

Pulping Processes and Their Effects on Cellulose Fibers and Nanofibrillated Cellulose Properties: A Review

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Abstract

Although pulping processes from wood are well-cemented technology, the emergence of bio-based nanotechnology, as well as the increase in concern about the environmental impact that these processes can have, calls for a reevaluation of the impacts that the traditional pulping methods have on the surfaces of the fibers and how variances will then affect the generation and properties of the nanocellulose materials, that will then impact the different applications that can be derived from them. Since literature tends to focus on one method and then characterize it, the aim of this review is to discuss the properties that have been reported of different fibers and nanofibers depending on the wood source, the chemical pulping method selected (kraft or sulfite methods), and the bleaching or lack of it and then compare the effects that these can have in properties such as crystallinity, chemical composition, surface charge, and functional groups present on the surface.

Cellulose is an abundant and natural material, which has been used for centuries to supply human necessities and as the primary source for the production of pulp and paper (Klemm et al. 2005, Dufresne 2017). The first paper-based material was developed around 105 BCE in China; at that time, paper makers unconsciously took cellulose properties into consideration (Sixta 2006). The paper manufacturing process was based on the hydration of plant tissues in water, followed by cutting and pressing the material. By doing this, a thin network of cellulose fibers was formed onto a fabric leading to the production of the first paper sheet. Over the centuries, the production of pulp and paper has evolved into the modern-day technologies; in addition, a variety of plants are now being used, as more sophisticated and complex industries have been initiated. These developments, along with cutting down the raw material and carrying out chemical treatments, have made the cellulose industry a wide-ranging and profitable business. With a broad spectrum of final products, this industry is now able to produce more specialized merchandise, from thick boards to very thin and soft skin care tissues, as well as cellulose pulps with diverse chemical composition and properties.

During the last century, there was enormous growth and industrialization of societies, and the use of petroleum-based materials started to predominate. These changes resulted in a dependence on oil for energy and materials, concern for the long-term availability of such resources, and consequent calls for their replacement with renewable and more environmentally friendly resources. The amount of biomass globally available at relatively low cost makes biomass an

appealing option for the replacement of petroleum-based materials, chemicals, and energy.

As mentioned before, cellulose, in particular from wood sources, is one of the most abundant natural and renewable resources on the planet. The current main use of cellulose is to produce the most common commodities, such as pulp, paper, board, and tissue. With the decline of paper consumption and digitization of information, the pulp and paper industry, with extensive efforts by the academic and industrial sectors, has been actively seeking new alternative processes and products from cellulose with improved properties and to develop value-added and high-performance products (Xu et al. 2013, Li et al. 2015).

With the emergence of nanotechnology, the possibility of applications at this scale has been a research topic of increased importance for different proposed uses (Moon et

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al. 2006). Nanotechnology is concerned with the ability to process materials at scales of 100 nm or lower (Kamel 2007), and with all these materials, properties at the most fundamental levels show behavior that is distinctly different from those in bulk (Kamel 2007). Following this trend, cellulose shows remarkable improvements in its mechanical and surface properties at the nanoscale, properties that can be advantageous for a wide variety of applications.

At a very fundamental level, intermolecular interactions play a very important role in the properties of cellulose, since they are the main drivers for material behavior and final properties. Surface properties dictate the interactions that materials will have toward the medium in which they are placed and with other components (Ratner et al. 2013).

The aim of this work is to provide an overview of how the different modifications that occur during the kraft and sulfite pulping processes will affect the end fiber properties, including crystallinity, chemical composition, and functional groups.

Wood as Raw Material

Within natural and biodegradable sources, there are diverse feedstocks that can be used as cellulose sources such as sisal, linen, sugarcane bagasse, pineapple, straw, and cotton, among others (Morán et al. 2008, Cherian et al. 2010, Abraham et al. 2011, Mandal and Chakrabarty 2011, Morais et al. 2013, Visanko et al. 2017). Centuries ago in the pulp and paper industry linen and cotton rags were used as the basic fiber sources. With the necessity to increase production and to improve specific properties of paper, wood became the principal source of cellulose (Sjöström 1993, Koch 2006).

Wood is an anisotropic and hygroscopic material, in which the chemical composition can vary with tree, species, environment, age, geographic location, soil conditions, and weather (Pettersen and Rowell 1984). The variability within the tree is perhaps the largest source of variation and can follow specific trends both horizontally and vertically. For pines, the abrupt transition from earlywood to latewood will translate into lower and higher cellulose content, respectively. Pines can also exhibit increases in cellulose content with radial growth, while Chinese fir, for example, shows a decline in cellulose with age (Li et al. 2019). Conversely, for a diffuse porous hardwood, the chemical changes within a ring or with age can be more subtle due to a more homogenous fiber morphology.

Wood species can be classified in two groups, commonly known as softwood and hardwood. The former includes pine and spruce, while examples of the latter are birch and aspen. Based on the general amount of carbohydrates, lignin, and extractives of each class, each species differs in chemical composition (Table 1). In addition, one of the main differences between them is the fiber length: softwood has longer fibers (~2 to 6 mm), while hardwoods have short fibers (~0.8 to 1.6 mm; Solala 2011).

Constituents of Wood

The main components in wood fibers are carbohydrates and lignin, which are unevenly distributed within the cell wall layers (Fig. 1). In wood, 65 to 70 percent of the total dry weight is made up of cellulose and hemicelluloses, also known as holocellulose (Rowell et al. 2012). Understanding their structures and interactions within the fibers is crucial to

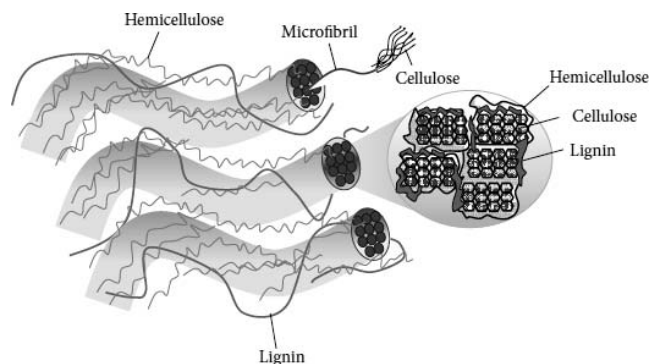


Figure 1.—Wood components arrangement on the cell wall layers and microfibrils cross section. Reprinted from Lee et al. (2014).

understand how the pulping process will affect their final properties for further applications.

Cellulose

Cellulose is a linear homopolymer made up of β -D-glucopyranose units which are linked together by (1-4) glycosidic bonds (Sjöström 1993, O’Sullivan 1997). The repeating β -D-glucopyranose units, together with the OH groups of the carbon atoms in position 4 and 1 (C4 and C1), are covalently linked through acetal functions, making an extensive and linear polymer (Klemm et al. 2005). In the repeating unit of cellulose, called cellobiose, two sugar units are held together by a β -(1-4) glycosidic bond (Fig. 2).

At the ends of the cellulose chain, C1 is the reducing end-group, with the presence of a hemiacetal. On the other hand, C4 behaves as an aliphatic hydroxyl with a nonreducing end (Koch 2006, Dufresne 2017). The OH groups present in the cellulose fiber structure give to this polymer certain polarity.

Within the molecular structure of cellulose, each anhydroglucose unit has three OH groups linked to carbons 2, 3, and 6 (C2, C3, and C6, respectively). The three OH groups are able to interact with hydroxyl groups from other anhydroglucose units forming intermolecular and intramolecular bonds within and between cellulose chains (Roman 2009; Fig. 3), conferring rigidity, stability, and water insolubility to the cellulose (Moon et al. 2011). Within these interactions, two are defined as intramolecular H-bonds occurring from O(3)–H to O(5) and O(2)–H to O(6), and one intermolecular H-bond taking place from O(3)–H to O(6)–H (Kontturi et al. 2003).

Within the cell wall, cellulose can be found in two different forms known as crystalline and noncrystalline regions, also called amorphous or disordered; the former are typically nonaccessible to water, chemicals, or microorganisms, while the latter are more easily accessible (Kondo et al. 2001, Rowell et al. 2012). Based on the arrangement and hydrogen bonds within and between the cellulose chains, different crystalline allomorphs, cellulose I, II, III_I, III_{II}, IV_I, and IV_{II}, exist that can be interconverted, by chemical or thermal treatments (Habibi et al. 2010).

Native cellulose is also known as cellulose I. Within its structure, the cellulose chains are organized in parallel, with two different crystalline forms, I α and I β (Fig. 4). The main difference between these is the hydrogen bonding patterns (Viëtor et al. 2000, Dufresne 2017). The importance of this packing resides in the fact that microfibrils formed by

Table 1.—Density, microstructure, and chemical composition of different wood species. Adapted from Naimi et al. (2016). Used with permission.^a

Species	Parameter	Density (kg m ⁻³)	MFA (°)	Fiber length (mm)	Fiber coarseness (mg m ⁻¹)	Glucan (%)	Glucan in cellulose (%)	Hemicellulose (%)	Lignin (%)
Douglas-fir ^b	Mean	716	32.1	1.31	0.11	38.17	35.38	28.49	36.13
	SD	113	4.8	0.05	0.00	0.15	0.14		0.15
	CV (%)	16	15	4	0	0.40			0.42
Pine ^b	Mean	550	29.9	1.17	0.11	37.87	34.86	30.29	35.03
	SD	69	5.5	0.09	0.00	0.06	0.06		0.15
	CV (%)	13	18	8	0	0.15			0.44
Aspen ^c	Mean	482	11.5	0.65	0.07	46.70	45.63	26.47	27.90
	SD	18	0.8	0.04	0.01	0.61	0.59		0.69
	CV (%)	4	7	6	8	1.30			2.48
Poplar ^c	Mean	473	24.4	0.73	0.08	50.37	49.2	24.27	26.53
	SD	40	2.7	0.03	0.01	0.50	0.50		0.60
	CV (%)	8	11	4	7	1.00			2.27

^a CV = coefficient of variation; MFA = microfibril angle.

^b Softwood.

^c Hardwood.

monoclinic cellulose will have different planes, where hydroxyl groups will be highly concentrated with a specific hydrophobic plane (2 0 0), which can have an impact in the interactions of the fibrils with surrounding molecules (Koyama et al. 1997, Hult et al. 2003). The different pulping methods will have an impact in the crystalline packing of the cellulose microfibrils. The chemicals used in the different treatments will interact with the fibrils for the removal of other cell wall components. The pulping chemicals will also penetrate the cellulose structure and rearrange it (Duchesne et al. 2001; Hult et al. 2001, 2003; Quiroz-Castañeda and Folch-Mallol 2013).

After cellulose is isolated from the cell wall, the interaction with specific chemicals will transform the native cellulose I crystals into different polymorphs. Cellulose II is the product of the recrystallization of the chains after sodium hydroxide mercerization. During this process, intermediate conversion stages are reached and different Na-cellulose compounds are formed. Finally, the mercerized cellulose is organized in an antiparallel mode (Revol and Goring 1981; Okano and Sarko 1984, 1985), which is the most stable allomorph (Kolpak et al. 1978, Kroon-Batenburg and Kroon 1997; Fig. 5). This process does not dissolve the cellulose chains, but only leads to fiber swelling (Dufresne 2017). Cellulose II can also be obtained by regeneration, where hydrogen bonds need to be broken to solubilize the cellulose. For this purpose, ionic liquids have been discovered to be effective alternatives (Swatloski et al. 2002, Turner et al. 2004, Brandt et al. 2013). Cellulose can then be precipitated in solvents such as water, acetone, or

ethanol (Zhu et al. 2006). Conversion reactions from cellulose I to II are irreversible, suggesting a higher thermodynamic stability based on the structure of cellulose II (Dufresne 2017). Cellulose III_I and III_{II} emerge after treatment of cellulose I and cellulose II, respectively, with ammonia, while cellulose IV_I and IV_{II} are obtained by heating cellulose III_I and III_{II}, respectively (Nelson and O'Connor 1964, Paakkari et al. 1989, O'Sullivan 1997, Konturi et al. 2006, Habibi et al. 2010, Ioelovich 2016).

Cellulose is further organized forming elementary fibrils with diameters between 3 and 5 nm. Elementary fibrils are combined into larger structures called microfibrils with diameters between 10 and 20 nm, which are further arranged together in a fibril-matrix-like structure mixed with hemicellulose and lignin that can be found in the cell wall layers (Postek et al. 2011). The fibril-matrix structures are treated by different pulping methods to obtain cellulose fibers with diameters in the range of micrometers. Furthermore, through chemical, mechanical, and/or enzymatic processing of the cellulose fibers, nanocelluloses can be obtained. Nanocelluloses are characterized by having at least one dimension within the nanoscale (Klemm et al. 2011). The higher surface area of the nanosized particles provides unique surface properties. Additionally, the chemistry of the pulping method chosen will provide additional functional groups available for modifications, inducing changes in charge density, zeta potential, and optical activity of such fibrils (Lagerwall et al. 2014, Salas et al. 2014). These unique varieties of properties, added to the inherent biocompatibility, biodegradability, sustainabil-

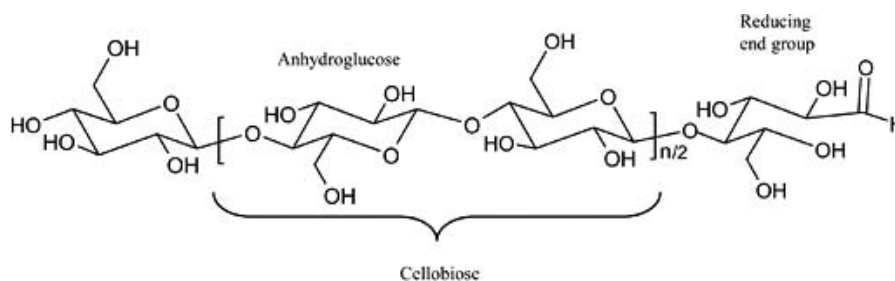


Figure 2.—Cellulose chain structure. Reprinted from Konturi et al. (2006) with permission from Royal Society of Chemistry.

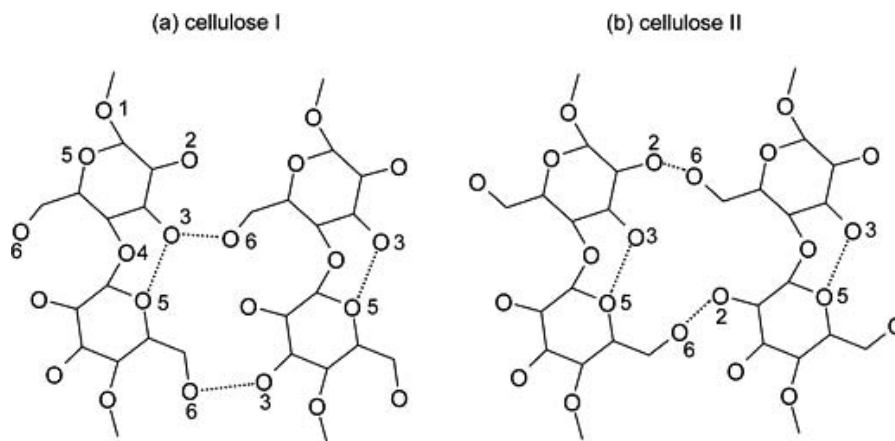


Figure 3.—Intramolecular and intermolecular interactions within and between cellulose chains. Adapted from Kontturi et al. (2003) with permission from Royal Society of Chemistry.

ity, and renewability of lignocellulosic fibers, open a new set of opportunities to use these materials in novel fields as wide-ranging as environmental remediation, biomedical devices, electronics, construction, or energy storage.

Hemicellulose

Hemicelluloses are the second most important polysaccharide constituent in lignocellulosic materials, belonging to the heteropolysaccharides, and they are usually branched (Klemm et al. 2005, Tunc and Van Heiningen 2008). They can have different structures and properties depending on the species from which they were obtained. In addition, the hemicellulose content can vary between species, such as softwood and hardwood, as presented in Table 1.

Hemicelluloses are natural polymers composed by two main sugar groups: pentoses, which contain five carbons (e.g., xylose and arabinose), and hexoses formed by six carbons (e.g., glucose, galactose, mannose; Rowell et al. 2012).

Hemicelluloses are branched and amorphous structures, usually constituted of different combinations of polymers, such as galactoglucomannans and glucuronoxylans. The less orderly arrangement of hemicelluloses compared with cellulose makes the former more accessible to chemicals, water, or microorganisms (Li 2011). In addition, hemicel-

luloses have lower degrees of polymerization when compared with cellulose, which makes them more soluble (Sjöström 1993).

By performing enzymatic hydrolysis, it has been demonstrated that hemicelluloses are mainly located between the cellulose microfibrils in the cell wall structure, while remaining hemicelluloses have been proposed to occur within the amorphous region of the cellulose microfibrils structure (Arola et al. 2013).

Although hemicelluloses and cellulose have an affinity for each other (Eronen et al. 2011), the former also can be found covalently linked with lignin, leading to the occurrence of lignin-carbohydrate complexes (LCCs; Paszczyński et al. 1988, Deshpande et al. 2018). Thus, hemicelluloses have been proposed as an intermediate compound, which has affinity for both lignin and cellulose.

A few studies have found that the presence of hemicelluloses plays a significant role in the properties of cellulose fibers. First, they improve pulp fibrillation due to reduction of coalescence between the fibers (Duchesne et al. 2001, Hult et al. 2001, Iwamoto et al. 2008); second, they tend to enhance the colloidal stability of a suspension due to the higher charge repulsion among the fibers (Hannuksela et al. 2003, Hubbe et al. 2008, Cheng et al. 2009, Tenhunen et al. 2014). As a result, the presence of hemicelluloses improves properties of the fibers such as thermal stability and strength (Iwamoto et al. 2008). Nevertheless, during the pulping process, a large amount of hemicellulose is degraded (Tunc and Van Heiningen 2008).

Lignin

Within the cell wall structure, lignin has been defined as the adhesive that holds together cellulose and hemicelluloses. Owing to its hydrophobic character, it can be used to modify the hydrophilic ability of cellulose (Bian et al. 2018). Lignin can be described as an amorphous and heterogenous polymer of phenylpropane units forming three-dimensional structures (Chakar and Ragauskas 2004). These structures are made up by C-O-C and C-C linkages (Rowell et al. 2012) between the monolignols, *p*-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol (Sjöström 1993; Fig. 6).

As mentioned previously, lignin and polysaccharides can be linked together by covalent bonds, forming LCCs

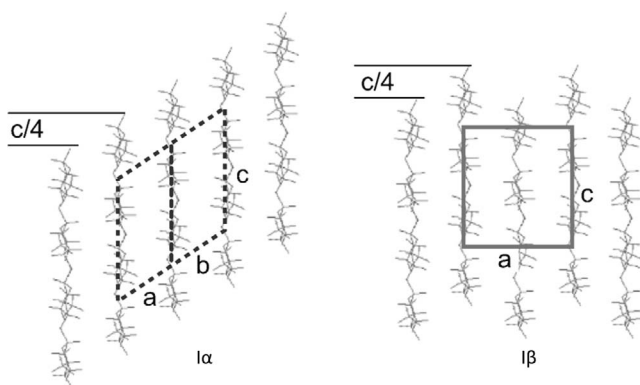


Figure 4.—Hydrogen bonding patterns for I α and I β . Adapted from Moon et al. (2011) with permission from Royal Society of Chemistry.

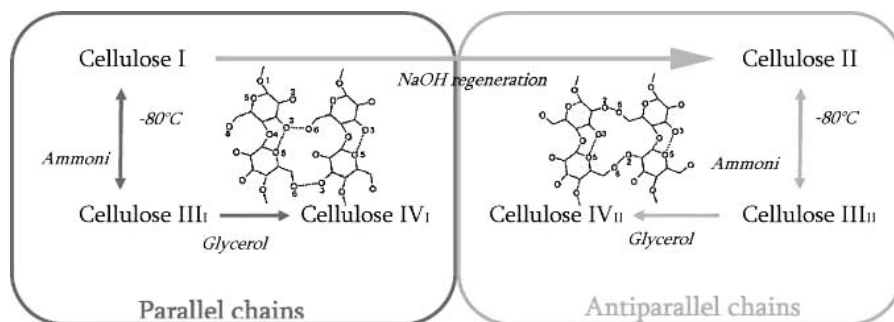


Figure 5.—Polymorphs of cellulose and their obtaining sequence. Reprinted from Lavoine et al. (2012) with permission from Elsevier.

(Paszczynski et al. 1988) linked by ether, ester, or even glycosidic bonds (Paden et al. 1983, Sjöström 1993).

Although lignin has been studied for decades, due to its complex structure and the changes this biomaterial undergoes after the pulping process, the exact original chemical structure remains unknown. In a recent study, a constitutional structure for kraft lignin from softwood was proposed. Nevertheless, the study authors stated that the obtained lignin fraction after the pulping process has very little in common with the material it came from because of its highly heterogeneous nature (Crestini et al. 2017).

Pulping Methods

During wood pulping, the primary objective is to keep the structure of wood fibers intact, while enhancing the removal of lignin as extensively as possible (Gratzl and Chen 1999, Smook 2016b). Because of the different percentages of the wood components (Table 1), diverse methodologies have been developed for the removal of lignin and extractives, depending on their suitability to different species. Hemicelluloses are usually retained to different degrees according to the final end-use of the fibers, and even though the degree of polymerization is lower, hemicellulose contains a high amount of surface hydroxyl groups that can interact with the cellulose fibers or other materials (Suurnäkki et al. 1997, Hult et al. 2001, Toivonen et al. 2015).

Pulping methods can be classified in three principal categories: chemical, mechanical, and semichemical. The most commonly used chemical methods are kraft and sulfite. Even though the kraft and sulfite methods are the most used in the pulp and paper industries, organosolv extractions and enzymatic isolation are also important when non-wood-

based biomass is used as a starting material for producing pulp that can further be used for nanocellulose materials (Nascimento et al. 2014, 2016; Vallejos et al. 2016). Based on the method used to produce the cellulose fibers, they will be suitable for different applications as the fiber properties will be modified (Sixta et al. 2006).

During the chemical pulping process, lignin must be removed to allow for the separation of cellulose fibers. When the removal of lignin reaches a certain value, the undesired effects of degradation of hemicelluloses and cellulose begin. Owing to polysaccharide(s) degradation, chemical reactions have to be stopped at some target molecular weight that is usually controlled by the H factor. This parameter takes into consideration the time (h) and temperature (K) as the main variables during the cooking process (Eq. 1). The H factor value is targeted as standard through the downstream production (Sixta et al. 2006).

$$H = \int_0^t e^{(43.2 - \frac{16115}{T})} dt \quad (1)$$

Decades ago, a study compared the different pulping processes in terms of production in tons per year, showing, at that time, the kraft process was responsible for about 78 percent of the total pulp capacity (Kepple 1970). More recently, a study published by the Food and Agriculture Organization of the United Nations (FAO) estimated that in 2020, the kraft pulp production (bleached and unbleached) in the United States will be 99.5 percent compared with 0.5 percent for bleached sulfite pulping (Fig. 7; FAO 2016).

Kraft pulping

In 1884, Carl Ferdinand Dahl patented the production of cellulose from wood, commonly known as the kraft process. At that time, the cooking liquor contained sulfate of soda, soda carbonate, soda hydrate, and sodium sulfide (Dahl 1884). Over the years, this process has been modified, and efficient alternatives have been developed. Currently, this alkaline method consists of a cooking liquor containing sodium hydroxide (NaOH) and sodium sulfide (Na₂S) with operational conditions ranging from 2 to 4 hours at temperatures between 170°C and 180°C (Li 2011, Smook 2016c).

As an indicator of the prominence of kraft pulping, a more recent comparison between the number of kraft and sulfite mills in North America in 2016 was made, showing

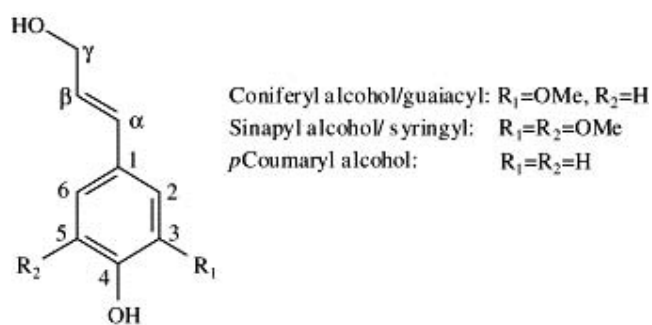


Figure 6.—Three lignin precursors. Reprinted from Chakar and Ragauskas (2004) with permission from Elsevier.

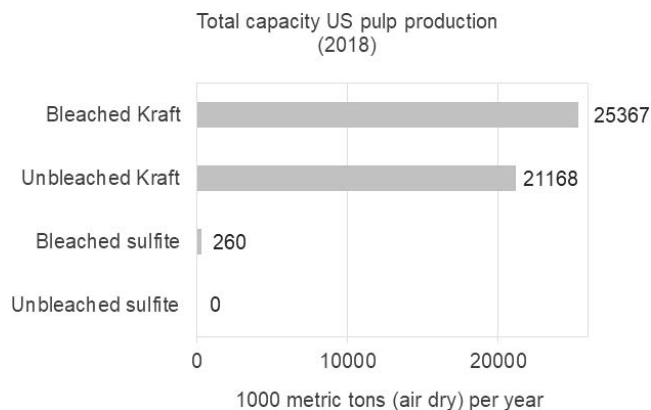


Figure 7.—Estimated total capacity US pulp production (2020). Information adapted from the Food and Agriculture Organization of the United Nations (2016). Accessed June 2018.

that from a total of 100 mills, 95 used a kraft process, while only five used the sulfite process (Smook 2016a). The increased tendency toward the use of kraft pulping over the other methods can be explained mainly by three factors: (1) efficient recovery of the chemicals, (2) good quality of the produced fibers, and finally, (3) the opportunity to use different types of woods (Kepple 1970, Smook 2016b).

During the kraft process, fibers are subjected to very alkaline conditions, high temperatures, and mechanical stress (Vänskä et al. 2016). The key reactions during this procedure involve the cleavage of lignin, where the rupture of the structure is mainly through the C–O–C linkages. However, the active chemicals used, NaOH and Na₂S (in the presence of hydrosulfide ions [HS⁻], a product of the reaction between Na₂S with water), are mainly responsible for the lignin cleavage reactions (Smook 2016c). As a secondary effect during kraft pulping, a higher aggregation of the fibers occurs during the initial step, increasing the diameter of the microfibrils (Hult et al. 2001, 2003), which has been proposed to be the result of the elimination of hemicelluloses and lignin, which allows greater contact between the fibers and, thus, among the aforementioned OH groups.

Sulfite pulping

Benjamin C. Tilghman patented his finding in pulping methodology, establishing the bases for the production of delignified pulp from wood and fibrous materials (Phillips 1943). Currently, this process has been further studied and refined. The general concept is still based on the use of SO₂, obtained from (HSO₃⁻), for the modification of lignin, and the use of some cationic base (Ca⁺², Mg⁺², Na⁺, NH₃⁺) for the prevention of chromophore formation from the residual lignin on the fibers and its later hydrolysis. The difference in the cationic base allows the pulp to cook at a wider range of pH that can improve yield and fiber properties (Smook 2016a). Typical cooking is done at low pH (~1.5), which has the drawback that the integrity of the fibers can be compromised due to hydrolysis reactions. The use of the alternative cationic bases helps to increase the pH up to 5. Standard operating temperatures range from 130°C to 140°C for 6 to 8 hours at a pressure of 100 psi (689.5 kPa; Poletto et al. 2011, Smook 2016a).

Other modifications of the sulfite process have been developed ever since, mainly to increase the operational pH to reduce corrosion and improve the integrity of the fibers. Two processes are mainly used, neutral sulfite pulping and alkali sulfite, which are applied in semichemical processing where the sulfite process softens the fibers prior to the grinding of the pulps (Gümüşkaya and Usta 2006, Patt et al. 2006, Forouzanfar et al. 2016). The resulting semichemical pulps have a higher lignin content in order to improve yield rather than the complete isolation of the cellulose fibers.

At the present time, even when paper making is a large share of the final end product for sulfite pulps, the different surface properties of the fibers have marked a rapid increase of its use for dissolving pulps (Sixta 2000). Furthermore, there is an increase of its use for the use and consumption of wood-derived materials (Quintana et al. 2015).

Effects of Pulping on Surface Properties of Cellulose Fibers

Crystallinity

During the pulping processes, undesired reactions of the polysaccharides, such as peeling and hydrolysis, are common. These reactions are the result of interactions between OH⁻ ions, with (1) the reducing ends of the cellulose chains and (2) at some random points on the cellulose chain (Strunk 2012).

In the case of cellulose, due to its high crystallinity and compact structure, there are fewer adverse effects compared with hemicelluloses, which, due to their lower degree of polymerization and branched structures, are reduced approximately 40 to 50 percent during the early stages of the cooking process (Smook 2016b).

Analyzing the crystallinity in terms of the type of pulping process, it has been demonstrated that kraft pulps exhibit a higher crystallinity than sulfite fibers as a result of a better arrangement between the fibers, which can be correlated with their higher mechanical properties (Hult et al. 2001, 2003). Since sulfite pulping uses strong acid conditions, the effects on the supermolecular structure of the pulp is mainly due to changes in the degree of polymerization and the polydispersity (PD) of the samples. This effect is a consequence of two aspects of the acidic pulping: (1) the random hydrolysis, which is more common in sulfite process than in alkaline kraft process, and (2) the dissociation of the primary cell wall, which frees those smaller fibers from the bundles, while increasing the PD and inducing a lowering of the molecular weight in suspension (Sixta et al. 2006, Duan et al. 2015, Benítez and Walther 2017). During kraft pulping, a higher concentration of the Iβ crystalline form is conserved, while during sulfite more Iα are preserved, the latter of which have smaller length and diameter when compared with the cellulose from the kraft process; but the aspect ratio of both is in the same order of magnitude (Young 1994; Hult et al. 2002, 2003).

Surface functionalized groups

Another important effect that pulping processes have on fiber morphology is the resulting functional groups on the surface. Such charged groups are related to many of the surface properties of the fibers and to their reactivity. Sulfite pulps have higher contents of carboxylic and carbonyl groups when compared with those of pretreated and nonpretreated kraft pulps (Young 1994, Sixta et al. 2006,

Strunk 2012). Additionally, because of the use of sulfuric acid and its sulfite derivatives, sulphate groups occur on the fiber surface, increasing their reactivity and capability for further modification (Sjöström and Enstrom 1966, Young 1994, Östenson et al. 2006).

During the sulfite process, ether groups of lignin are cleaved by the acidic conditions of the medium, and lignosulfonate compounds are formed due to the reaction of lignin with bisulfite ions (HSO_3^- ; Smook 2016a). The presence of lignosulfonates promotes fiber swelling, making fibrillation and beating responses easier and faster, since the fibrils have more repulsive interactions between them (Chakar and Ragauskas 2004). In papermaking, this surface functionality facilitates the interactions between different additives and the cellulose fibrils (Young 1994, Schwikal et al. 2011, Smook 2016b).

On the other hand, during the kraft cooking process, hydroxide and hydrosulfide anions present in the white liquor are able to cleave lignin, giving rise to the formation of free phenolic hydroxyl groups, which increase the hydrophilicity of lignin and, consequently, its solubility (Chakar and Ragauskas 2004).

Chromophores groups

An additional, and not necessarily desired, consequence of the pulping methods during cooking is the formation of chromophoric groups responsible for the darker color of the fibers. These chromophores are derived from oxidation reactions that convert the phenolic groups of lignin into quinone-like substances, which are mainly responsible for the absorption of light (Smook 2016d). Although chromophores groups occur in both types of pulps, kraft pulps are characterized by a darker color after pulping when compared with sulfite pulps.

Lignin-carbohydrate complexes

Other side reactions that occur during pulping are so-called condensation reactions, which are responsible for recombining and forming new C-C bonds, resulting in more insoluble compounds (Chakar and Ragauskas 2004). Additionally, while β -O-4 linkages of lignin are broken, new phenolic hydroxyl groups appear in the structure (Lawoko et al. 2005), resulting in fibers with a higher surface deposition of extractives and lignin, especially in the case of kraft pulps, leading to a higher number of surface hydroxyl groups. Such effects can be explained by the higher alkaline conditions of the process and due to condensation reactions of the components (Shen and Parker 1999, Gustafsson et al. 2003).

Regarding the effects of the process conditions, the higher the delignification, the lower the selectivity, in terms of cellulose yield, of the kraft process, and the higher the condensation reactions (Baptista et al. 2008). By lowering the concentration of hydroxide ions during kraft pulping, a higher carboxylate content can be reached, conferring higher tensile strength to the individual fibers (Dang et al. 2006).

General properties

Although kraft pulping has been widely adopted by the industry for its ease of chemical recovery, sulfite pulping allows a more efficient elimination of lignin, which impacts

the lignin solubility and consequently results in pulps that are easier to bleach (Hult et al. 2003; Smook 2016a, 2016c).

The different types of hemicelluloses in wood are characterized for their impact on fiber properties. Reports have shown that the kraft process retains a higher amount of xylose than sulfite pulping, but sulfite retains more mannose. When kraft pulp is pretreated, as is usually now the case for high-value pulps (such as dissolving pulp), then this relationship is inverted, since the objective of the pretreatment is to eliminate the hemicellulose and improve the purity of the pulp (Sixta 2006, Strunk 2012, Duan et al. 2015). Another important saccharide is glucose, which, as the monomer of cellulose, is shown to be more conserved in sulfite pulping (in percentage ratios; Hult et al. 2003, Strunk et al. 2012).

In both cases, the lignin content of sulfite pulp is always lower, since the chemistry behind it improves the solubility and surface modification of the lignin polymer, which also generates different possibilities for the use of the residual stream (Page 1983, Fardim and Durán 2004, Rojo et al. 2015, Smook 2016a). On the other hand, brightness values are similar for the pretreated kraft and sulfite pulping methods (Sixta 2006, Strunk 2012).

Important findings regarding the coalescence of the fibers after the pulping processes have been reported. Alkaline sulfite pulps have shown higher coalescence of fibers when compared with those neutral or acidic sulfite pulps, due to the effect of their surface functionalities (Hult et al. 2002, 2003; Pönni et al. 2012). As expected by the combination of chemical and mechanical processes, the neutral sulfite semichemical fibers (NSSC) show a higher content of lignin and hemicelluloses, since the process is less focused on the pulp purity than in process yield, which has also been reported to be improved when compared with kraft pulps (Masura 1998, Shen and Parker 1999, Smook 2016a). Cellulose and lignin have surface energies of 56.6 and 48.2 mJ/m^2 , respectively. Considering the surface energy of NSSC hardwood pulp and kraft hardwood pulp, it was found that they exhibit values close to those reported for cellulose (Shen and Parker 1999).

Bleaching Process

Even when chemical pulping methods provide cellulose fibers with good mechanical properties, lignin is still present on the fibers. Consequently, the implementation of bleaching technology is needed in order to eliminate residual lignin without impacting the fibers' mechanical properties (Sixta 2000, Smook 2016d).

The most commonly used oxidizing agents during the bleaching steps are chlorine dioxide (ClO_2), oxygen (O_2), ozone (O_3), and hydrogen peroxide (H_2O_2). The interaction of the fibers with oxidizing agents and alkaline washing cycles generates changes to the surface as these processes aim to modify the existing lignin while increasing its solubility.

Although bleaching processes are often used for pulp and paper production, among the main concerns are the environmental issues involving this practice. To address this, there has been a reduction in the use of chlorine and derivatives in favor of the oxygen-based methods (Serkov and Radishevskii 2009, Khakimova and Sinyaev 2014). Resultant pulps from this bleaching sequence are commonly known as total chlorine free (TCF) pulps.

Surface Properties after Bleaching

Bleaching is normally done as a series of four to six steps, usually starting with an oxidative step, followed by an alkali wash for the maximization of lignin solubility and removal. Depending on the choice of chemical used in each step, these sequences will then be followed to produce fibers with different lignin contents. As an example, in a study published by Khakimova and Sinyaev (2014), six bleaching steps were performed on bisulfite pulp using the following sequence: peroxide with sodium molybdate (acid medium; Pa), alkali extraction (E), sodium chlorite (Ct), alkali extraction enriched with peroxide (EP), and a final stage of sodium chlorite (Ct). These data showed 36.9 percent delignification and a decrease of 1.8 μm in the mean width, also with some loss in mechanical properties, which can be linked to the decrease in crystallinity (Khakimova and Sinyaev 2014). Similar processing, but with chloride dioxide instead of Ct, showed a higher purity in sulfite-derived pulps than in those coming from pretreated kraft, but more extractives remained in the surface of the sulfite pulp than in the kraft. This can be explained by the difference in surface reactivity, larger pores, and consequent water retention values (Duan et al. 2015).

The totally chloride-free (TCF) oxidative sequence is made up of oxygen delignification (O), an oxygen, peroxide-enriched alkali extraction (EOP), followed by ozonation (Z), and a final EOP. In some cases, the extraction stage can be enhanced with enzymes to eliminate hemicelluloses and amorphous cellulose as well as the residual lignin and lignin-derived chromophores (Serkov and Radishevskii 2009, Quintana et al. 2015).

For the more traditional pulp and paper industry, the main finding was an impact to the fibers as a reduction in brightness and whiteness of the pulp obtained by the TCF method, even at the same levels of lignin content as in chlorine-treated pulps. This reduction is proposed to be a consequence of the decrease in the molecular weight of the pulp during the ozone step. Smaller fiber size causes a decrease in the scattering coefficient, affecting the interaction of fibers with light and the brightness/whiteness and a subsequent increase of transparency of the fiber suspension. Even though this is an effect of ozonation, the base used in the previous alkali extraction stage has a strong influence in this outcome.

Bleaching processes have a direct impact on crystallinity of the cellulose fibers, with kraft fibers showing higher crystallinity, which is expected due to the removal of amorphous lignin and hemicelluloses (Popescu et al. 2008).

Nanocellulose

Based on renewable, biodegradable, and biocompatible sources, lignocellulosic materials with nanoscale dimensions are known as nanocellulose. The methods applied to obtain nanocellulose usually involve chemical, mechanical, and enzymatic treatments, or a combination thereof, giving rise to different types of nanocellulose types. Most commonly, the term nanocellulose refers to cellulose nanocrystals (CNC) and cellulose nanofibrils (CNF).

The main process to obtain CNC is based on acid hydrolysis of the cellulose fibers, where the less ordered regions of the fibrils are degraded (Habibi et al. 2010, Lu and Hsieh 2010, Postek et al. 2011). Carrying out this process, only the crystalline region of the fibers remains,

forming rod-like structures 10 to 2 nm in width and several hundred nanometers in length (Xu et al. 2013). On the other hand, by performing a mechanical treatment, with or without enzymatic or chemical pretreatment, both regions of the elementary fibrils remain in the structure, leading to the production of CNF. CNF particles are long flexible structures when compared with CNC, with similar or larger diameters (Xu et al. 2013).

Nanocellulose can be used in novel applications such as packaging, functional nanocomposites, and emulsion stabilizers, as well as in the pharmaceutical and medical fields, due to its unique properties such as high aspect ratio, high strength, low density, and high capacity for chemical modification (Spence et al. 2010, Klemm et al. 2011, Moon et al. 2011).

Particularly for the production of CNF, the chemical composition and properties of the starting lignocellulosic material will play an important role in the behavior of the resulting materials after fibrillation, since the individual components interact at a very fundamental level.

During the early 1980s, Turbak et al. (1983) and Herrick et al. (1983) were the first to develop cellulose microfibrils by homogenizing cellulose pulp suspensions under pressure. At that time, they found that beating and refining the cellulose pulp using only mechanical treatment was inefficient because large amounts of energy were needed to produce these small particles, resulting in high production costs (Ankerfors 2012). However, during the last few decades, efforts have been focused on the development of different types of treatments along with the emergence of new technologies that have made it possible to obtain cellulose nanofibrils (CNF) in techno-economically feasible ways. Presently, the two machines most commonly used to produce CNF are: (1) the microfluidizer, where the cellulose suspension is forced to pass through a small chamber allowing the fracture of the fiber into smaller portions (Lavoine et al. 2012), and (2) the supermasscolloider, where the suspensions are ground when passing between one stationary and one rotating stone, which allows breaking and delamination of the fibers (Solala et al. 2012).

Today, nearly all CNF grades are produced from fully bleached chemical pulps that contain only trace amounts of residual lignin (<1%), which are called bleached cellulose nanofibrils. Thus, the different processes to isolate lignin from the cellulose pulp, closely related to the further bleaching step, have been developed in order to eliminate the lignin content of the cellulose fibers as an initial step to obtain CNF, conferring to the cellulose nanofibrils different surface properties. Nevertheless, by changing the harshness of the pulping process and restricting the use of bleaching steps, not all the lignin and hemicellulose present in the cellulose fibers need to be removed, providing new surface properties. Consequently, the nanocellulose made thereof, commonly known as lignin-containing cellulose nanofibrils (LCNF), will have improved properties such as lower water absorption and lower oxygen permeability (Ferrer et al. 2012, Rojo et al. 2015). Moreover, the use of LCNF, which contains not only lignin but also hemicelluloses, opens new opportunities for its incorporation in diverse composite materials (Sun et al. 2014, Delgado-Aguilar et al. 2016, Ferrer et al. 2016, Wang et al. 2016). Furthermore, from an environmental point of view, the production of LCNF could be beneficial, since the processes of lignin removal as well as the following bleaching steps are no longer necessary

(Rojo et al. 2015), contributing to a practice more friendly to the environment (Spence et al. 2010).

Conclusions

Herein it was shown how the two most important pulping methods have a direct impact on fiber properties, not only in mechanical and structural areas, but in surface properties as well. Different impacts of the pulping processes have been pointed out as the main characteristics that affect the cellulose fibers, such as crystallinity, deposition of groups on the surface, and chromophores groups.

Kraft pulping is a very complex process in which variables such as time, chemical concentration, pH, and temperature can be modified resulting in cellulose fibers with different properties. In addition, a wide variety of raw materials can be used, increasing the variability of the final properties of the material. Sulfite pulps have great surface availability, reactivity, and better swelling properties than kraft pulps, making them ideal for dissolving pulps and for papermaking.

It is worth mentioning that both kraft and sulfite pulping are integrated procedures where not only chemical treatments are performed, but also several mechanical steps are used to improve the even distribution of chemicals and to get better dispersion of the fibers. While mechanical treatment can isolate the individual fiber components in different ways, chemical treatments modify the chemistry of its surface.

By adequately combining mechanical and chemical treatments during the production of cellulose fibers, desired properties can be imparted to the fibers. By knowing how the specific components of each raw material are modified after the pulping and bleaching process, a better understanding of the subsequent cellulose nanofibers' properties can be reached. Thus, this review provides a good overview of the work that has been performed in the area and to which properties attention should be drawn in order to better select them and improve the wide capability of the pulping of wood-based fibers.

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