached fibers higher swelling results in higher strength properties, no correlation between WRV and tensile index was observed in this work (Figure C-2b). Similar findings were described by Esteves et al. (2021) for fibers with kappa numbers ranging from 23 to 57, which exhibited similar tensile strength despite significant differences in WRV. Therefore, even if high degrees of swelling are attained in unbleached fibers, the lignin content seems to be the primary factor limiting high fiber flexibility and conformability, elements needed to render a denser paper web with high strength (Laine and Stenius 1997b). In the case of mechanically treated pulps, the increase of strength stems from the surface fibrillation and delamination of the fiber cell wall upon application of the mechanical action that increases fiber flexibility, collapsibility, and bonding ability (de Assis et al. 2019).

Compared to sheets from chemically treated pulps, refined pulps of higher kappa number resulted in sheets with higher bulk at a given tensile index (Figure 7-3a). Similar results were obtained for sheets from chemically treated pulps for a given treatment. This can be explained by the higher rigidity and lower conformability of fibers having a higher lignin content, which

results in bulkier fiber networks. Sheets from refined pulps also showed a higher tensile index at a given bulk. This occurrence, which has also been reported elsewhere (Esteves et al. 2021; Nordström 2014), could be related to the straightening of the fibers imparted by mechanical action, as shown by the reduction in curl and kinks of refined fibers (Table A2). More straight fibers will have a better stress distribution upon loading, resulting in a higher tensile strength (Dasgupta 1994; Page 1969; Page et al. 1985). Conversely, the chemical treatments, which did not significantly impact the fiber morphology, resulted in fibers with higher curl and kinks than the mechanically treated fibers. Another factor likely contributing to the higher strength of mechanically treated pulps could be associated with their higher concentration of fine particles (Table A2), which helps to reinforce the fibrous assembly by increasing the total bonded area within the structure (Gharehkhani et al. 2015; Taipale et al. 2010; Zambrano et al. 2021b).

All the treatments evaluated enabled strength levels before creping that are suitable to match the strength target of commercial bleached tissue products made from virgin and recycled fibers. The latter considering that creping reduces strength between 63% and 74% (de Assis et al. 2020; Gonzalez et al. 2020) and that the average tensile index for bath tissue and paper towels in the consumer segment are ca. 5.9 N.m/g and 7.8 N.m/g, respectively (de Assis et al. 2019; Wang et al. 2019). These results show the high strength inherent to OCC pulp and suggest that the upcycled pulp could be incorporated in a tissue-making operation without affecting strength specifications.

7.4.3.2 Freeness

Figure 7-3c shows the variation of freeness with tensile index. The increase in tensile index induced by the treatments was accompanied by a reduction in water drainage from the fiber slurry, as shown by the decrease in freeness. Such a reduction is related to the densification of the wet fiber mat that stems from the increase in fiber conformability, which increases the flow resistance through the capillaries, hindering the passage of water (Hubbe and Heitmann 2007). In addition, the increase in fiber hydrophilicity of the chemically treated pulps compared to the untreated pulp, as reflected by their higher WRV (Figure 7-2c), also contributes to the lower drainage. A higher WRV implies a better affinity of water towards the cellulosic fiber, suggesting that larger amounts of water get "trapped" into the fiber cell wall and attached to the fiber surface during the draining process.

From a practical standpoint, the development of sheet strength needs to be achieved while minimizing adverse effects on drainage, i.e., freeness losses. In tissue making operations, a high drainage rate is desired since it enables high machine speed, high productivity rates, and reductions in drying energy and mechanical dewatering (lower pressing of the wet web translates into higher sheet bulk and better product quality) (de Assis et al. 2018b; Gonzalez et al. 2020). When comparing the chemically treated pulps with the mechanically treated pulps, the former yielded higher drainage over a wide range of tensile index values. The lower drainage of the latter can be primarily attributed to the increase of fines content in the pulp with refining. In addition to increasing the overall surface area of the fiber slurry, fine particles, which are generated from the removal of the fiber cell wall's primary layer and fiber cutting (Gharehkhani et al. 2015), increase the tortuosity of the flow channels, hindering the release of water from the wet mat (Zambrano et al. 2021b). Conversely, the fines content in the chemically treated pulps

remained constant across the different treatments and conditions evaluated (Table A2). A lower fines content is generally preferred since it prevents runnability issues related to low drainage, poor solids retention during sheet formation, particle build-up in process waters, higher consumption of functional additives, and higher drying energy requirements (Hubbe and Heitmann 2007). Therefore, the higher drainage of the chemically treated pulps reflects one important advantage of these pulps over the mechanically treated ones.

7.4.3.3 Softness

Figure 7-3d shows the tradeoff between softness and tensile index. These properties were inversely correlated, i.e., the strength development resulted in reduced softness (as reflected by the increase in TS7). The inverse relationship between softness and strength is a common phenomenon widely reported in the literature (de Assis et al. 2019; Chang et al. 2018; Fišerová et al. 2019; Hollmark and Ampulski 2004; Prinz et al. 2020; Wang et al. 2019; Zambrano et al. 2021b). Interestingly, differences in the surface chemistry of the fibers, considering the different nature of the treatments applied, did not seem to have an effect on the softness-strength relationship. Instead, the results indicate that the mechanisms of softness in tissue paper are primarily governed by the physical features of the fiber network. Accordingly, the reduction in softness can be explained by the densification of the fibrous assembly, which causes an increase in the structure's flexural rigidity (Figure 7-3e). A higher flexural rigidity, which translates into a higher intensity of vibrations and thus a higher TS7 peak, is associated with a greater resistance of the tissue sheet to be crumpled by the hand, a feature related to a lower perceived softness (Hollmark and Ampulski 2004; Lyne 1950).

7.4.3.4 Water absorption capacity

The performance of a tissue paper relating to its ability to pick up and retain fluids is dictated by the absorption capacity and the absorption rate. The former relates to the amount of fluid that the fibrous structure can store, whereas the latter accounts for the speed at which the fluid can penetrate into the structure (Zambrano et al. 2021a).

Figure 7-3f depicts the tradeoff between water absorption capacity and tensile index. Unlike softness, which was primarily governed by physical properties of the fiber network, absorption capacity showed variations based on the type of treatment applied. This indicates that both components, viz. structural and chemical characteristics of the fibrous assembly, play a critical role in determining the absorbency features of the paper web. Therefore, differences in absorption capacity observed among treatments may be explained based on these two characteristics.

Effect of structural components of the paper web

In general, there was a reduction in absorption capacity compared to the untreated OCC. From a structural standpoint, the reduction in the bulkiness of the paper web following the treatments is linked to a reduction in the pore volume within the fibrous assembly that is available to absorb and hold water. Several authors have also reported reductions in absorption capacity, which are proportional to the degree of densification of the structure (de Assis et al. 2019; Dhiman and Chattopadhyay 2020; Zambrano et al. 2021b). Accordingly, the higher bulk of the sheets made from O-treated pulp may explain, to a certain degree, their higher absorption capacity compared to sheets made from P and Z-treated pulps that showed lower bulk, respectively (Figure 7-3g). Overall, the absorption capacity of sheets from high lignin-containing OCC was similar to that of sheets from fully bleached OCC (5.8 g/g) (Zambrano et al. 2021a),

which can be attributed to the higher bulk (+5.2%) of the former that compensates for their lower swelling ability of the bleached fibers. A detailed explanation of the effect of the lignin content on absorption capacity is provided by Zambrano et al. (2021a).

Effect of fiber wettability

From a fiber chemistry standpoint, it is essential to consider the fiber wettability towards water since this aspect provides an indication of the water's ability to penetrate and be retained within the fiber upon swelling of the cell wall (Hubbe et al. 2015; Laine and Stenius 1997a; Maximova et al. 2004). The apparent contact angle of water on the cellulosic substrate was used as an indicator of fiber wettability. A reduction in apparent water contact angle was observed following the application of the treatments (Figure 7-2d). Such reduction was accentuated with increasing chemical charges for P and Z treatments. However, this was not the case for the O treatment, which showed an important reduction in contact angle with the lowest chemical charge applied and then minor differences upon the progression of the treatment. The enrichment of the fiber surface in hydrophilic moieties (Figure 7-2b) may explain the remarkable reduction in contact angle of the treated pulps (up to 55%) in comparison with the untreated OCC with higher lignin content. It is important to highlight that the term "apparent" was adopted in accordance with previous literature (Hubbe et al. 2015; Kutnar et al. 2012; Rossi et al. 2012) since the rough, porous, swellable, and absorptive nature of the cellulosic substrates, makes the measurements difficult to be regarded as ideal or equilibrium quantities (Kamdem and Riedl 1992).

Oxygen delignification generated pulps with the lowest water contact angle among the treatments evaluated (Figure 7-2d). Hence, in addition to the higher bulk, the highest wettability of the O-treated pulps towards water may explain the higher absorption capacity exhibited by

these sheets. Likewise, the lower wettability of Z-treated pulps, which also showed the lowest sheet bulks, may be the reason for their lower absorption capacity. Sheets from P-pulp with intermediate contact angles and bulks showed an absorption capacity that was between the absorption capacities obtained from the previous pulps. The higher contact angle observed for the Z-treated pulp may be related to the presence of oxidized lignin fragments that failed to solubilize given the acidic pH of the ozonation and remained in the pulp even after washing, as previously mentioned (Pouyet et al. 2014; Tripathi et al. 2020).

Compared to the sheets made from mechanically treated pulp, the chemically-treated pulps did not show major advantages in terms of absorption capacity. These results suggest that, for the set of conditions evaluated, the absorption capacity is primarily governed by the structural characteristics of the paper web (pore volume) rather than the chemical characteristics (fiber chemistry). These findings align with previous works, where most of the absorption capacity was ascribed to the pore volume of the paper web (de Assis et al. 2019; Dhiman and Chattopadhyay 2020; Zambrano et al. 2021a). Conversely, the improvement in fiber wettability derived from the chemical treatments had important repercussions on the absorption rate, as described in the following section.

7.4.3.5 Water absorption rate

In our previous work, we reported that although mechanical refining could be regarded as a suitable treatment for developing strength of OCC, the limited absorption rate of tissue sheets from refined OCC made this pulp non-competitive against bleached OCC pulp (4.2 $mm/s^{0.5}$) and deinked pulp (4.6 $mm/s^{0.5}$) with higher rates (+81% and +99%, respectively). Therefore, this was a feature requiring improvement, should the utilization of OCC be considered for the

manufacture of high-performance tissue grades, particularly paper towels (Zambrano et al. 2021a).

Figure 7-3h shows the tradeoff between absorption rate and tensile index. Overall, the absorption rate of chemically treated pulps was significantly higher in comparison with the untreated and mechanically refined OCC pulps (+55% and 36% on average, respectively). Despite the increase in absorption rate, bleached OCC and DIP still displayed higher absorption rates than the chemically treated pulps (+33% and 46%, respectively), which is expected considering the lignin-free nature of bleached OCC and DIP. However, the treatments applied allowed reducing by 48% the initial difference observed between refined OCC and bleached OCC and by 53% the one between refined OCC and DIP. Hence, it is demonstrated that the treatment methods proposed herein can produce OCC pulps with improved absorbency rates, highlighting the potential that tailoring the fiber chemistry has on enhancing absorbency features of high-lignin containing pulps.

The improvement observed in absorption rate was primarily related to the increase in fiber wettability towards water as indicated by the reduction in contact angles following the treatments (Figure 7-2d). From the standpoint of surface interactions, higher exposure of polar groups, primarily C−OH and C=O, present in cellulose and hemicellulose, as well as oxidized lignin structures, increases the wettability of the fiber by water (Pipon et al. 2007; Yang et al. 2003). O-treated pulps showed the highest absorption rates among the chemically treated pulps, which may be ascribed to the higher fiber wettability (lower contact angle) obtained following this treatment. It is worth noting that the major benefits in absorption rate were obtained with the lowest chemical load applied for each treatment. Unlike tensile strength, which greatly benefited from the lignin removal (Figure 7-3b), no additional improvements were obtained in absorption

rate from extended delignification and increased fiber hydrophilicity. Conversely, there was a slight reduction in absorption rate with treatment progression. The increase in fiber wettability was accompanied by a reduction in the fiber network's pore size (Figure 7-3h), which is known to hinder wicking due to an increase in viscous drag (Aberson 1969). The results suggest that such reduction in pore size was the effect dominating the wicking mechanism, and thus further increasing the fiber wettability is needed to compensate for the reduced pore size. Zambrano et al. (2021a) reported a significant increase in the absorption rate of OCC pulp having contact angles below 30° despite the lower pore size of those sheets (between 15.7 μm and 18.9 μm) compared to the ones obtained in this study.

The absorption rate of refined OCC showed a particular behavior with an increase followed by a reduction as the strength of the fiber web was developed. This occurrence, previously reported in the literature (Aberson 1969), is related to the effect of gravity on the vertical wicking process. The densified fibrous assembly obtained at the highest refining level contains a distribution of narrow pores which are little affected by gravity (Figure C-5). By reducing refining, the pores become wider, which causes the observed increase in absorption rate; however, there is a limit where the effect of gravity in the wider pores becomes dominant, and there is a reduction in the absorption rate.

7.4.4 Practical implications for the tissue paper industry and end consumers

A summary of the tissue and slurry properties of upcycled OCCs and some process features of the different treatments studied are outlined in Table 7-3. Overall, the treatments generated OCC pulps with improved strength properties. In the case of chemically treated pulps, the strength development in the tissue sheets was proportional to the extent of delignification. The O treatment led to the best combination of tissue properties (highest absorption capacity and

rate), followed by P and Z (highest brightness). In this regard, the results indicate that O treatment is the best candidate from a product performance standpoint. However, P presents an easier implementation and lower capital cost as compared to O (high-pressure vessels, longer retention times, and high temperature) and Z (vessel under atmospheric pressure, ambient temperature, shorter retention time but higher reagent costs) (De Assis et al. 2017; Esteves et al. 2021; Sharma et al. 2020). On-going work on the kinetics of P for treating OCC indicates that all the peroxide is consumed after 15 min of the reaction starting time. This suggests that this treatment could be carried out directly in the mill hydropulper, which operates at low retention times and medium temperature (Tendulkar et al. 1995). Further research is needed to explore the feasibility of this concept.

Regarding chemical use and effluents, O and P require high charges of NaOH, and thus pulp washing stages and neutralization of liquid effluents (Sharma et al. 2020). Z incorporates a double pH adjustment sequence using HCl and then NaOH (acidic before Z and neutral after Z) (Abadie-Maumert and Soteland 1985; Tripathi et al. 2020). All the treatments generate little to non-polluting effluents that can be processed in conventional wastewater systems (Hubbe et al. 2016; Sharma et al. 2020). In case a more effective utilization of reagents is desired, P also requires pretreating the pulp in a chelation stage due to the high sensitivity of the peroxide to transition metals (Pipon et al. 2007; Zanuttini et al. 2009a).

As for the mechanical treatment, refining offered a good tradeoff between strength and absorption capacity but lower absorption rate and freeness. From a process standpoint, the main advantage of this treatment is the ease of implementation and lack of effluents, in addition to being a state-of-the-art technology (Gharehkhani et al. 2015; Gigac and Fišerová 2008). Therefore, given the pros and cons provided, the selection of the most feasible scenario for a

commercial tissue mill operation requires performing integrated techno-economic and environmental analyses of the different treatments evaluated.

Table 7-3: Summary of tissue properties (evaluated at a given tensile index) and process features of treatments for upgrading OCC into high-performance brown fibers

	Tissue and slurry properties					**Process features** [a]			
Treatment	Softness	Absorption capacity	Absorption rate	Brightness	Freeness	Ease of implementation	Effluent quality	Capital cost	Operating cost [b]
O_2 delignification (O)	++	+++	+++	++	++	+	++	+	+++
O_3 (Z)	++	+	+	+++	++	+	++	+	+
Alkaline H_2O_2 (P)	++	++	++	++	+++	++	++	++	++
Mechanical refining	++	++	+	+	+	+++	+++	+++	+

Legend: +++ Best, ++ medium, + worst; [a] Consulted references: (De Assis et al. 2017; Dence and Reeve 1996; Fisher International 2021; Hubbe et al. 2016; Sharma et al. 2020); [b] Refers to chemical costs for TCF treatments and energy costs for mechanical refining.

The technical feasibility of the treatments explored is not the only variable to consider when evaluating industrial implementation. The possible acceptance of alternative brown tissue products in the market is also of utmost importance. Consumer preferences and consumption of eco-friendly tissue paper have increased in recent years and will continue to grow (Barbarossa and De Pelsmacker 2016). Recent consumer perception trends indicate that more than 80% of consumers have a willingness to pay a price premium for environmentally-friendly packaging (Ketelsen et al. 2020), 55% for items containing biodegradable packaging (increasing from 15% since 2019) (Kitz et al. 2021), and 71.9% for products with certified elements linked to sustainability (Esposti et al. 2021). Studies indicate that some tissue papers labeled as sustainable, which contain only 5–10% non-wood or unbleached fibers and 90–95% of conventional wood fibers, have retail prices 48% higher than traditional products while exhibiting lower performance (de Assis et al. 2018a; Hensley et al. 2020; Wang et al. 2019). In this sense, the characteristics of the processes evaluated (i.e., proven technologies in the pulp and industry), the improvement obtained in the performance of high lignin-containing pulps, and the

increasing trend of consumers to purchase products and services perceived as eco-friendly (Barbarossa and De Pelsmacker 2016), indicate an opportunity to upcycle OCC into alternative fibers suitable for the manufacture of high-performance brown tissue paper.

7.5 Conclusions

This research evaluated chemical and mechanical treatments for upcycling OCC pulp into a suitable feedstock for the manufacture of high-performance brown tissue papers. Among the strategies studied, mechanical refining was the easiest process to develop strength; however, the refined pulp had limitations related to low water absorption rate and drainage of the fiber slurry. It was demonstrated that different total chlorine-free processes (TCF), viz. oxygen delignification (O), alkaline hydrogen peroxide (P), and ozonation (Z), can improve the brightness, absorption rate and freeness of OCC pulp as compared to refining. Moreover, these treatments were also effective at developing the strength of the tissue web and slightly enhancing brightness. The improvement in absorption rate was highly related to the increase in fiber wettability, as indicated by the reduction in water contact angles following the oxidative treatments. The strength development primarily resulted from the removal of lignin, which improves flexibility and conformability of more swellable fibers, leading to a larger bonded area within the fiber network. Among the TCF treatments evaluated, O provided the best tradeoff between water absorbency (capacity and rate), softness, and strength, followed by P and Z. Although this treatment was the best candidate from a product performance standpoint, P is likely a more straightforward process to implement in a tissue manufacturing operation, considering that it also offered an adequate performance tradeoff. Moreover, while strength greatly benefited from lignin removal, the highest absorption rates were obtained with the lowest chemical load applied. This suggests that mild chemical treatments with lower environmental

impact than full bleaching sequences can be used to improve fiber wettability and that the development of the web strength can be achieved via mechanical refining. We believe that the strategies herein presented for upcycling OCC provide an opportunity to produce high-performance pulp from an alternative fiber with the potential to compete in the growing market of unbleached tissue products while also contributing towards efforts in the circular economy.

7.6 Acknowledgments

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8 CONCLUSIONS AND FUTURE WORK

Tissue manufacturers have major challenges in minimizing costs and regulating pricing as a result of the increasing cost of raw materials, the shrinking supply of recycled fibers from high-grade recovered papers, the increase in private label offering, changes in consumer behavior, and growing demand for sustainable products.

This research explored the development and application of strategies to reduce market effects on the profitability and stability of the hygiene tissue business.

The first strategy developed involved the reduction of manufacturing costs by optimizing the utilization of fibers in the tissue product. It was demonstrated that by extensively refining a fiber fraction of the tissue furnish to freeness levels unusual in tissue-manufacturing (between 50 and 390 mL CSF) or to convert it to micro- and nanofibrillated cellulose, it is possible to reduce by 10 to 15% the fiber content of tissue products without impairing product performance. The extensively refined fiber fraction promotes significant strength gains in the tissue sheet that are offset by reducing the fiber content in the sheet until reaching the functional target strength required for proper performance. Moreover, the adverse effects on drainability of the fiber slurry derived from the use of highly refined fibers are counteracted by the addition of a cationic polymer to the fiber slurry, ensuring that total freeness remains at a suitable level for proper machine runnability.

The second strategy explored relied on the use of alternative fibers to improve the flexibility of the fiber supply chain. To that end, old corrugated containerboard (OCC) was upcycled into a high-quality pulp for tissue manufacture. Two OCC pulp grades were produced, namely, bleached OCC and upgraded brown OCC. Bleached OCC (ca. 75% ISO-brightness) was obtained using elemental chlorine-free bleaching sequences ($D_0(EP)D_1P$ and $OD_0(EP)D_1P$).

Overall, bleaching significantly increased tensile index, water absorption rate, and brightness while having adverse effects on bulk and softness and minor impacts on water absorption capacity. Compared to deinked pulp (DIP), bleached OCC showed higher tensile index, higher freeness, and similar absorption capacity but slightly lower brightness and softness. Compared to southern bleached softwood kraft (SBSK), bleached OCC showed higher absorption capacity and similar softness but lower freeness at a comparable tensile index. Mechanical refining was also used as a treatment for upgrading unbleached OCC. Although the refined OCC showed high strength and high absorption capacity, it had limitations regarding a low absorption rate and low freeness. To address this issue, upgraded brown OCC (unbleached) was produced through the application of total chlorine-free treatments, namely, oxygen delignification (O), alkaline hydrogen peroxide (P), and ozonation (Z). The TCF-treated OCCs showed improved absorption rate and freeness as compared to mechanically refined brown OCC. These treatments were also effective at developing the strength of the tissue web and slightly enhancing brightness.

Findings from this second strategy show how OCC can be upcycled into a high-quality pulp suitable for tissue paper manufacture, which can serve three purposes: (1) ensure the availability of recycled fibers in the face of the shortage of high-grade recovered paper, (2) provide an alternative brown fiber with the potential to compete in the growing market of unbleached tissue products, and (3) alleviate the waste management of excess packaging waste in the US.

Ultimately, this research presents alternatives to offset price volatility of market pulps and recycled fibers, thus providing opportunities to drive cost savings, protect profit margins, and create value in the hygiene tissue industry.

Limitations and proposed suggestions for future work follow.

8.1 Fiber reduction in tissue sheets

Although the fiber reduction (FiRe) technology was successfully demonstrated in one tissue mill, tissue-making is a highly complex operation with process variables that can change dramatically from one mill to another. In this respect, to ensure the robustness of the technology in its translation from bench-scale to commercial scale, there are remaining upscaling tasks needing attention:

8.1.1 Validation of FiRe using industrial-scale refining (strength development and fines generation)

The application of FiRe requires the generation of a highly refined fiber fraction. For the technology development, refining conditions were tested using laboratory-scale refiners, obtaining efficient strength development and low fines generation. High strength development is desired as it allows higher levels of fiber reduction. In contrast, the presence of fines is undesirable as it reduces drainage and slows down the tissue machine, hurting production. It is important to validate those similar results hold true when using industrial or pilot-scale refiners having different plate designs, operating conditions (consistency of the feed stream and energy input) and processing different wood fiber species.

8.1.2 Testing of FiRe under different mill process water conditions (anionic demand)

The application of FiRe requires using a cationic polymer to facilitate drainage of the pulp slurry containing the highly refined fiber fraction. The performance of the polymer is very sensitive to the quality of the water in the pulp slurry. Clean water will favor high efficiency of

the polymer, whereas water with a high content of dissolved and colloidal substances (mill process water) will hinder the action of the polymer. FiRe was initially developed using clean tap water. Subsequent exploratory experiments using process water from a recycled tissue mill significantly hindered the performance of the CPAM, requiring very high dosages of polymer to achieve the target freeness values. In this regard, it is necessary to evaluate the performance of different cationic polymers (individually or formulations including more than one) with different process waters (from virgin and recycled operations) by building drainage profiles and measuring anionic demand (optimum polymer dosage) to determine the appropriate dosage/type of polymer for the application of FiRe at commercial scale.

8.1.3 Application of FiRe at commercial scale (drying, machine speed, web breaks, creping/caliper)

The impact of the fiber reduction on the wet strength of the paper web and its influence on web breaks and machine speed is an aspect requiring further investigation. Although it is thought that the reduction in basis weight could have a positive impact on drying energy requirements, there is also a possibility that the increase of fines content in the paper web could be detrimental for drying. Therefore, the influence of applying the FiRe technology on the tissue machine's drying energy needs to be verified. Finally, it is expected that the reduction in the sheet caliper upon application of the technology can be compensated by optimizing the creping operation to produce a coarser crepe structure. This is a concept requiring validation.

8.2 Upcycling OCC for tissue paper applications

The tissue-making potential of both unbleached and bleached OCC was demonstrated using tissue handsheets entirely made from these fibers; however, typical tissue-making slurries are composed of a blend of fibers to impart distinct characteristics to the tissue sheet. In addition, the treatment conditions applied throughout the upcycling processes may not necessarily be commercially scalable. Suggestions for addressing these limitations in future research are proposed below.

8.2.1 Optimization of process-related aspects

An extended oxygen delignification stage can be applied to further reduce the kappa number of OCC (from a Kappa of 90 to 15 – 30) before entering the ECF bleaching sequence. This could optimize the bleaching sequence by reducing chemical charges and potentially help achieve higher brightness (> 75% ISO). Considering the rising interest in TCF bleaching, it is also worth comparing the development of tissue properties of ECF vs. TCF bleached OCC.

In the upcycling process to obtain a high lignin-containing OCC pulp, no additional benefits were attained regarding an improved water absorption rate with increasing chemical charge. In this regard, it was proposed that a high-performance brown OCC pulp could be obtained via a hybrid process (oxidative chemical treatment followed by mechanical refining). In addition, it was suggested that the alkaline hydrogen peroxide treatment could likely be the method with the most straightforward implementation in a recycling operation since the treatment could be carried out directly in the hydropulper. Both concepts need to be validated.

8.2.2 Evaluation of fiber furnish formulations for tissue-making containing upcycled OCC

It was proposed that bleached OCC could be used as a substitute for DIP and SBSK; however, it is important to verify the extent to which these fibers can be replaced without impairing product performance.

Regarding the upcycled OCC with high lignin content, although the oxidative treatments explored improved the water absorption rate of tissue sheets made from these unbleached pulps, it was still lower than sheets made from DIP. Formulating furnishes containing upcycled brown OCC and DIP could help further improve the water absorption rate of the tissue product. In addition, a comparative study on the performance of these recycled products vs. virgin products could elucidate the extent to which these alternatives furnishes could be commercially competitive.

8.2.3 Techno-economic and life cycle analysis on upcycled OCC

It is necessary to perform a techno-economic analysis to evaluate the capital and operating expenditures of upcycling OCC into a tissue-making quality fiber. The scenarios assessed should consider both bleached and unbleached (upgraded) OCC. In addition, given that brown fibers are typically perceived as sustainable, it is essential to evaluate the true sustainability of upcycled OCC pulp to avoid greenwashing (misleading statements for consumers).

APPENDICES

APPENDIX A: Supplementary information to Chapter 4

MICRO- AND NANOFIBRILLATED CELLULOSE FROM VIRGIN AND RECYCLED FIBERS: A COMPARATIVE STUDY OF ITS EFFECTS ON THE PROPERTIES OF HYGIENE TISSUE PAPER

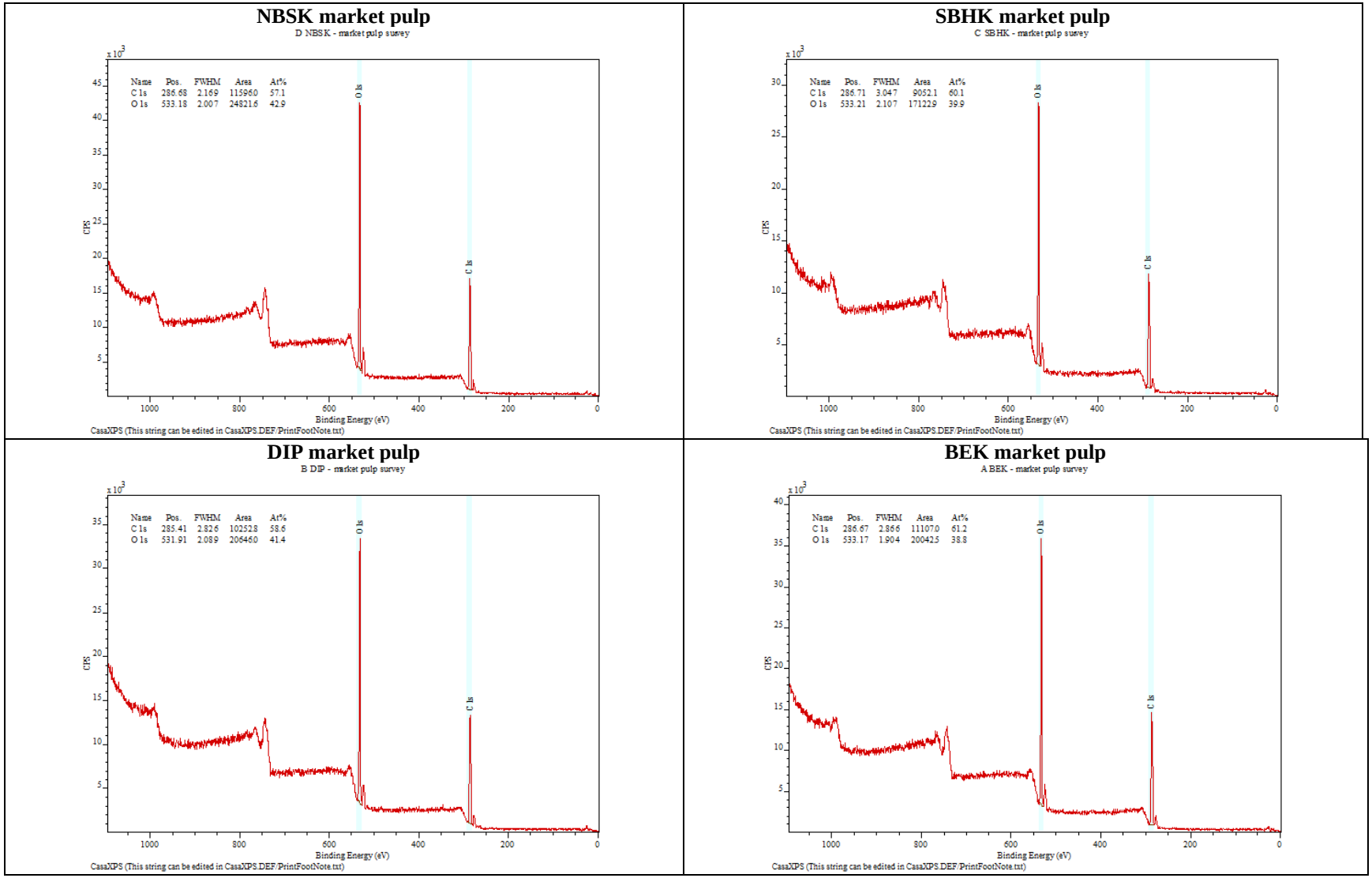

Figure A-1: Low-resolution survey spectra of market pulps

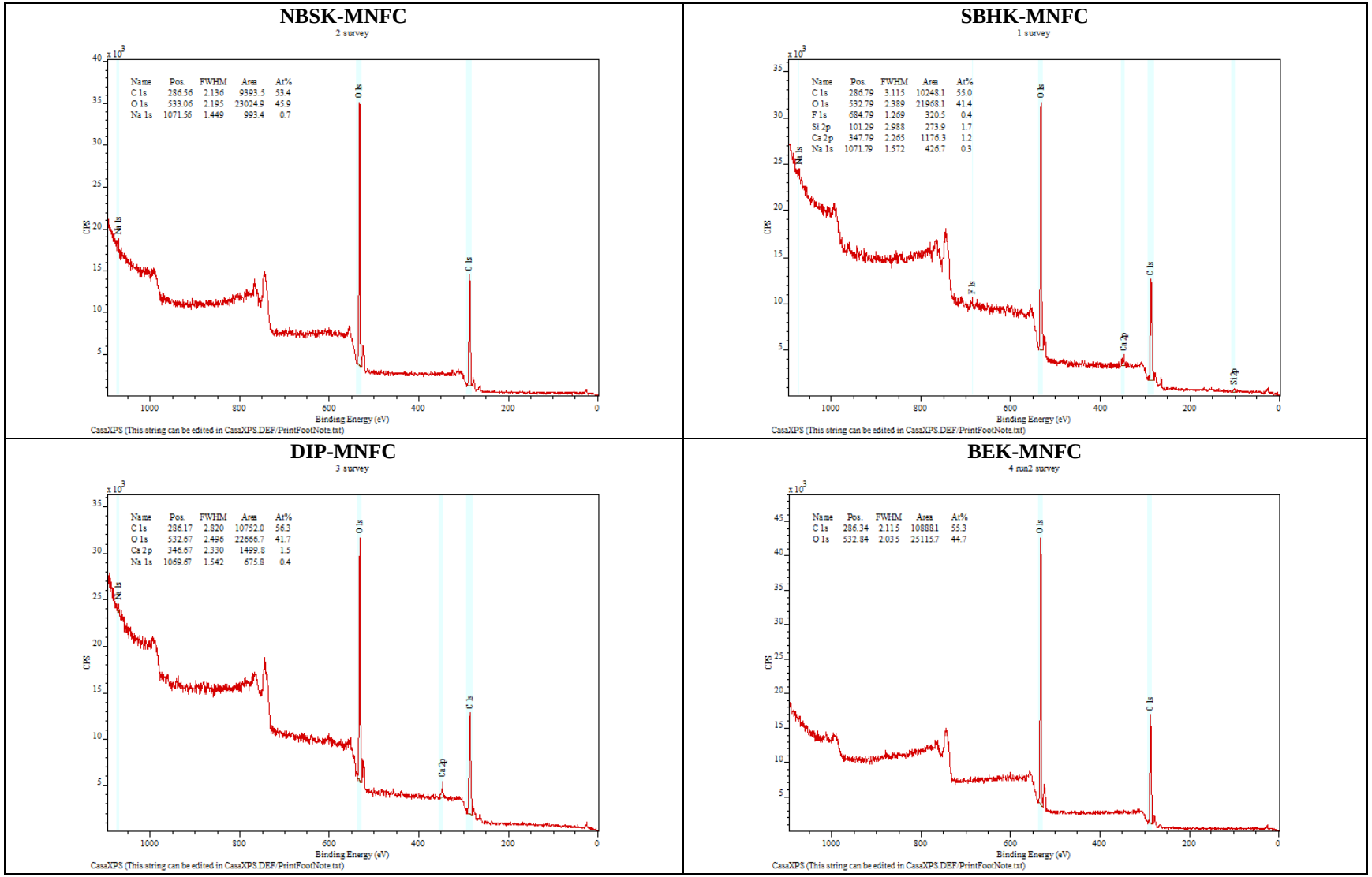

Figure A-2: Low-resolution survey spectra of MNFC dispersions

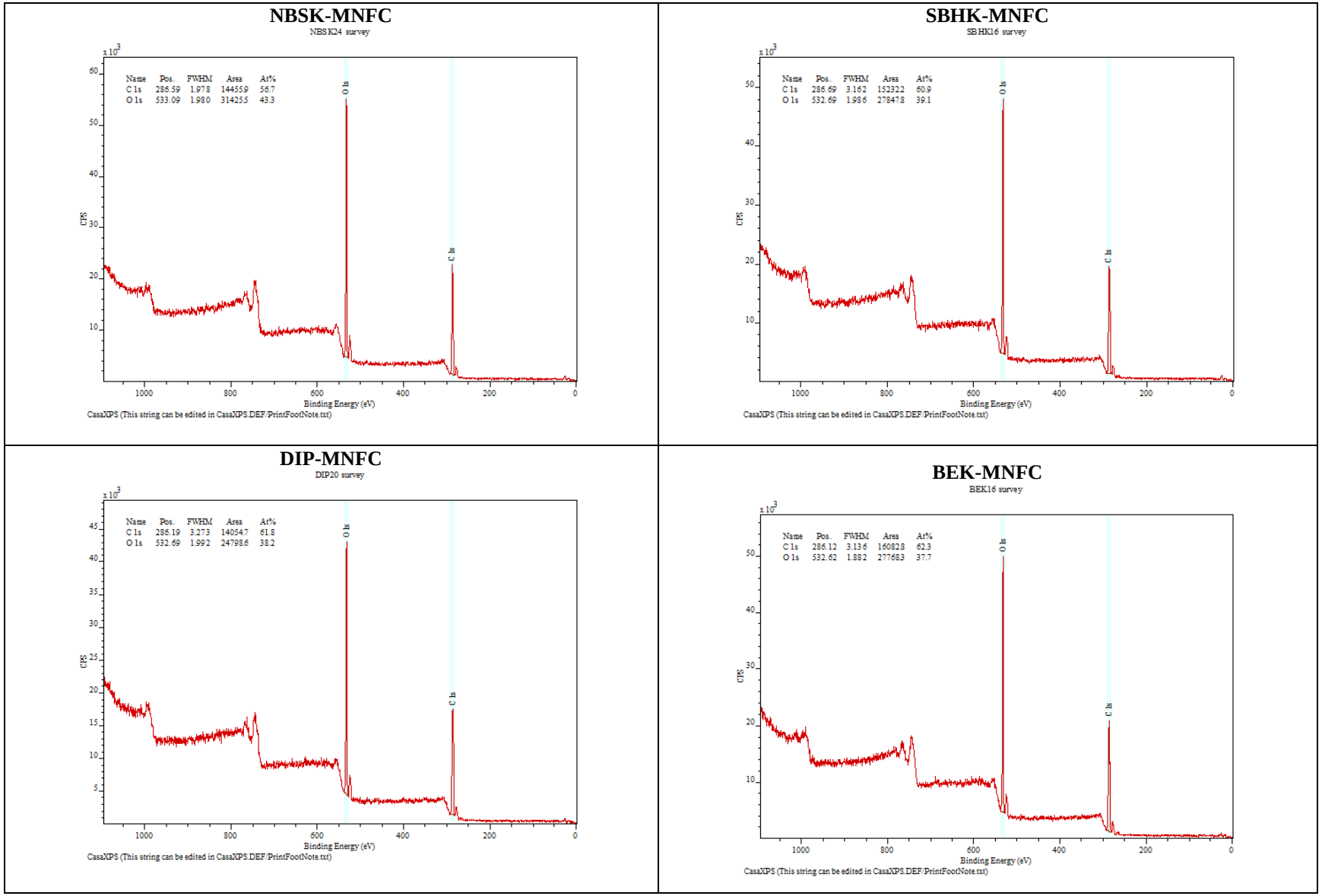

Figure A-3: Low-resolution survey spectra of air-dry MNFC films

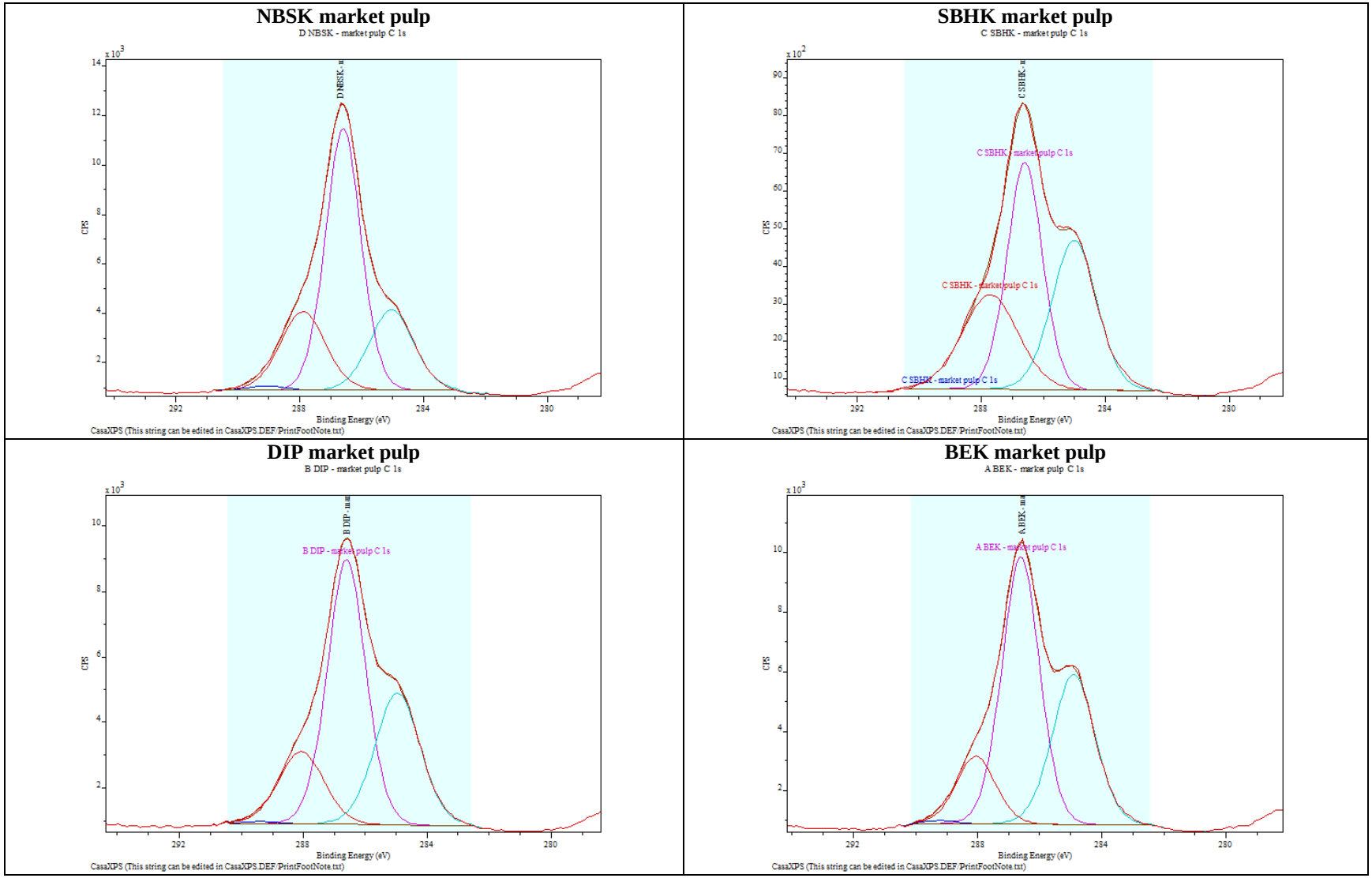

Figure A-4: High-resolution carbon C1 spectra of market pulps

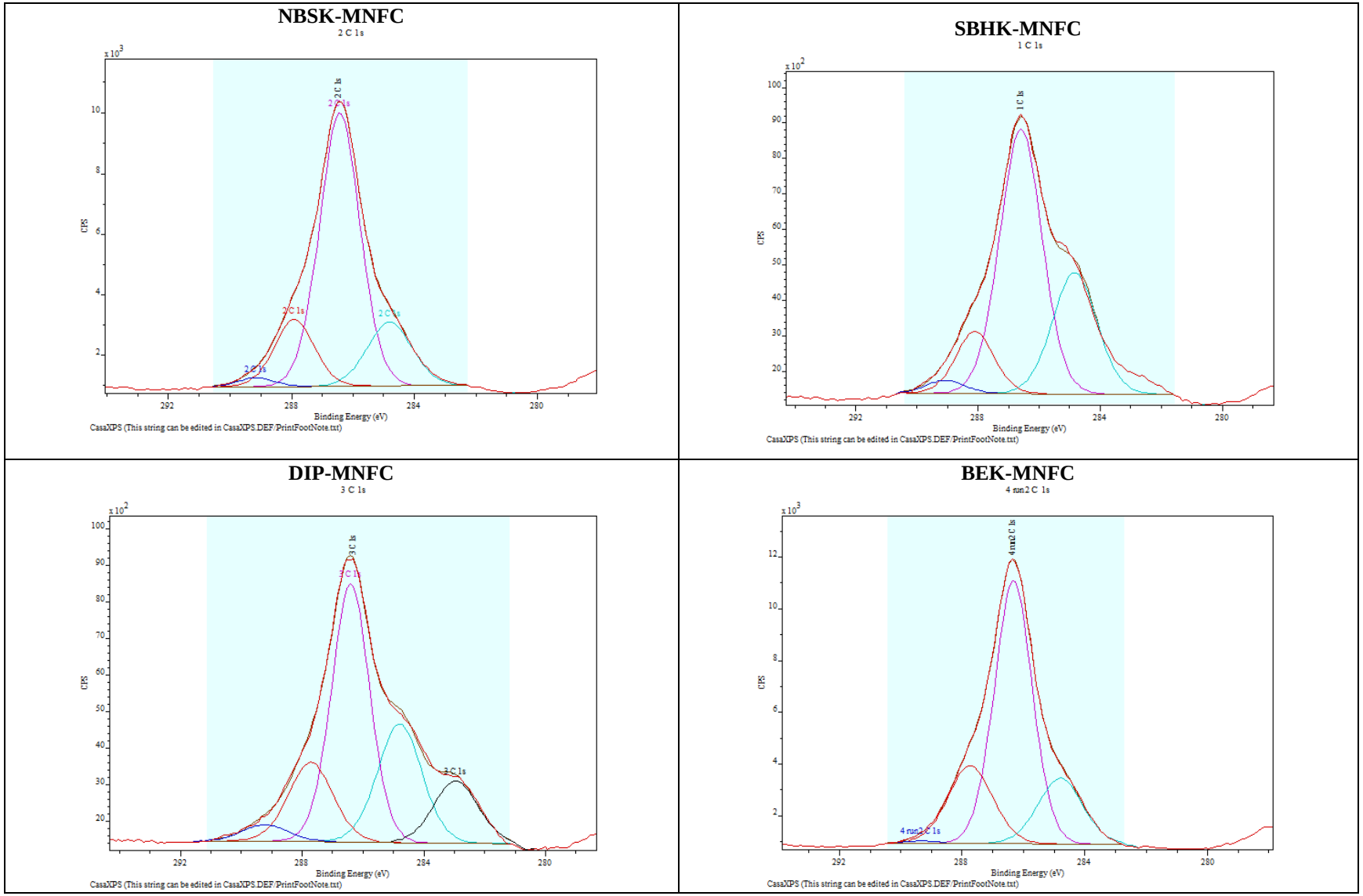

Figure A-5: High-resolution carbon C1 spectra of MNFC dispersions

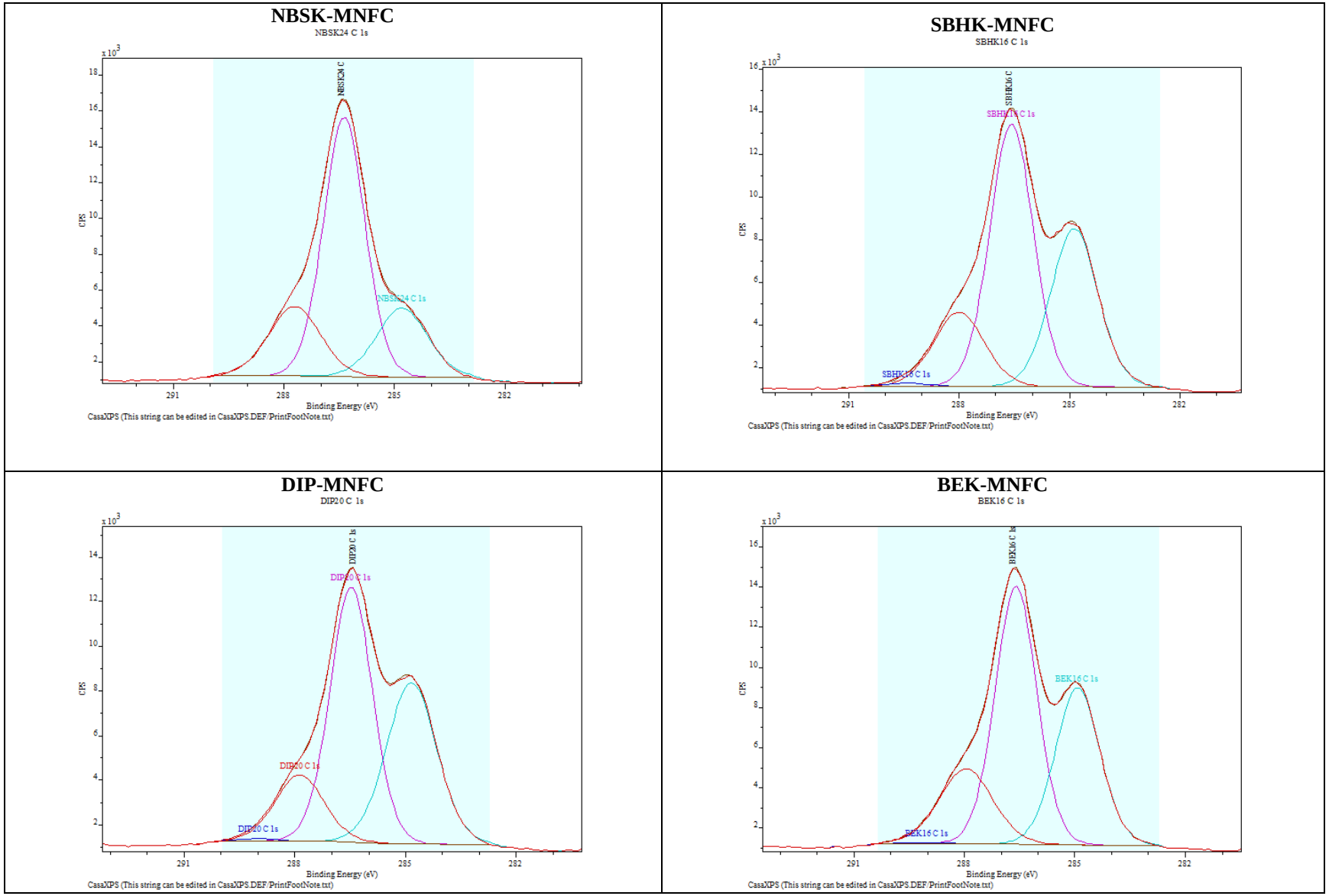

Figure A-6: High-resolution carbon C1 spectra of air-dry MNFC films

Table A-1: Surface functional group composition and O/C ratio of air-dry MNFC films

	% C1 (C–C, C–H)	%C2 (C–O, C–OH)	%C3 (C=O, O–C–O)	%C4 (O–C=O)	
Binding energy (eV)	285.0	286.4	287.9	289.2	O/C
NBSK-MNFC	20	60	20	0	0.76
SBHK-MNFC	33	50	17	0.6	0.64
DIP-MNFC	36	49	15	0.4	0.62
BEK-MNFC	32	49	18	0.3	0.61

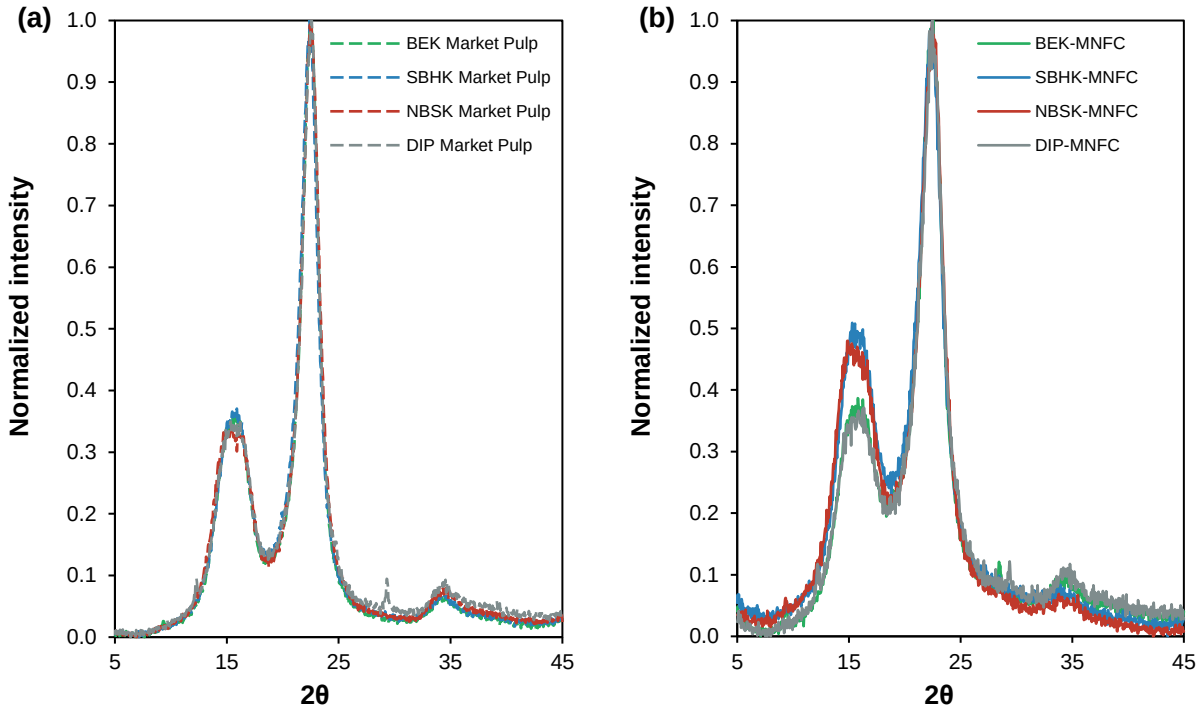

Figure A-7: Normalized XRD patterns of (a) market pulps and (b) corresponding MNFCs

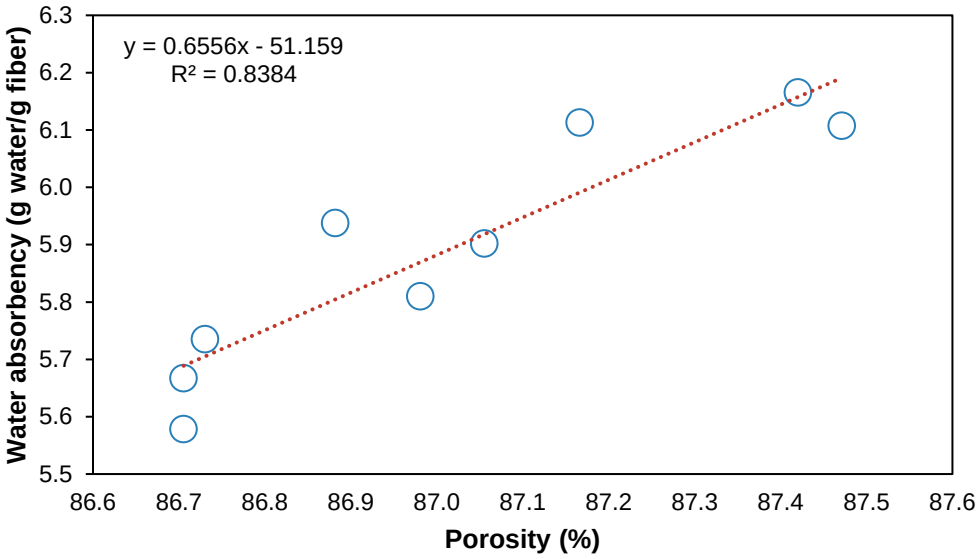

Figure A-8: Correlation between water absorbency and porosity for MNFC-containing sheets and refined control. Since porosity is calculated from the sheet bulk, the same R^2 is obtained when correlating water absorbency and bulk.

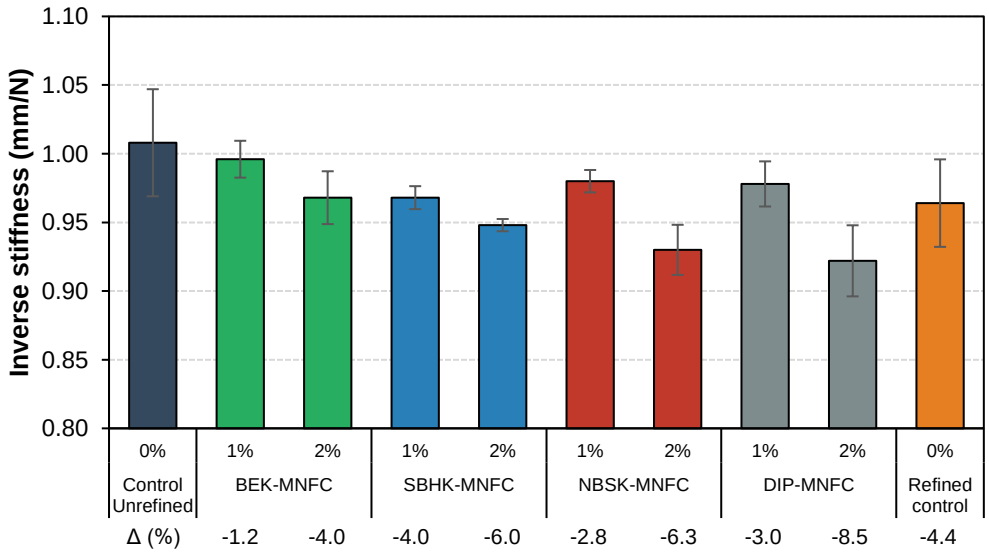

Figure A-9: Effect of the addition of MNFC on inverse stiffness. Δ is the percent difference in the property with respect to the control (unrefined). Error bars indicate standard deviation. The inverse stiffness was measured using a Tissue Softness Analyzer (Emtec Electronic GmbH, Leipzig, Germany). A perpendicular force from 100 mN to 600 mN is applied to the sheet and the vertical displacement is recorded. The inverse stiffness is calculated as the ratio between the sample displacement and the applied force. Inverse stiffness is an indicator of bulk softness.

APPENDIX B: Supplementary information to Chapter 6

UPCYCLING STRATEGIES FOR OLD CORRUGATED CONTAINERBOARD TO ATTAIN HIGH-PERFORMANCE TISSUE PAPER: A VIABLE ANSWER TO THE PACKAGING WASTE GENERATION DILEMMA

Table B-1: Standard deviations associated with the WRV, zero-span breaking length and sheet swelling across the bleaching sequences $D_0(EP)D_1P$ and $OD_0(EP)D_1P$

		$D_0(EP)D_1P$				$OD_0(EP)D_1P$				
Pulp characteristics	**Unbleached**	**D_0**	**(EP)**	**D_1**	**P**	**O**	**D_0**	**(EP)**	**D_1**	**P**
WRV, g/g	± 0.02	± 0.01	± 0.06	± 0.02	± 0.01	± 0.04	± 0.01	± 0.01	± 0.02	± 0.03
Zero-span breaking length, km	± 0.5	± 0.4	± 0.4	± 0.6	± 0.6	± 0.3	± 0.5	± 0.5	± 0.4	± 0.5
Sheet swelling, %	± 0.1	± 0.1	± 0.5	± 0.2	± 0.7	± 0.2	± 0.1	± 0.2	± 0.8	± 0.6

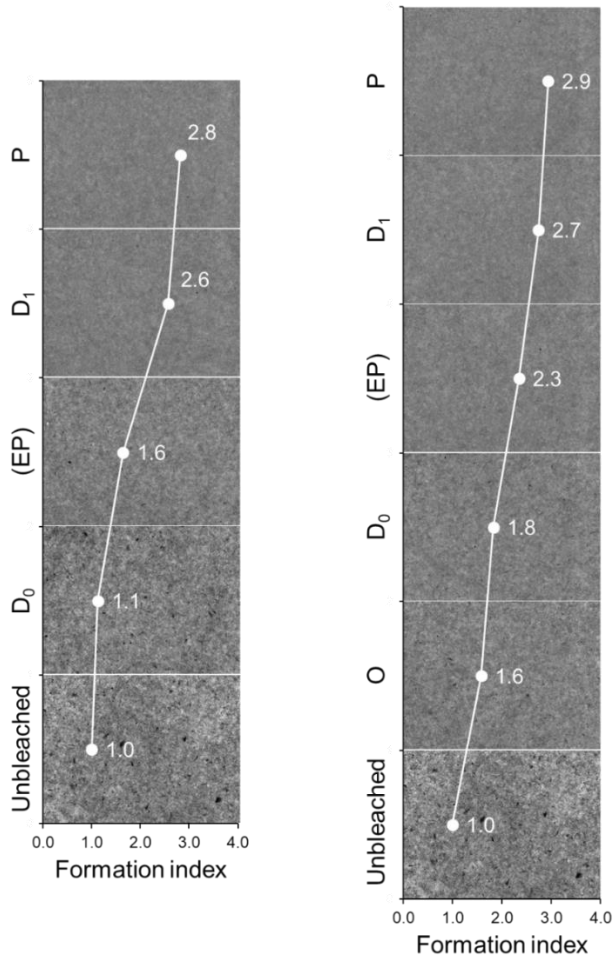

Figure B-1: Evolution of the formation uniformity across the bleaching sequences $D_0(EP)D_1P$ (left) and $OD_0(EP)D_1P$ (right). The pooled standard deviation of the formation index was ± 0.1. Formation uniformity was determined with a Paper PerFect Formation Analyzer PPF-LPA07 (OpTest Equipment Inc., Hawkesbury, ON Canada). Unbleached OCC was used as the reference sheet. A formation index greater than 1 indicates that the formation of the tested sheet is better than the reference paper. The formation index was calculated as the average of the relative formation values for floc sizes over a range of 0.5 mm to 60 mm.

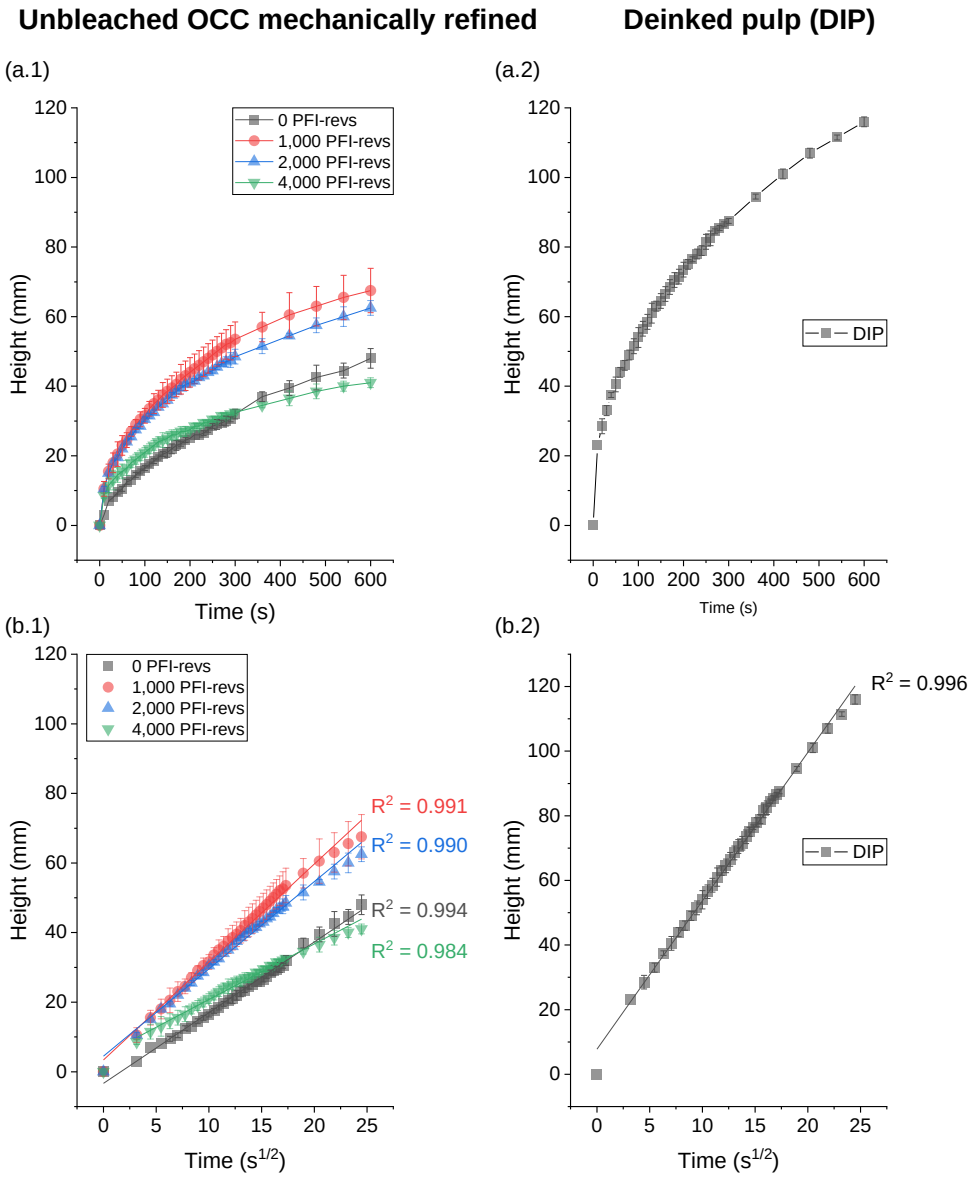

Figure B-2: (a) Capillary rise for unbleached OCC mechanically refined and DIP and (b) corresponding Lucas-Washburn plots

APPENDIX C: Supplementary information to Chapter 7

DEVELOPING ALTERNATIVE, HIGH-ABSORBENCY BROWN FIBERS: TISSUE PAPER FROM UPCYCLED CORRUGATED PACKAGING WASTE TO MEET NEW CONSUMER TRENDS

Table C-1: Fiber mass distribution of unbleached OCC pulp and morphology of fiber fractions

Fiber fraction	Weight percent (%)	Fiber length (mm)	Width (μm)
Unfractionated	-	1.66 ± 0.01	22.3 ± 0.2
>14 mesh	42.0 ± 2.0	2.62 ± 0.02	26.6 ± 0.2
14-28 mesh	13.5 ± 0.3	1.73 ± 0.03	24.2 ± 0.2
28-48 mesh	13.8 ± 0.8	1.05 ± 0.02	20.2 ± 0.1
48-100 mesh	7.2 ± 0.1	0.69 ± 0.01	18.5 ± 0.1
100-200 mesh	2.5 ± 0.1	0.46 ± 0.01	17.8 ± 0.1
<200 (Fines)	20.8 ± 0.2	-	-

Fiber mass distribution determined using a Bauer-McNett classifier according to TAPPI 233 cm-95 (1995)

Table C-2: Fiber quality analysis of OCC treated under different conditions

		Fiber length[1] (mm)		Width (μm)		Kink index (1/mm)		Curl index[1]		Fines content[1] (%)	
Treatment	**Condition**	**Avg[2]**	**SD[3]**	**Avg**	**SD**	**Avg**	**SD**	**Avg**	**SD**	**Avg**	**SD**
Base case	Untreated (0 PFI-revs)	1.66	0.01	22.3	0.2	1.60	0.03	0.106	0.004	13.5	0.3
Mechanical refining	1000 PFI-revs	1.48	0.01	22.3	0.1	1.19	0.02	0.066	0.002	16.6	0.8
	2000 PFI-revs	1.37	0.02	22.8	0.2	1.02	0.01	0.057	0.002	17.5	0.8
	4000 PFI-revs	1.34	0.06	23.7	0.4	0.91	0.02	0.051	0.001	17.1	0.9
Oxygen delignification (O)	2%NaOH - 100 psi O_2	1.51	0.02	21.6	0.1	1.60	0.01	0.113	0.003	15.6	0.1
	3.5%NaOH - 100 psi O_2	1.57	0.02	22.0	0.1	1.57	0.03	0.107	0.002	13.7	0.5
	5%NaOH - 100 psi O_2	1.59	0.02	21.8	0.3	1.58	0.02	0.112	0.002	13.4	0.4
Alkaline hydrogen peroxide (P)	2%H_2O_2 - 1.5%NaOH	1.55	0.04	21.8	0.1	1.64	0.04	0.110	0.004	14.9	0.2
	4%H_2O_2 - 3%NaOH	1.57	0.03	21.9	0.1	1.63	0.03	0.107	0.001	14.8	0.4
	8%H_2O_2 - 5%NaOH	1.61	0.01	22.1	0.1	1.65	0.01	0.104	0.002	13.9	0.3
Ozone (Z)	1.4%O_3	1.58	0.01	21.8	0.1	1.47	0.05	0.096	0.006	12.9	0.2
	2.9%O_3	1.59	0.06	21.6	0.2	1.58	0.04	0.100	0.002	10.7	0.1
	4.0%O_3	1.59	0.02	21.7	0.2	1.64	0.01	0.100	0.001	12.5	0.5

[1] length weighted; [2] Avg indicates the average measurement of 10,000 fibers; [3] SD indicates the standard deviation from at least 3 replicates

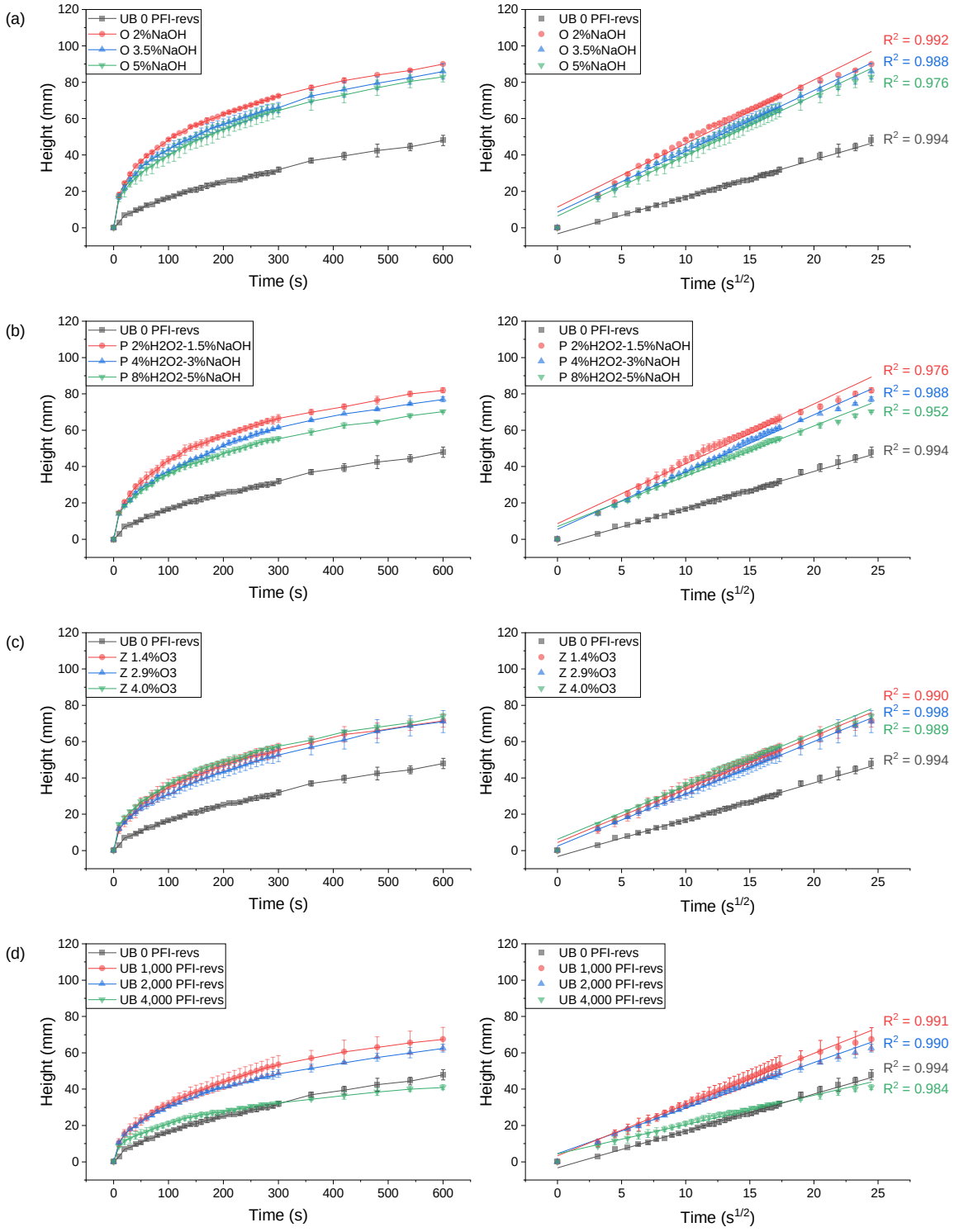

Figure C-1: Capillary rise (right) for handsheets from (a) O, (b) P, (c) Z, and (d) mechanically treated OCC pulps with corresponding Lucas-Washburn plots (left)

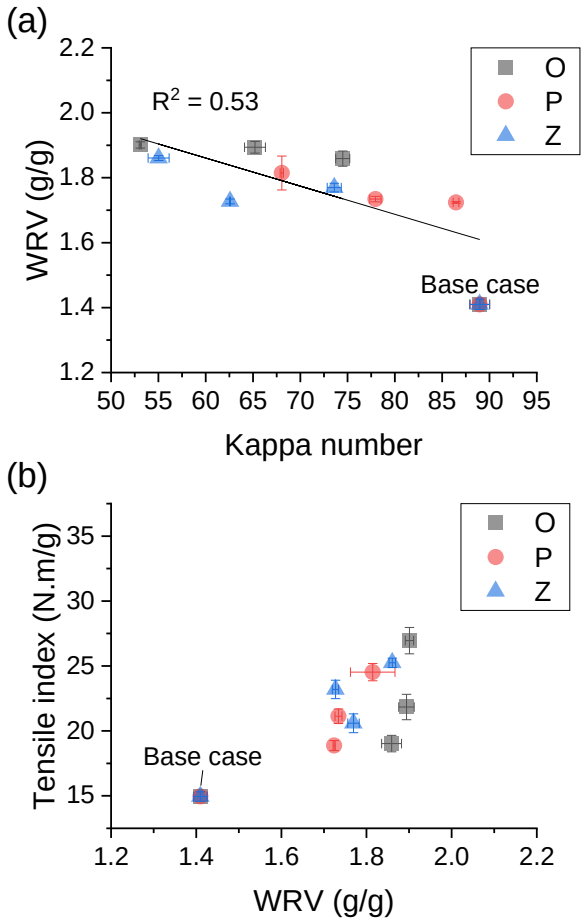

Figure C-2: Relationship between (a) kappa number and water retention value (WRV) and (b) WRV and tensile index

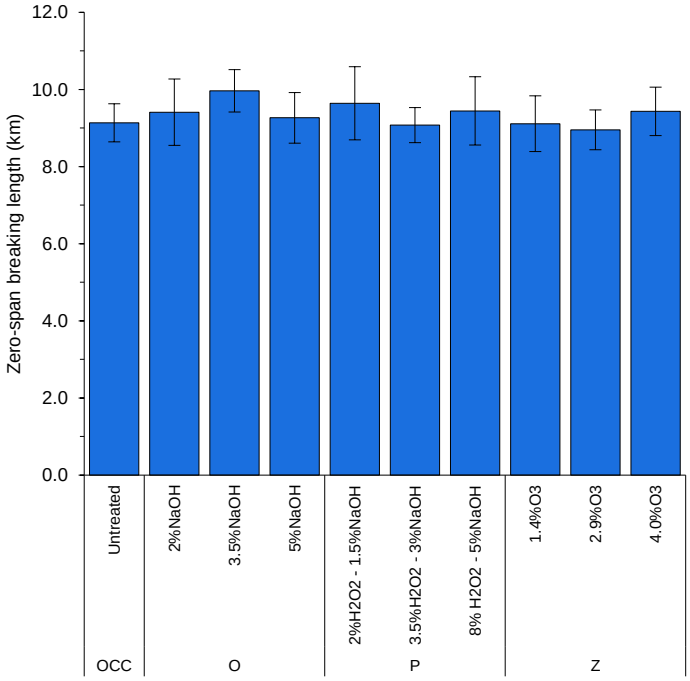

Figure C-3: Zero-span breaking length of OCC chemically treated OCC pulps

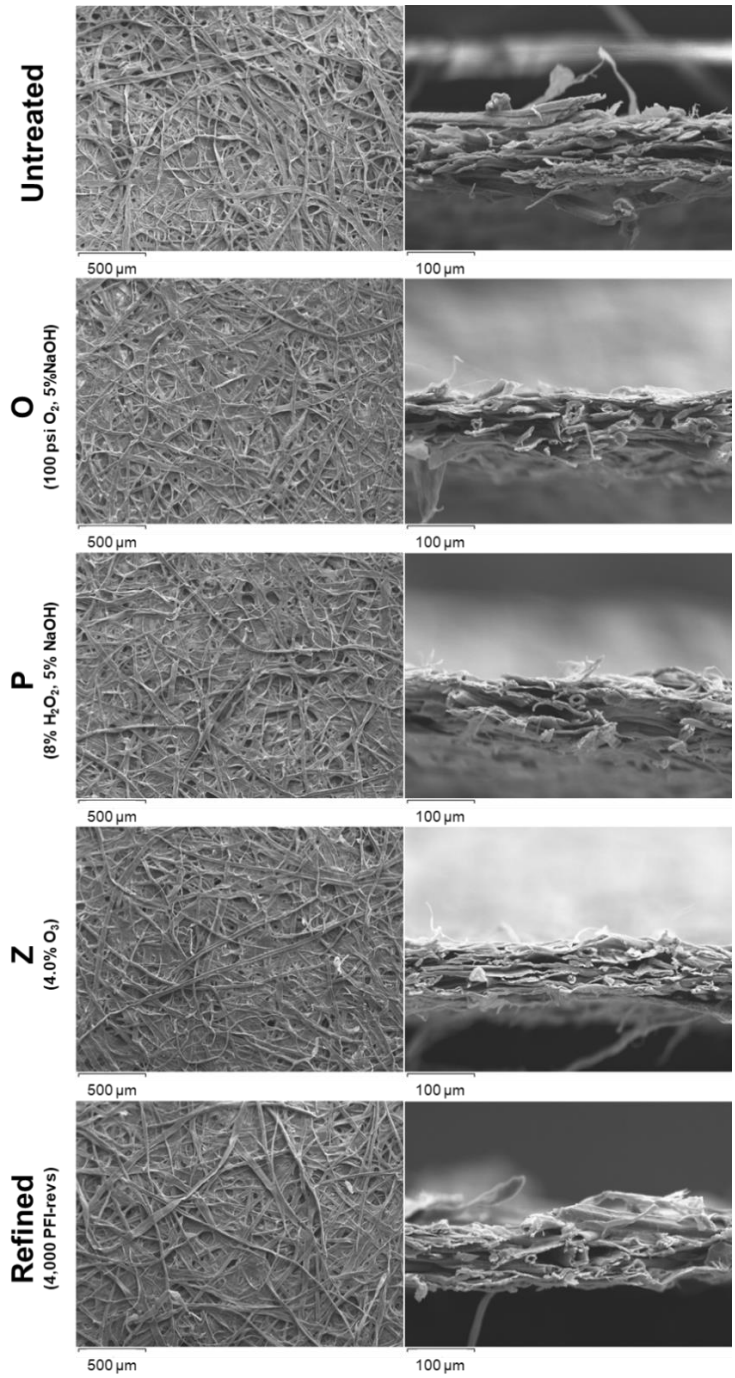

Figure C-4: SEM images of surface and cross-section of sheets made from chemically (O, P, Z) and mechanically (refining) treated OCC pulps. Imaging of the surface and cross-section of the handsheets was performed using a variable pressure scanning electron microscope (VPSEM Hitachi S3200 N, Hitachi High Technologies America, Schaumburg, IL). Samples for cross-section imaging were produced by cryofracture to avoid collapsing of the fiber network structure.

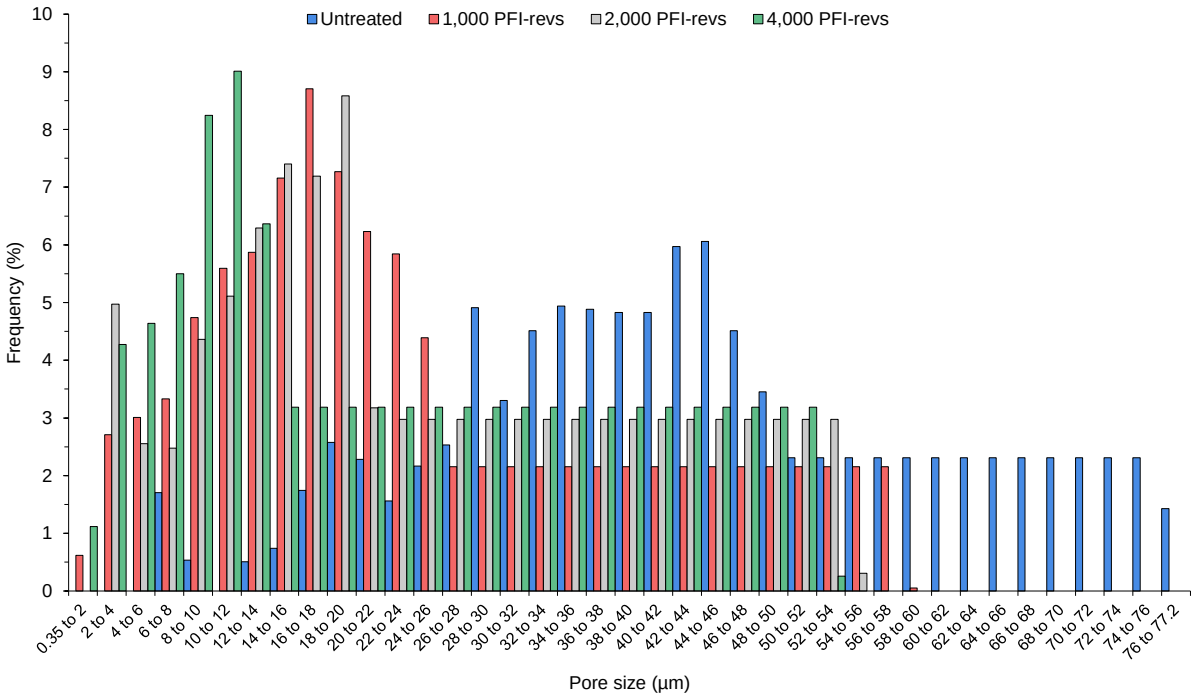

Figure C-5: Pore size distribution of tissue sheets from mechanically treated OCC