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THE EFFECT OF OXYGEN DELIGNIFICATION ON FIBER PROPERTIES IN KRAFT PULP PRODUCTION – A REVIEW

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ABSTRACT

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Fiber damages comprise fiber deformations, characterized as fiber curl, kink, dislocations and strength losses as well as some yet unidentified factors. This recently discovered phenomenon is especially evident in mill scale kraft pulps. Laboratory produced pulps tend to have less damages and superior strength properties compared to those produced in pulp mills.

Generally fiber damages pose a problem in the production of reinforcement pulp because they tend to decrease the ability of fibers to transmit load. Previous studies on fiber damage have shown that most of the fiber damages occur during brown stock processing starting from cooking and discharging. This literature review gives an overall picture on fiber damages occurring during softwood kraft pulp production with an emphasis on the oxygen delignification stage. In addition the oxygen delignification stage itself is described in more detailed extent in order to understand the mechanisms behind the delignification and fiber damaging effect.

The literature available on this subject is unfortunately quite contradictory and implicates a lot of different terms. Only a few studies have been published which help to understand the nature of fiber damages. For that reason the knowledge presented in this work is not only based on previous studies but also on research scientist and mill staff interviews.

Keywords: kraft pulp, brown stock, fiber damage, oxygen delignification, cellulose degradation, fiber swelling,

1 INTRODUCTION

Recently, the attention of scientists and pulp producers has been focused on the fiber damages that result during the mill processing of kraft pulp. Fiber damages lead to the loss of fiber strength and can be observed as a difference in strength between mill- and laboratory-produced pulps.

This work is a sub-project of the Fiber Treatment project, financed by TEKES and partners from industry, Metsä-Botnia Oy, Sunila Oy, UPM-Kymmene Oy, Stora Enso Oyj, Andritz Oy, Sulzer Pumps Oy and carried out by Lappeenranta University of Technology. The Fiber Treatment project aims at developing a way of simulating the fiber damages that occur during the mill-scale oxygen delignification of softwood pulps in order to gain better understanding of the mechanisms that lead to undesired fiber damage. This literature review sums up the existing knowledge of the stages of oxygen delignification and the fiber damages that occur in the manufacture of kraft pulp.

2 OXYGEN DELIGNIFICATION OF KRAFT PULP

Oxygen delignification uses oxygen and alkali to remove a substantial fraction of the lignin that remains after cooking in order to improve the brightness of the pulp. Oxygen delignification can be applied to all pulp types. The process uses an elevated temperature and pressure at high or medium consistency in single or multiple stages with or without additional chemicals for brightening and viscosity preservation /1/. The most common industrial application is at medium consistency in a single stage with delignification normally being in the range of 30%-50%. New applications for oxygen delignification commonly involve two reaction stages and extend the normal range of delignification to between 65% and 70% /1/.

2.1 PROCESS PARAMETERS

The key parameters used for controlling and optimising an oxygen delignification stage in a commercial industrial setting are the temperature, reaction time, chemical application rate, pH, reactor pressure and pulp consistency /1/. In today's processes, medium consistency treatment is more common due to lower capital costs, the ease with which pulp can be transported and improved selectivity /1, 2/. Kraft pulp mills, where the main emphasis in the pulp quality is on strength properties, tend to run the oxygen delignification stage at the lowest MC consistency level (8-11%) /2/. Based on experience, lower-consistency treatments give better pulp strength properties /2/. The reason for this is unclear. It has been speculated that low-consistency pulps contain less dissolved air, and the excess water also suppresses the effects of high shear forces on the fibers /2, 3/. On the other hand, according to the fluidisation theory, a decrease in the pulp consistency does not increase the effect of shear forces but decreases the fluidisation times. Also, the suppressive effect of water is related mainly to the water film on the fiber surface. The thickness of this water film does not depend on the consistency /4/.

Oxygen delignification is conventionally carried out at high alkaline pH, ranging from 10.3 to 12.1 /5/. A highly alkaline pH contributes to the formation of biphenyls that hinder oxygen delignification reactivity /5/. Oxygen delignification can also be carried out at acidic pH or neutral pH /5/. According to Ai Van Tran, lignin is more extensively degraded and solubilized at acidic pH oxygen delignification than at alkaline pH /5/. An acidic pH results in a lower content of total phenylic hydroxyl groups in the residual lignin, which corresponds to a higher degree of oxygen delignification. Ai Van Tran et al. suggested that the second stage of oxygen delignification can be successfully carried out in an acidic pH without adversely affecting the properties of the pulp or the degree of delignification /5/.

Pulp can also be pretreated before oxygen delignification in order to improve the efficiency of oxygen delignification. Pretreatment can be done using chlorine, acid peroxide, ozone or nitrogen dioxide /6/. According to Fossum et al, the pretreatment of pulp with nitrogen dioxide helps to preserve the strength qualities of the pulp while

reducing the kappa number to a lower level (75% delignification) than in conventional oxygen delignification without pretreatment /6/.

2.2 OXYGEN STAGE SYSTEMS

Today oxygen delignification process is commonly carried out at medium consistency using two stages. Figure 1 shows a typical two-stage medium-consistency oxygen delignification process.

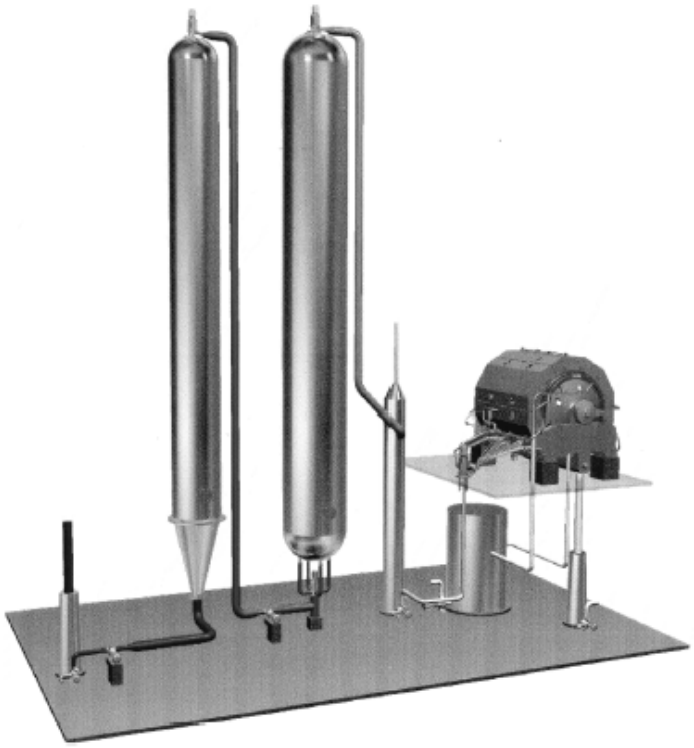

Figure 1. A two-stage medium-consistency delignification process /1/.

A typical two-stage system has a pump, usually a MC pump, before the first stage and a high-shear mixer before each stage. At the current level of development of two-stage systems, washing is optional between the stages. The first stage of a two-stage system is a high-pressure, high-alkali and low-temperature, short-residence time step that delivers a large kappa number reduction with only a modest drop in viscosity. The second stage incorporates the characteristics of an extraction step in that it uses a higher temperature, longer residence time and lower chemical concentration to extend delignification without drastically reducing the pulp strength. The second stage is

essentially the same as an existing single stage. A single-stage system approximates the conditions of a two-stage system with the depletion of alkali chemicals, reduction in pressure and increase in temperature as the retention time increases. The use of two separate reactors in two-stage system allows for the optimization of the reaction conditions /1/. After oxygen delignification, the pulp is effectively washed using usually at least two washing stages e.g. a diffuser and a two-stage DD washer /1/.

2.3 CHEMISTRY OF OXYGEN DELIGNIFICATION

Oxygen, in its normal state, is a weak oxidising agent, but its power is promoted by an increase in temperature and the use of a reactive substrate; this is achieved under alkaline conditions. Oxygen delignification can result in a very low kappa number, but however kappa reduction must be limited to 35…40% in order to preserve the strength properties of pulp /2, 6/.

During oxygen delignification, oxygen reacts predominantly with residual lignin, which structures contain a free phenolic hydroxyl group, through complex radical chain reactions /1, 7/. In the surface lignin, the content of free phenolic groups is low, and so oxygen does not react readily with surface lignin /7/. Oxygen delignification can reduce the total lignin content by about 50%, while the surface lignin content can be decreased only by 15% /7/.

Figure 2 illustrates the steps in the mechanisms of oxygen delignification, which is governed by the interplay between superoxide and the hydroxyl radical. In the first and second steps, the formed superoxide and the hydroperoxyl radical react at almost diffusion-controlled rate by dismutation, which produces oxygen and hydrogen peroxide /8/. The reaction properties of superoxide and the hydroperoxyl radical complement each other; whereas superoxide radical is mainly a reducing, selective, diffusible, delignifying and bleaching agent, the hydroxyl radical is strongly oxidizing, unselective, non-diffusible, partly delignifying and non-bleaching /8/. Superoxide can penetrate fibers and acts mainly as a reducing agent, but may also act as a weak oxidant of molecules with readily transferable hydrogen atoms /8/.

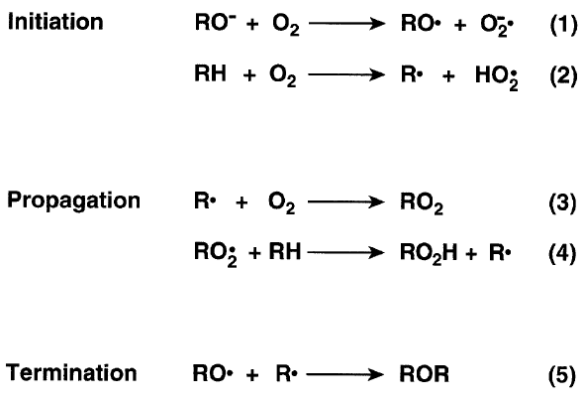

Figure 2. The steps in the mechanism of oxygen delignification /1/.

Oxygen delignification has its own limitations: For example, the condensed structures that remain in the fiber after cooking are resistant to oxygen degradation /9/. Also, one obvious limitation of oxygen delignification is the low reactivity of oxygen. Delignification proceeds at reasonable rate only at a high temperature and pH. However, these conditions favour carbohydrate degradation /8/. Delignifying under milder conditions requires the alternative activation of the substrate using special oxidation catalysts, e.g. enzymes, transition metal complexes, polyoxymetalates or photocatalysts /8/. These oxidation technologies do not require a high pH and temperature, and thus, the cellulose fiber can be expected to be less affected by deformation, curl and degradation by oxidation and alkaline hydrolysis /8/.

2.4 EFFECTS OF METAL IONS ON OXYGEN DELIGNIFICATION

The oxygen delignification process involves a gas, liquid and a solid phase. The solid phase is a heterogeneous composite of two intermixed organic polymer phases /10/. Given these conditions, it is obvious that much of the knowledge on the process is based on the empirical data. For example, the effect of metal ions in oxygen delignification is still not satisfactorily understood despite several studies /10/.

Generally, magnesium compounds are considered to be beneficial for oxygen delignification and are the only accepted reagents for improving the selectivity of the

process. Several theories have been proposed to explain the beneficial effects of magnesium:

1) The stabilization of intermediate radical species by magnesium /10/
2) The coprecipitation of transition metal ions with magnesium hydroxide which should stabilize hydrogen peroxide against decomposition to give hydroxyl radicals and achieve the redox stabilization of Mn^{2+} /8/.
3) The formation of Mg-cellulose transient complexes which protects cellulose against attacks from hydroxyl radicals /8, 10/.
4) The association of superoxide with the $Mg(OH)_2$ colloid may catalyse the proton-dependent dismutation of superoxide; i.e. the $Mg(OH)_2$ colloid mimics superoxide dismutase /8/.

Manganese, which is one of the transition metals, is considered to be benign or even beneficial, while iron and copper have been found to be detrimental to pulp strength, because they tend to react with cellulose in undesirable depolymerization reactions. Calcium has been found to be deterious to the pulp viscosity, either because it displaces beneficial magnesium or because it is inherently detrimental to cellulose during oxygen delignification /11/. Decreasing the calcium level of pulp while retaining beneficial magnesium does not appear to be an easily attainable goal. It may be that the most practical approach that can be taken to limit the amount of calcium present in brown stock is to ensure that the calcium levels in the white liquor are kept as low as possible /11/.

3 FIBER DAMAGE

3.1 THE NATURE OF FIBER DAMAGE

Various types of stress can induce deformations in wood fibers. The fiber deformations already present in a living tree may be enlarged by the mechanical and chemical treatment during pulp processing. Also, new deformations may develop, which leads to reductions in the fiber strength /12/. The wood species, growth conditions and fiber properties all affect the susceptibility of fibers to damage during pulp processing. For example, thick-walled fibers are more susceptible to fiber

damage due to mechanical processing than are thin-walled fibers, which can bend elastically /12, 13/.

Previous studies into fiber damages in the brown stock line during kraft pulp processing have shown that no single process step can be identified to be the source of damage. Damages in the fiber form occur in many steps; for example, in the blow valve, blow tank pump and valve, screening and the oxygen stage /14/. It has also been confirmed that the discharge of cooked chips from the digester results in numerous irreversible fiber damages /12/.

The true nature of fiber damages is not yet completely clear /15/. All fiber properties may vary, and many of them correlate vaguely with the loss of fiber strength measured in terms of the wet zero-span, tensile and tear strength. The strongest correlations with the loss of fiber strength are evident with fiber deformation indexes such as curliness and the fiber dislocation index /15/. In addition to fiber curl and dislocations, twists, kinks, bends, holes in the cell wall, swelling, microcompression, collapsed cell walls and cut fibers are other examples of fiber form defects /16/.

Fiber deformations decrease the ability of fibers to transmit load, which is seen as decrease in paper strength properties; tensile strength, tensile stiffness and burst strength /17/. The strength of pulps consists of at least three components; single fiber strength, fiber-fiber bond strength per unit area and the total fiber-fiber bonded area /18/. Individual fiber strength properties are a direct result of the initial fiber strength in the original woodchips, and of the chemical and mechanical treatment in the mill. Once the pulp has left the process, it is not possible to improve an individual fiber strength /18/. Furthermore, the detection of single fiber strength losses using conventional test methods is difficult. For example, in zero-span measurement, the fiber strength has to be calculated based on a number of assumptions, e.g. the fiber distribution, fiber network properties etc. /18/. The other two components, the bond strength and bonded area are considered to be less influenced by the process conditions, and these components can be influenced after the fibers have left the process /18/.

3.1.1 Dislocations

Dislocations are already common in native softwood tracheids. Scientists suggest that dislocations are a product of the growth or wind stress of a tree and that dislocations and zones of dislocations can give rise to microcompressions under drying stress /19/. During mechanical treatment, i.e. chipping, pulping and pulp processing, dislocations arise in pulp fibers due to the compressive stresses acting on the fiber wall /20/.

Fiber failure starts from microscopic damage in the fibrils. The axial compression of fibers results in dislocations and misalignments. After this, the fiber does not carry as much load as does the undamaged fiber /15/. The fiber wall becomes weaker, and this weakening cannot be explained by viscosity or chemical composition, nor by the 3-D shape of the fibers /15/. Dislocations make fibers more flexible and sensitive to chemical attack with an accompanying improvement in the binding capacity /12/. Tracheids tend to swell, bend and rupture at the sites of dislocations, thus resulting in the decreased strength capacities of the pulp. Figure 3 illustrates a fiber that contains dislocations that result from longitudinal compression.

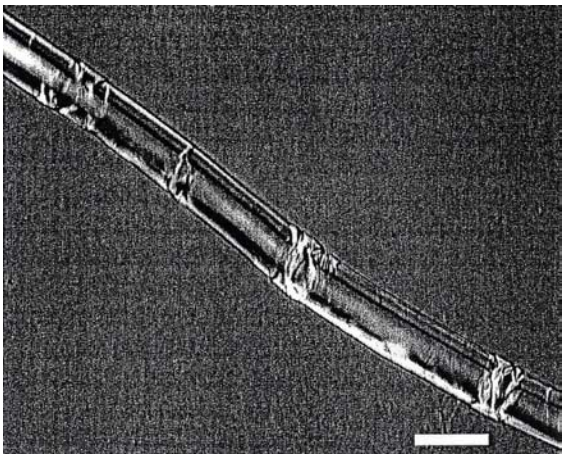

Figure 3. Dislocation areas across the width of a spruce fiber (scale bar = 40 μm) /12/.

Dislocations that result from the longitudinal compression of wood can be seen, according to W. Robinson, as bright, linear regions in the fiber wall when viewed under polarized light /21/. The observed white lines presumably relate to the structural changes initiated in the S_1 layer /12/. It is likely that the differences in microfibril

orientation in the S_1 layer govern the direction of the dislocations. Increased longitudinal compression can eventually lead to the separation of the S_1 and S_2 layers and, finally, to gross buckling, severe folding and the complete failure of fibers /12/.

According to Forgacs, the size of dislocations varies a lot, and their length may be 5-30 μm in fibers the width of which is around 30 μm /22/. According to Nyholm et al., the average length of dislocations (microcompressions) is 20-120 μm /12/. Smaller dislocations, often called slip planes, are approximately 1 μm in width, and can be seen as both single and double minute compression failures /12/. Single compressions are considered to be single folds that are associated with kinks in the fiber wall. Double compressions are found with the angle opening either towards the lumen or outer cell wall, which is caused by a thickening in the direction in which the angle opens. Dislocations occur with equal frequency in both early- and latewood tracheids but are more pronounced in latewood tracheids, probably because of their thicker cell walls /22/. However, it has been found that beaten earlywood tends to exhibit more dislocations than latewood fibers /12/.

Most scientists, who study fiber dislocations, believe that there is a correlation between dislocations and ray crossings /12/. When studying spruce fibers, researchers found that weak planes and most discontinuities occur preferentially near ray pit fields /12/. The edges of ray cross-field pits are areas where wood tends to fold and fracture under tension and compression /12/. When applying compressive strength on wet wood, dislocations appear at sites of fiber/ray cell contact in latewood rows. Normally, rays have a major role in radial shear parallel to the grain, and step-wise failure results due to the area of weakness they represent /12/. Areas of weakness are also found close to the tracheid ends, where the cells often deviate from their vertical alignment and are heavily pitted /12/.

3.1.2 Fiber Curl and Stretch

Curly fibers are a problem as they tend to lead to weaker anisotropy in paper properties than straight fibers /23/. Fiber interactions and flocculation resist the

rotation of fibers, and fibers may therefore bend during drainage /23/. In a low-density network, fiber curl and wrinkles reduce the critical buckling stress /1/. Fiber curl is especially undesired in pulp intended for carton board production, as it tends to decrease the elastic modulus of the pulp and thus increase the stretch of carton board /2/.

Fiber curl occurs when the fiber microstructure changes, i.e. inner fibrillation unfolds. This happens especially in alkaline conditions. When the alkali is removed, the reactive sites of the fibrils bond with each other. The bonding, however, does not occur at original sites for many reasons; for example, lignin or hemicellulose has been removed from the fiber leaving an open reactive site, or the mechanical forces have twisted the fiber so that sites physically close to each other are susceptible to bonding. The factors that affect this bonding are largely unclear, as is the time in which this reattachment happens /13/.

Pulp curl seems to be yield-dependent, i.e. the lower the yield, the curlier are the fibers /17/. Sundquist and Tikka observed that fiber curling occurs mainly during brown stock processing and can be up to 130-150% /13, 14/. Fiber curliness also tends to vary a lot in pulp samples from different mills depending on the process /13/. However, it is common for all pulp samples that the curliness of the final pulp tends to reach a "minimum" curliness level despite different processing conditions /13/.

The degree of fiber curl can be changed through beating the pulp to different degrees depending on beating conditions /17/. Laboratory-scale PFI beating produces straight and evenly treated fibers; however, according to Mohlin et al., mill-scale beating has a weaker fiber straightening effect /17/. Fiber deformations may also "heal" during the drying process in paper manufacturing /24/. The straightening of fibers in macroscopic drying increases the elastic modulus, and the fiber becomes better aligned. In some paper grades, fiber curl can even be beneficial by adding more porosity and bulk to the paper sheet /2/.

3.2 SWELLING OF FIBERS

The water intake and swelling of pulp fibers are important factors which have a strong influence on the consolidation and bonding of the fibers in the web and are, thus, important for the final quality of paper products /25/. Water is held by the fibers in many different ways; in the amorphous polymer parts of the fiber cell wall, in cracks and pores in the lumen and on the surfaces of the fiber, as well as by the fibrillar surface gel /25/.

The cell walls of dry fibers do not contain any pores. During the growth and the formation of the cell wall, the removal of water brings the structural elements together, and consequently, the cell wall shrinks. Subsequently, cell wall pores develop in the fiber during swelling, caused by water, which pushes the fibrils apart, allowing the structure to return, at least partly, to its original state /26/. The pores in the swollen, delignified cell wall appear to be rather uniform with an average size of around 100 nm in diameter, with the exception of possible micropores of an equivalent cylindrical size of around 2 nm /26, 27/. Figure 4 shows a picture of a swollen fiber surface.

Fibers immersed in water swell until equilibrium is established between the water in the fibers and the water in the surrounding solution, i.e. until the chemical potential of the water is the same everywhere /25/. According to Scallan et al., swelling results from the osmotic pressure generated within the fiber wall when the counter-ions of the acidic groups are exchanged from hydrogen to sodium form /27/. The degree of swelling depends on the temperature, ionic strength, chemical composition and internal fibrillation of the fibers, as well as on the mechanical restraints to the swelling of the wood fiber material /25/.

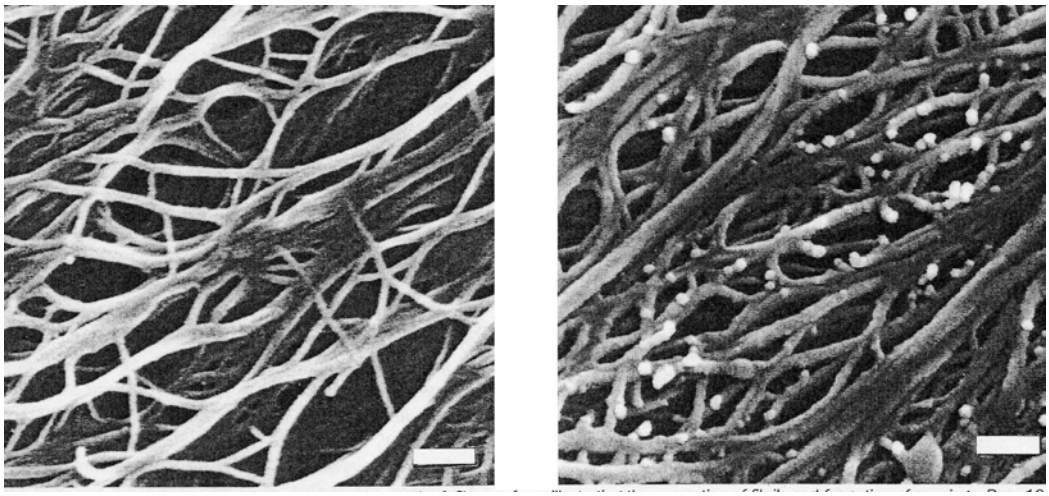

Figure 4. SEM micrographs of a freeze-dried, swollen unbeaten kraft fiber surface, illustrating the separation of the fibrils and the formation of openings (bar 100 nm) /26/.

In the beginning of delignification, the amount of bound water increases, which is a reflection of an increase in the amorphous (cellulose and hemicelluloses) carbohydrate content /25/. The presence of water converts the ligno-hemicellulose (located in the pores) to a micro-porous gel, where lignin acts as a cross-linking agent within the wall and hemicellulose acts as a coupling agent between lignin and cellulose /27/. Hemicelluloses promote fiber swelling, and lignin inhibits it /24/. In the later state of delignification, when the hemicelluloses have been removed, the remaining wood polymers are less water-absorbing due to their higher content of crystalline cellulose /25/. The pore volume also increases at first, due to the cavities developed when lignin is removed /28/. However, extensive delignification leads to a collapse of these cavities, lowering the amount of pore water /25/. It is probable that with progressive lignin removal, small pores develop into larger ones; also, the cell wall may collapse at low yields /25/. Furthermore, fiber damages lead to a decrease in the ability to retain water /29/.

Hartler suggested that swelling in a wood fiber can only take place towards the lumen and is, therefore, the only possible direction of expansion of the fiber cell wall /30/. According to Scallan et al., swelling occurs principally in a direction transverse to the microfibrils. In addition, as swelling progresses, the elastic nature of the cell wall resists the expansion until equilibrium is achieved /27/. The modification of the ligno-hemicellulose gel, for example during pulping, reduces the cross-linking effect of

ligno-hemicellulose, leading to a drop in the elastic modulus /27/. Thus, low-yield pulping leads to the collapse of pulp fibers /27/. The elastic modulus can, however, be increased through drying-and-rewetting, due to the formation of hydrogen bonds between the microfibrils /27/.

The swelling of fibers can cause them to straighten /24/. Swelling also yields more flexible fibers, and the increased fiber flexibility promotes conformability, thus allowing the fibers to form more fiber-fiber contacts and achieve a better web strength /31/. Certain chemical groups - such as carboxylic groups - dissociate in water, promoting fiber swelling and contribute to the improved flexibility and conformability of the fiber wall /24/. High contents of carboxylic acid groups on fiber surfaces may also increase the inter-fiber bonding strength /32/.

3.3 ANALYSIS METHODS OF FIBER DAMAGE

The deterioration of the pulp strength tends to vary in different mills and processes. However, the reduction of the tensile and tear strength and the Zero Span, which describes the deterioration of the fiber strength in the brown stock line, are common to every process. The most important task of fiber deformation analyses is to evaluate the effect of fiber deformation on the ability of the fibers to take up load and to transmit load /17/. When studying fiber damages most commonly used analyses are pulp viscosity, tensile and tear strength measurements, zero-span, wet zero-span, fiber curl and stretch. A more novel method of testing individual fiber strengths is the Single Fiber Fragmentation Technique (SFF), which enables the evaluation of the effect of an individual fiber strength on the loss in pulp strength /18/.

Fiber curl and dislocations can be determined via microscopic analyses, and nowadays, also automatically (Pulp Expert). The strength deterioration of individual fibers can be measured using wet zero span, however the local defects found in fibers probably have no effect on the zero-span measurement /12/. According to Mohlin et al., wet zero span is a good way of measuring the ability of fibers to carry load, as it is not affected by fiber-fiber bonds /17/. In fact, in their studies, they observed a good correlation between wet zero-span values and curl and kink indexes /17/. However,

although a change in the visual deformation of fibers is related to changes in their ability to transmit load, their shape (curl and kink indexes) cannot be used as a general measure when different pulps are to be compared /17/.

The curl and kink indexes are defined as follows:

Curl index = (fiber contour length / longest dimension)-1

Kink index = $(N_{10\text{-}20}+2N_{21\text{-}45}+3N_{46\text{-}90}+4N_{91\text{-}180})$ */ total fiber length*,

Where N is the number of kinks with an angle in the interval indicated by the subscript /17/.

Fiber dislocations and microcompressions can be determined using staining analyses. Poorly oriented and loose cellulose regions of cell walls stain more strongly than do the surrounding intact walls. For example, Congo red have be used to indicate cell wall discontinuities i.e. dislocations /12/.

Tracheids are susceptible to chemical attacks at sites of dislocations. The separation of cell wall microfibrils or bundles or the change of the direction of microfibrils lead to the breaking of hydrogen bonds, which results in a higher accessibility of cellulose to chemical hydrolysis /12/. The influence of acids, enzymes and other agents is related to the extent of the structural changes, with larger deformations increasing the accessibility of cell wall elements /12/. This feature can be used in studying fiber dislocations with the help of cellulase treatment. Cellulases are able to attack structurally irregular zones in the fiber wall, and penetrate the ruptured S_1 layer. This results in localized sites of degradation and, eventually, in the more rapid degradation of the fiber /12/.

3.4 POSSIBLE CAUSES FOR FIBER DAMAGE

The development of pulping technology has lead to dramatic changes in digester designs and volumes /33/. A major step towards modern digester technology was the shift from moving reactors to stationary ones, which enabled greater capacities and higher levels of production /15/. Serving as the first and main delignification and

defibration step, the digester is in a crucial position in the control of the pulp strength /15/.

So far, apart from already known detrimental effects of prolonged delignification, no single process has been clearly found to be the source for fiber damage in the downstream brown stock line. Changes in fiber properties occur in many steps and are usually caused by several factors. Pulping chemistry alone cannot explain the loss of mill pulp strength. Generally it can be said that treatments, which require high shear forces, high pH levels and temperatures, high consistencies and amounts of chemicals, and which contain contaminants or other impurities, result in fiber damages /2/. For example, Tikka et al. observed that dissolved solids and ion concentration play important roles in the genesis of the strength losses /15/. Fiber damages can occur in the fiber line between the digester and the oxygen stage if the temperature or pH is too high, especially when the pulp fibers are subjected to simultaneous intensive mechanical action /18/. Mechanical treatment can lead to increased curl and micro-compressions, which can decrease the sheet tensile properties /18/.

After the introduction of medium consistency pumping and high shear force fluidization, some questions were raised about their effects on the quality of the pulp /15/. These questions have mostly remained unanswered, because true chemical and physical mill conditions have not been or could not be used in laboratory-scale studies /15/. In the brown stock line, the pulp is repeatedly subjected to fluidization, pumping, mixing and washing. However, when testing single processes, such as fluidization and MC pumping, the occurrence of fiber damages due to these treatments is not clear /34/. Even rather harsh fluidization does not affect the length of the fibers, but can cause bending and deformation on the micro scale /35/.

The superior strength of laboratory pulp and never discharged basket pulp inside batch digesters points to the conclusion that the causes of strength losses must be sought among the mechanical phenomena that take place in certain chemical media and temperatures /15/. All downstream processes have their own strength-diminishing characteristics. Blow valve, blow tank pump and valve as well as oxygen stage all are known to cause fiber damages. The screening and washing process areas cause strength losses when processing high-strength softwood pulp produced at very high

digester strength delivery /14, 15/. Also valves used for flow rate regulation can cause fiber damage /2/. The tightening of valves leads to a sudden change of the pressure in the pipelines /2/. It can be hypothesized that sudden pressure changes within the process can cause damage in fibers by releasing dissolved gas from fibers causing cell wall ruptures /2/.

Tikka et al. have made some hypotheses concerning the sources for fiber damage:

1) The stronger the pulp, the easier it is for it to lose strength. Thus, high-strength pulp must somehow be more vulnerable to damage. After losing the first 20% of its strength, the pulp seems to become more durable. This means that conventional cooking should cause a certain kind and amount of fiber changes, which only appear in the later part of the process, if avoided in high strength delivery cooking /15/.
2) High efficiency pulping is too intensive. Repeated high-power, high-shear-force machine elements damage the fiber structure and weaken the pulp /15/.
3) The chemical process conditions are too severe, too concentrated. High concentrations of ions, alkali and high temperature in the brown stock operation due to closed cycles and the counter-current high recovery of dissolved solids with a low washing dilution factor render the pulp vulnerable to morphological changes in the fiber structure and ultimately impair the pulp strength /15/.
4) The unknown chemistry in closed-cycle mills, which is, for example, caused by radicals and ions /15/.
5) Non-uniform delignification may lead to over-cooking and damage in the fiber structure in the outer part of the chips, while the chip cores remain under-cooked and require more cooking in order to achieve a reasonable degree of pulping /15/.
6) Unknown and uncontrolled combinations of the above factors /15/.

4 EFFECT OF OXYGEN DELIGNIFICATION ON FIBER PROPERTIES

Oxygen delignification systems are known to reduce viscosity and cause strength losses if delignification is prolonged /15/. According to Elias Salvador et al., oxygen delignification has different effects on different types of pulp. In softwood, oxygen delignification leads to fiber flexibility and bonding potential, but decreases fiber rigidity /36/. In general, the effects of oxygen delignification are apparent in unbleached pulps, but substantially minimized or disappear completely after bleaching sequences /36/.

4.1 DISSOLUTION OF CARBOHYDRATES

Carbohydrates are attacked during oxygen alkaline delignification, more so than in many other bleaching chemistries /1/. In other words, the oxygen delignification stage tends to have poor selectivity, which is expressed as the ratio of attacks on lignin to attacks on carbohydrates ($\Delta\gamma/\Delta\eta$). The main problem in oxygen delignification is, in fact, related to its selectivity, which is affected by the process conditions and pulp contaminants /1/. The attack intensifies as delignification proceeds, as a result of which oxygen delignification has to be stopped when about half of the residual lignin has been dissolved in conventional alkaline conditions /1/.

Cellulose and hemicelluloses are, at least partly, bound to lignin, which would explain the difficulty of achieving selective delignification /37, 38/. Residual lignin may be trapped in amorphous regions in proximity to, or even linked to, hemicelluloses or cellulose /37/. Lignin-to-carbohydrate linkages seem to resist degradation by superoxide free radicals /38/. J. Buchert et al. observed that xylans can even inhibit delignification /39/. Haixuan Zou et al. also demonstrated that hemicellulose polymers, which are present in the pulp, and specifically xylan, can act as protective factors against cellulose degradation and losses of viscosity /38/.

The exact mechanism for the observed results is unknown, but several mechanisms have been proposed: The hydroxyl and organic radicals are formed *in situ* during oxygen delignification /38/. The hemicellulose polymers, which have a low molecular weight, compete with the cellulose for free radicals and, thus, prevent the undue loss of molecular weight of the cellulose /38/. Thus, high-yield pulping, e.g. anthraquinone pulping, appears to decrease carbohydrate degradation during oxygen delignification /38/. Secondly, the hemicellulose polymer present in the pulp undergoes competitive reactions with the alkali present in the pulp. The peeling reactions of hemicelluloses consume caustic, and thus lower the alkalinity in the oxygen stage; as a result, there is less alkali available locally to react with the cellulose. This results in less cellulose degradation, but the oxygen delignification is also low /38/. Other proposed mechanisms are related to the structure of hemicelluloses. For example, due to transport limitations, chemical reagents are physically present in higher concentrations in the amorphous regions in the fiber cell wall as compared to the cellulose crystallites /38/.

Xyloglucans have been found to acts as "tie molecules" in connecting cellulose microfibrils to each other /37/. Next to hemicelluloses, amorphous regions of cellulose microfibrils may act as tie molecules between the crystalline regions /37/. The degradation and dissolution of these tie molecules leads to a decrease in the fiber strength /37/. Thus, it can be stated that the dissolution of carbohydrates bound to lignin leads not only to yield loses, but also to fiber strength degradation and fiber form alteration during oxygen delignification.

4.2 FIBER CURL, LENGTH AND CRYSTALLINITY

If extended to 50-% delignification, oxygen delignification introduces fiber curl and compromises the ability of fibers to form bonds /40/. The resulting reductions in fiber strength become evident when the pulp is being compared to pulps prepared by conventional chlorine dioxide bleaching, which is known to be very selective /40/.

High alkali charges and high treatment temperatures during oxygen delignification lead to low kappa and high cellulose chain degradation, which can be seen as a drop

in linear viscosity. According to Fiskari et al., extensive oxygen delignification, accompanied with high shear mixing, results in fiber curliness and viscosity drops in Scandinavian softwood pulp /40/. The more severe the oxygen treatment, the greater is the introduction of curl and the decrease in the fiber length /40/. Fiskari et al. observed that extensive mixing in a laboratory-scale device resulted in considerable curl /40/. Furthermore, the fiber length was decreased, which is apparently an artifact of the measurement method, as curled fibers are not aligned within the plane of measurement and, thus, project an apparent length that is less than their true length /40/.

It has been observed that cellulose crystallinity, expressed as the crystalline/amorphous cellulose ratio, is affected during oxygen delignification in mill-scale treatments. However, in laboratory oxygen delignification, cellulose crystallinity remains somewhat at its original level, probably because of more gentle treatment than in mill-scale conditions /40/. Generally, the results regarding cellulose crystallinity changes due to delignification are, to some extent, confusing, since some scientist have observed the difference in cellulose crystallinity before and after delignification while others have not.

5 CONCLUSIONS

Softwood fiber damages, usually characterized as fiber curl, kink, dislocations and strength losses, pose a problem, especially in the processing of reinforcement pulp, as they tend to decrease the ability of fibers to transmit load. The damages in fibers occur mainly in the S_1 and S_2 layers when the microstructure of the fibers changes due to mechanical and chemical actions during pulp processing. Fiber deformation starts in alkaline conditions when the inner fibrillation of swollen fibers unfolds. When the alkali is removed, the reactive sites of the fibrils tend to rebond at new sites, due to mechanical forces, hemicellulose and lignin removal. Thus, the fiber form changes, which is seen in the form of increased curliness and dislocations.

According to several studies, alkaline processes, high temperatures, high shear forces and prolonged delignification all promote the formation of fiber damages. The more

severe the conditions are the more fiber damage occurs. The fiber damaging effect of oxygen delignification seems to be related mainly to the dissolution of carbohydrates. It has been observed that hemicelluloses, especially xylan, protect fibers against cellulose degradation and viscosity losses. Thus, the extensive dissolution of hemicelluloses during cooking can promote the occurrence of fiber damages during oxygen delignification. Furthermore, more if oxygen delignification is extended to 50%, with the accompanying high-shear mixing, more widespread fiber damages can be expected.

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