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## ÚSTAV PROCESNÍHO INŽENÝRSTVÍ
INSTITUTE OF PROCESS ENGINEERING

## ÚPRAVA BĚLÍCÍ TECHNOLOGIE PŘI VÝROBĚ BUNIČINY Z JEDNOLETÝCH ROSTLIN
MODIFICATION OF BLEACHING TECHNOLOGY IN PRODUCTION OF ANNUAL PLANTS PULP

**DIPLOMOVÁ PRÁCE**
MASTER'S THESIS

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# Assignment Master's Thesis

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SIXTA, H. (editor). „Handbook of Pulp". 2006, Wiley-VCH Verlag GmbH &Co. KGaA, Weinheim. ISBN: 3-527-30999-3.

TIKKA, P. (editor) "Chemical Pulping Part 1, Fibre Chemistry and Technology (2nd ed.)". 2008, book series: Papermaking Science and Technology, book 6.

BELTRAMINO, F., RONCERO, M.B., VIDAL, T., VALLS, C. "Facilitating the selection of raw materials: Evaluation of the effects of TCF and ECF bleaching sequences on different wood and non-wood pulps". Afinidad, [online], 2018, Vol. 75. https://www.raco.cat/index.php/afinidad/article/view/338228.

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# ABSTRACT

The diploma thesis deals with the bleaching process in paper production. The main goal of this work is to evaluate the current state of bleaching technology in the company OP Papírna, s.r.o. and to propose a modification that will lead to the higher efficiency of this technology. To solve the assignment, a search of technological principles of bleaching and laboratory experiments were performed to find the appropriate solution. The contribution of the experiments was supported by technological calculations. The results of experiments have shown that the current state of bleaching technology can be made more efficient in several ways. It was proven that the submitted proposals have the potential for large economic and chemical savings. The reader of this thesis will get a basic overview of pulp and paper production technology with a focus on the bleaching process and gain knowledge of its balance calculations.

# ABSTRAKT

Diplomová práce se zabývá bělícím procesem při výrobě papíru. Hlavním cílem práce je zhodnotit současný stav bělící technologie ve firmě OP Papírna, s.r.o. a navrhnout úpravu, která povede k větší efektivitě této technologie. K vyřešení zadání byla provedena rešerše technologických principů bělení a dále provedeny laboratorní experimenty s cílem najít vhodné řešení. Přínos experimentů byl podpořen technologickými výpočty. Výsledky experimentů ukázaly, že současný stav bělící technologie lze několika způsoby zefektivnit. Bylo ukázáno, že podané návrhy mají potenciál velkých ekonomických i chemických úspor. Čtenáři práce se dostane základního přehledu technologie výroby buničiny a papíru se zaměřením na bělící proces a získá znalost jeho bilančních výpočtů.

# KEYWORDS

paper production, pulp bleaching, bleaching experiment, bleaching technology, paper mill

# KLÍČOVÁ SLOVA

výroba papíru, bělení buničiny, bělící experiment, bělící technologie, papírna

## BIBLIOGRAPHIC CITATION

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# DECLARATION

I declare that I have prepared this diploma thesis on the topic of Modification of bleaching technology in production of annual plants pulp independently under the guidance of Ing. Vojtěch Kunert using professional literature and sources listed in the list of literature cited.


In Brno on May 21, 2021　　　　　　　　…………………………………………

Bc. Čeněk Kouřil

## ACKNOWLEDGMENT

# CONTENT

# 1  INTRODUCTION

Paper products have accompanied us for at least 5000 years across different areas of our lives. The first uses in form of papyrus are dated back to the year 3000 BC in ancient Egypt. It is basically a thin sheet of cellulose fibers made from wood, cloth rags, or herbaceous plants which are transformed into pulp from which the paper sheets are made. Paper is used in many areas of human life toiletry, packaging, communication, information storing in form of books and office paper, paper money, and many others.

Throughout history, humanity has been developing different kinds of paper from various plants like mulberry, hemp, bamboo, etc., and materials like fishing nets, old rags, or even animal skin. Followed by the beginnings of making paper from the wooden pulp in the early second century AD, paper production was slowly reaching the modern types of paper as can be seen in everyday life of the 21$^{st}$ century. In the year 1806, the first Fourdrinier-type paper-making machine was patented. The current state of the technology will be discussed later in the thesis.

Ancient Japanese papermakers tried to bleach the paper using high mountain streams containing ozone and therefore are the first using oxygen for bleaching. The first efforts to bleach the paper using chlorine are recorded in 1774. The first uses of calcium hypochlorite as a bleaching agent at U.S. mills are dated back to the year 1804. As time went by, people wanted the paper to be brighter. At the time, only single-stage bleaching with the help of chlorinated lime was enough to meet brightness requirements. New methods of making the pulp have resulted in the pulp that was harder to bleach and only one bleaching stage was not enough. Therefore, at the beginning of the 20$^{th}$ century, the bleaching process was evolved into multi-stage chemical treatment. The first bleaching sequence arrangement was the calcium hypochlorite stage followed by the alkaline extraction stage and again subsequent calcium hypochlorite stage. Chlorine dioxide came to use in the 1940s. Nowadays the use of elemental chlorine is prohibited in many countries due to its negative environmental effects. (*History of Paper*, n.d.) (U.S. Congress, Office of Technology Assessment, 1989)

For an overview of paper production, a comparison of places on Earth with the largest paper production is given. The long-term development of current paper production in the EU is shown in Figure 3. The trend of pulp production is growing due to efficient processes despite the reduction of the total number of paper production mills. Figure 1 and Figure 2 showing regions and European leaders with the largest amount of pulp production. There can be seen that Nordic countries are current leaders in the field of the European pulp-making industry.
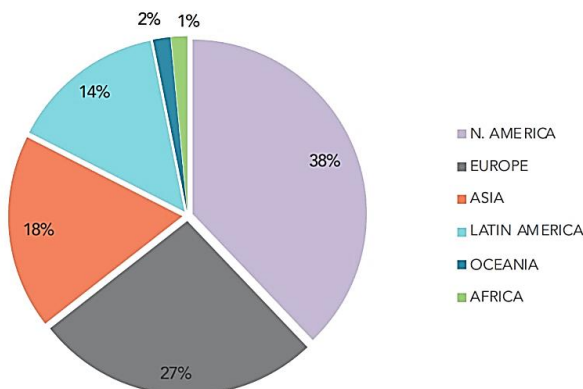




*Figure 2. Global pulp production by regions in 2014 (Haggith, Martin, 2018)*
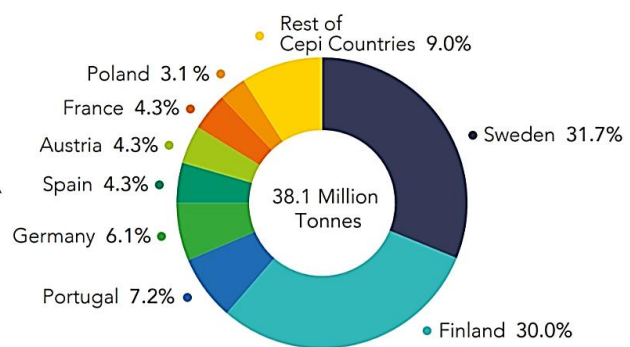
*Figure 1. Total pulp production by country in 2019 (Cepi, 2020)*
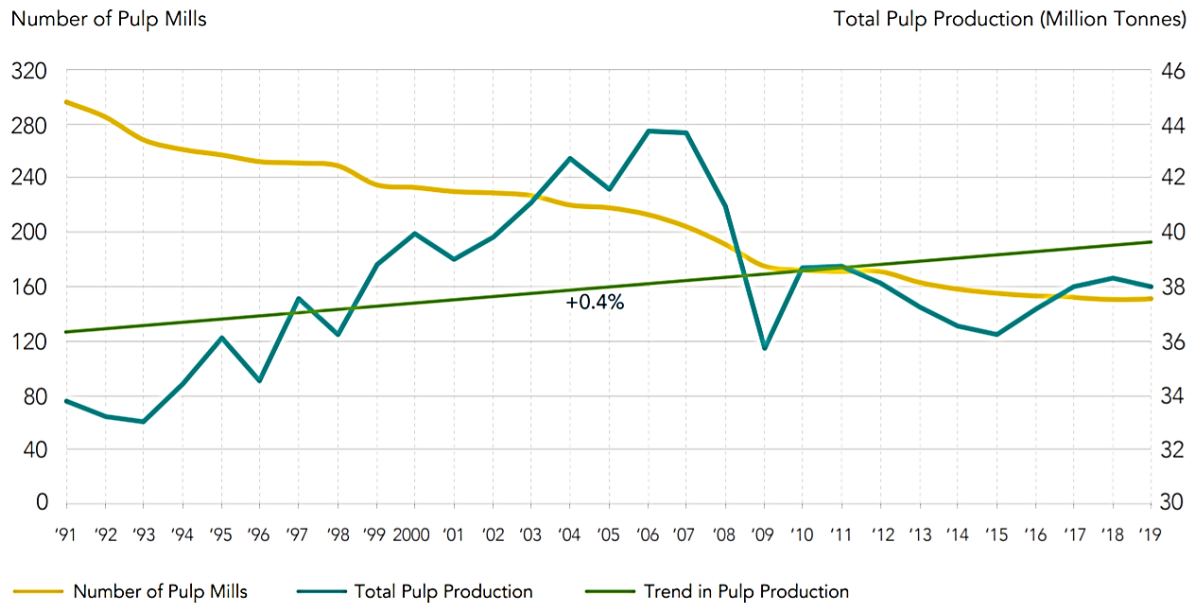
*Figure 3. Number of pulp mills and total pulp production in EU (Cepi, 2020)*

## 1.1  Pulp mill

The flow diagram for a pulp mill is shown in Figure 4. The part of the production on which this thesis is focused is highlighted by a red line. The input to the pulp mill could be wooden logs or tow from some annual plants. The process of making the pulp from these materials called the kraft process will be described later. The diagram shows the whole process with the main outputs. The process is based on recirculation and recovery of used liquids and chemicals in order to reach minimal heat losses and waste production. Some of the liquids pass sewage treatment plant and others are combusted to recover heat and some valuable solid contents. The main wastes produced by the mills are dregs, lime mud, slaker grits, and pulp mill sludge. Some of this waste can be recycled. For example, lime mud can be used in agriculture and construction in form of soil fertilizers or as a construction material substitute for calcium carbonate. Pulp sludge is proposed for use as fertilizer, but more widespread use is in construction as a filler. (Simão et al., 2018)



*Figure 4. Kraft pulp mill flow diagram (Mathews et al., 2013)*

The bleached pulp is then introduced to a machine called the Fourdrinier machine. The machine diagram is shown in Figure 5. The pulp is diluted at first and then formed, pressured, and dried on series of cylinders. The final wounded paper tambor can be cut to the required format of packed and handed for storage or transport. (Miranda et al., 2008)



*Figure 5. Fourdrinier paper making machine (Miranda et al., 2008)*

**Company collaboration**

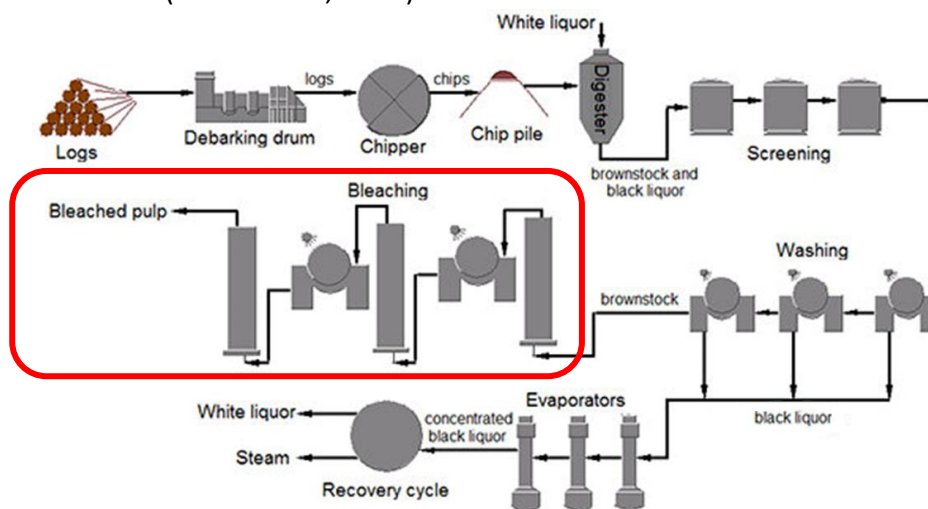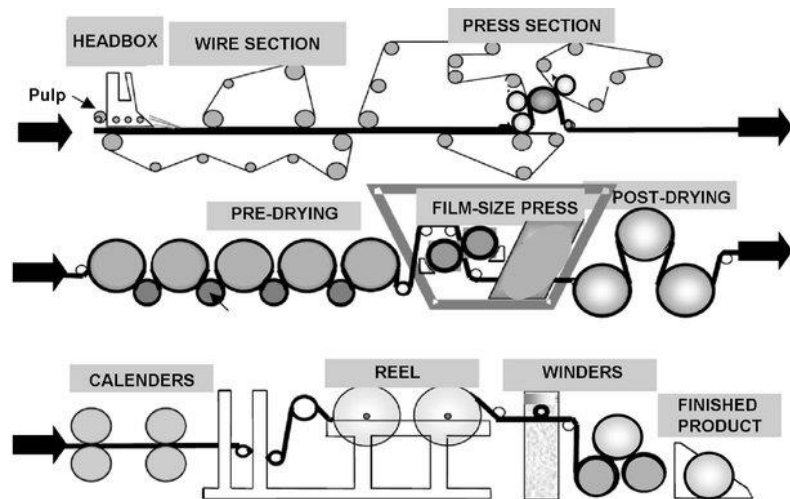This thesis was developed in collaboration with the company OP Papírna, s.r.o. which is part of the worldwide Delfort group. It is located in a village called Olšany in the Olomouc region. The mill consists of a kraft pulping line that processes annual plants and three paper machines processing the wooden pulp. The input materials for the pulping line are mainly flax and hemp tow. Later in the thesis will be performed experiments using the flax tow. The flax tow used is basically residue from the textile industry, which processes fibers of higher quality. The main products of the company are paper used for making cigarette paper, medication package insert, light book paper etcetera. Considering the nature of the final products which have to be clean, the mill does not process wastepaper (Delfort, n.d.).

## 1.2  Motivation and goals

The motivation behind this thesis is an optimization of the current bleaching line of the OP Papírna, s.r.o. pulping line. The bleaching process is a demanding operation that requires experiments in order to find optimal conditions. The intention is to find out, if the arrangement of the bleaching stages, washing quality, and other variables can lead to savings in form of energy, amount of chemicals, and finance.  The main goals of the thesis are these:

- theoretical research of the bleaching process and its possibilities,
- experiments verifying the proposed changes in the technology,
- mass and heat balance calculations in order to evaluate the proposed ideas.

Any positive results could eventually lead to real changes and possible investments in the modernization of the bleaching technology. The experiments expect that by using less amount of chemicals and thorough washed pulp for the goal of reaching the same or similar pulp brightness, at least 40 % of the expanses can be saved.

## 2 WOOD AND ANNUAL PLANTS PROCESSING

At first, before the bleaching process itself is described, it is appropriate to state some basics of materials entering the bleaching process and how they are acquired. Bleaching is applied to pulp formed by delignification of wood or annual plants. The difference between wood and annual plats is that wood (e.g., spruce, pine, redwood, etc.) has a distinct structure and composition of the strain unlike the structure of the stem of annual plants (e.g., hemp, flax, jute, etc.). Later this work will deal with bleaching of pulp made of annual plants, but the basics properties of the process are the same for wood and annual plants. This chapter discusses the process of making the pulp (pulping) from wood and its treatment preparation for bleaching, alongside with same basics of wood structure, respectively annual plants.

### 2.1 Wood structure

The basic element of wood is long fiber. Fibers are hollow tapering cells similar to a tube called tracheids. The length of tracheids can vary from short (earlywood) to long (latewood). The structure of wood is illustrated in Figure 6. The amorphous layer located between the cells is called middle lamella (ML or M). It has very high lignin content and can be imagined as a glue between individual tracheids. The tracheid itself consists of a primary wall (P) and secondary wall (S) which is divided into three separate layers ($S_1$, $S_2$, $S_3$). These layers are composed of microfibrils, which are bundles of cellulose, hemicellulose molecules, etc. Relating to thickness, the outer wall ($S_1$) and inner wall ($S_3$) are thinner than the middle layer ($S_2$). The cross-section of the wood cell is shown in Figure 7. To make pulp from wood, only the bark is removed, and the rest of the wood can be effectively used in a form of wooden chips (Tikka, 2008). In the next subchapters, the main chemical components of the cell wall will be described.
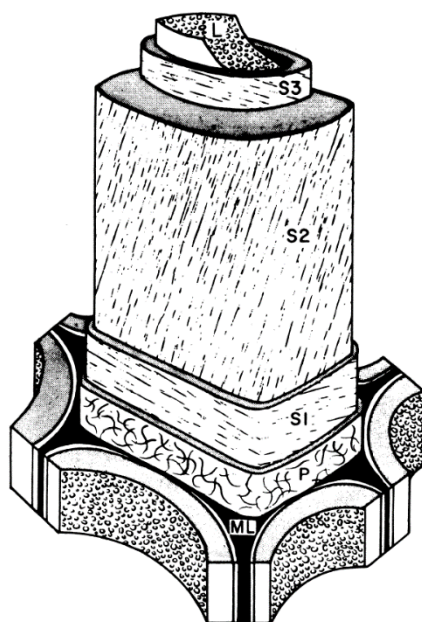


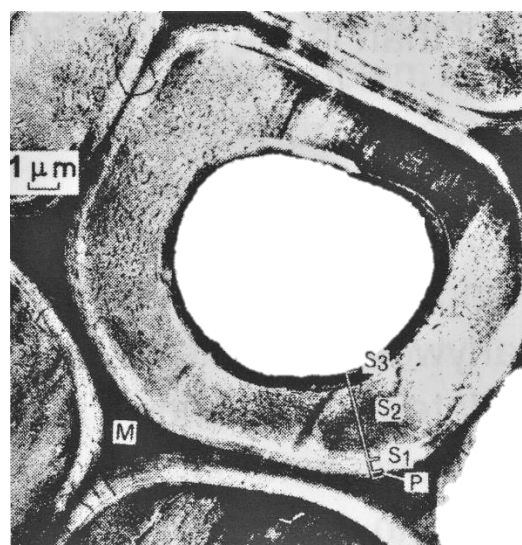*Figure 6. Schematic diagram of wood cell wall structure (Baillie, 2004)*

*Figure 7. Cross section of wood cell wall (Tikka, 2008)*

## 2.2 Annual plant structure

The structure of annual plants differs from the wood structure. It contains smaller amounts of lignin and the processing of annual plants provides better yield. But compared with wood, the pulp-making process is more difficult and also more expensive. The basic elements are not long woody fibers but so-called bast fibers. The stem of annual plants (Figure 8) consists of bast and wooden structure. The outer layer of the stem forms the epidermis (a). The outer surface of the epidermis is a resistant wax layer (cuticle), which protects the stem. Under the epidermis are bundles of bast fibers (d) bound by pectins arranged in rings and parenchyma (c). Closer to the center of the stem, underneath the cambium (b) which surrounds the bast layer, is located the woody layer (e) which is by its nature different from the wood cells. In the center of the stem is a hollow space called the lumen. The ideal part of the stem for pulp making are the bast fibers, which are easier to cook than the woody cells so-called shives. (Rouette, 2001)
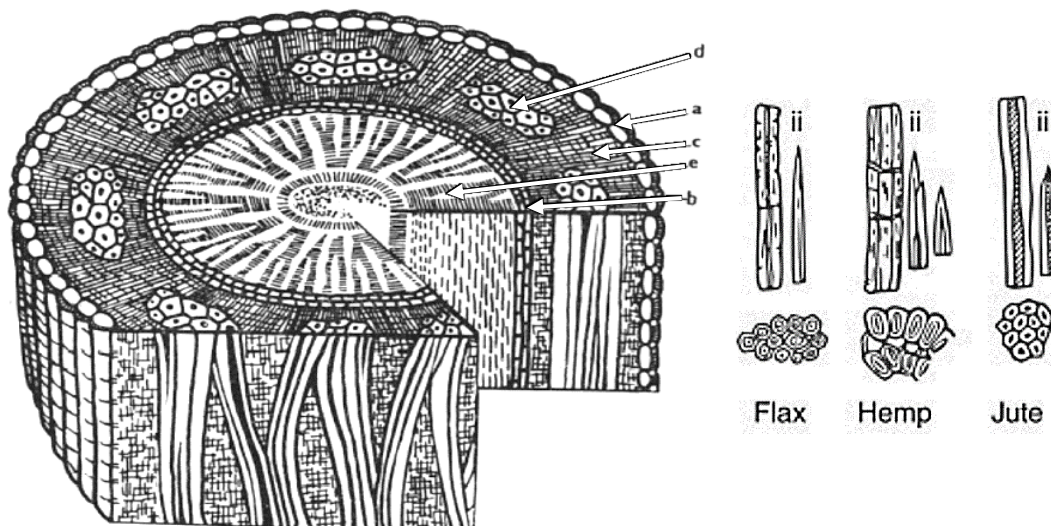


*Figure 8. Stem and cell structure of annual plants (Sain, Faruk, 2015)*

## 2.3 Chemical components of wood and plant structure

There are three main components in the structure of annual plants and woods – cellulose, hemicellulose, and lignin. Cellulose is a component, which should remain untouched by cooking and bleaching, and its strength preserved because it is the main component of paper production. On the other hand, hemicellulose and lignin should be removed from the pulp for a purpose of getting paper with the required optical and physical properties.

### 2.3.1 Cellulose

Cellulose is a polymer made of cellobiose, which makes these fibers usable for the papermaking process and also determines their properties. It characterizes the fiber strength of cellulosic materials. In pulping and bleaching operations, the goal is to minimize splitting and breaking cellulose chains, which can cause a reduction of fiber strength. (Smoke, 2016)

## 2.3.2 Hemicellulose

**Hemicellulose** is a polymer of five different sugars (cellulose contains only glucose) which form various polymeric structures. It can be degraded more easily than cellulose which leads to lesser content in pulp than in original wood. (Smoke, 2016)

## 2.3.3 Lignin

**Lignin** is amorphous, highly polymerized substance. Lignin is an important component of wood and is (after cellulose) the second most prevailing natural polymer on earth. Its main role is to solidify plant stems (Smoke, 2016). The chemical components distribution in cell wall layers is shown in Figure 9. Even though lignin concentration is highest in the middle lamella and in lowest in $S_2$ and $S_3$, more lignin amount is contained in these secondary walls than in middle lamella. Layer $S_2$ also contains most of the cellulose.

Flax and hemp plants have a small amount of lignin content (< 5 %) compared to wood and are difficult to delignified due to technological differences in the process. Other plants like jute or sisal have a higher amount of lignin (> 10 %) and are more easily delignified. For example, Norway spruce has a lignin content of 28 % and Silver birch 20 % (José et al., 2006).
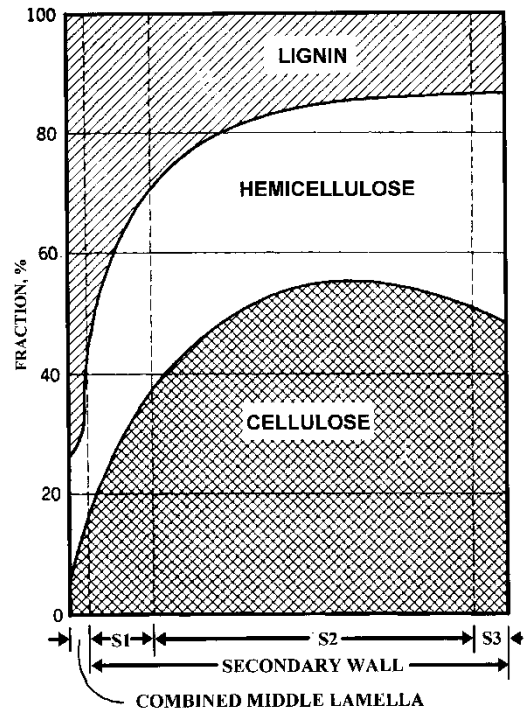


*Figure 9. Chemical distribution of tracheid wall (Tikka, 2008)*

## 2.4 Kraft process

The following description is targeted at making pulp from wood. The process of making pulp from annual plants is based on this process. With some modifications including change of chemicals rate addition, cooking time, temperatures, etc., the process itself is applicable for annual plants as well. Before the kraft process itself, the wood has to be prepared. Preparation compromises debarking and chipping of the wood following by screening of chips. Screening eliminates fine material and chips that are too big for the process. Prepared material is then introduced to the kraft process. It is fed to a pressure vessel called a digester used for cooking chips into pulp. The air in the chips is eliminated using direct contact by steam. The digester is filled with cooking liquor at a temperature between 80° and 100°C. The cooking is done in an alkaline solution of hydroxide (NaOH) and sodium sulfide ($Na_2S$) where the main active chemical agents are OH- and HS- ions which are present in the cooking liquor. The liquor consists of regenerated white liquor and black liquor from the previous cook. The contents are then heated to the required temperature (160-170°C). This can be done by direct steam or circulation of liquor extracted from the digester through a heat exchanger. This cooking temperature is maintained until the desired degree of delignification is reached. Bajpai

explains that "**delignification** is a process of breaking down the chemical structure of lignin and rendering it soluble in a liquid" (Bajpai, 2018, p. 313). For tracking the degree of delignification, the Kappa number is introduced. **Kappa number** expresses the amount of residual lignin presented of the pulp. It is an indirect measuring method, which applies the amount in milliliters of potassium permanganate consumed per one gram of lignin in the pulp by titration (Bajpai, 2018). Later on, measuring the Kappa number will be executed in laboratory experiments to find optimal conditions for bleaching stages.

The digester contents then go to a blow tank, which is a cylindrical vessel that receives hot pulp from the digester. In this blow action, the wooden chips are shattered into pulp-like material. The heat of the hot gases and volatile compounds are recovered in the blow heat recovery system. From the blow tank, the pulp goes through washing and screening where spent liquor is recovered and incompletely delignified wood chips and other impurities (bark, shives) are separated. Pulp is then stored and prepared for further processing (washing, oxygen delignification, bleaching) (Tikka, 2008). An example of the kraft process is shown in Figure 10.

The kraft process is the most significant pulp technique utilized – this technique takes 68 % of world pulp production. It is due to higher quality pulp than other pulping processes (sulfite and other techniques). Nevertheless, the fact that fibers were strong after the cooking is why the process bears the name "kraft" from the German word for strong. However, the pulp is much darker and harder to beat and bleach. (Triantafyllidis et al., 2013)

In the next subchapter, lignin, and carbohydrates reactions during the kraft process will be described.
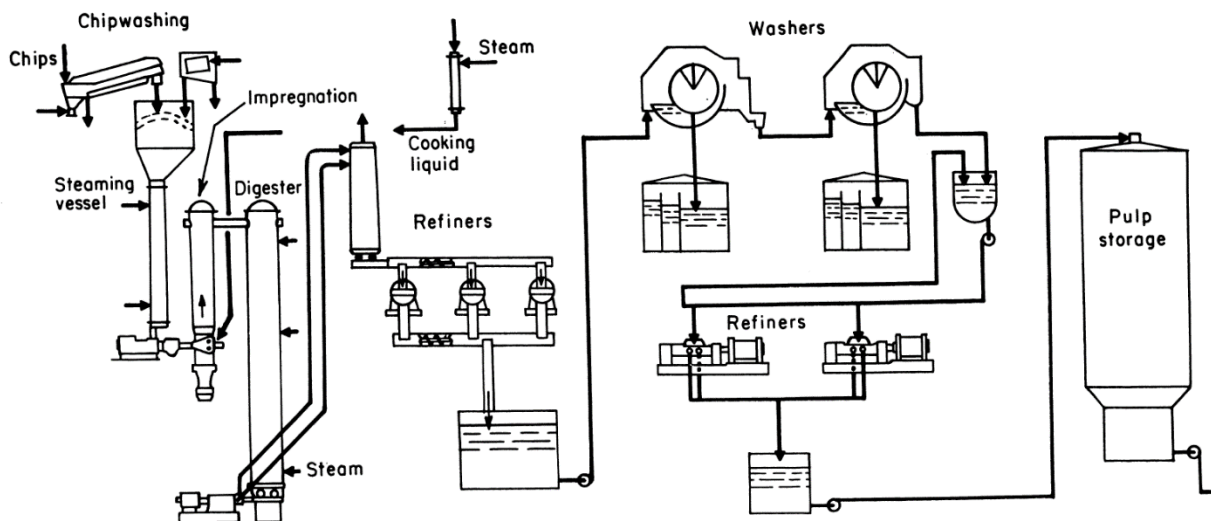


*Figure 10. Flow diagram of kraft process (Smoke, 2016)*

## 2.4.1 Lignin reactions

The objective of the kraft process is to remove as much lignin as possible. Concerning this, it is necessary to chemically reach not only the fiber walls but the middle lamella as well. This can be done by transporting chemicals and energy equally through the cell walls of each chip all the way into the middle lamella. This is possible at two major stages:

- *impregnation stage* – chips are soaked with liquid cooking chemicals before the beginning of delignification,
- *cooking phase* – constant chemical diffusion into the middle lamella.

After completely filling the chips with cooking liquor, the liquor can start penetrating the middle lamella and the delignification can begin. The lignin in the cell walls is then dissolved first. Dissolution of lignin in the middle lamella follows. The lignin in the middle lamella holds the fibers together, which shows that wooden chips can hold their wood-like structure even when 80 % of lignin is removed. This is consistent with the lignin distribution showed in Figure 9. shows three phases of the lignin reactions:

1.  Initial delignification – lignin dissolution starts during the impregnation stage before the cooking temperatures are reached (<140°C). In this phase, only small lignin fragments are decomposed, and the overall dissolved amount varies between 20-25 %. Corresponds to the first hour of Figure 11.
2.  Bulk delignification – when the cooking temperature is reached, the delignification rate rapidly increases. Starting with lignin in the cell wall, continuing into the middle lamella, about 70-80 % of total lignin is dissolved. This phase continues until approx. 90 % of the lignin is dissolved.
3.  Residual delignification – after the bulk phase, the residual delignification significantly slows down. However, it is important not to deplete all available alkali. It would lead to recondensation of dissolved lignin and eventually to preventing the dissolution. (Tikka, 2008)
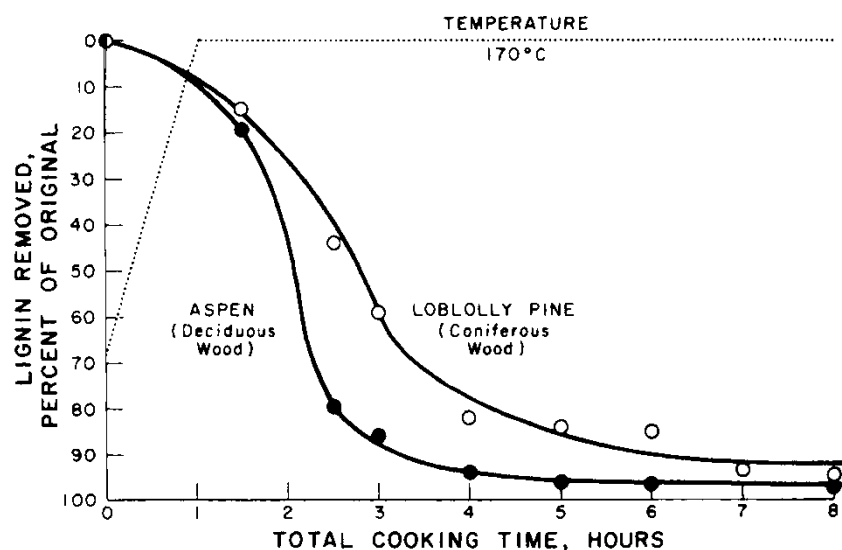


*Figure 11. Phases of lignin delignification (Tikka, 2008)*

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## 2.4.2  Hemicellulose reactions

During the alkaline cooking process, removing hemicelluloses is essential. The dissolution of hemicellulose leads to three important points:

- increasing the pore size in cell walls,
- increasing the overall rate of delignification,
- increasing the rate of delignification of the fiber wall concerning that of the middle lamella. (Kerr & Goring, 1974)

In the initial delignification phase, a large number of hemicelluloses are dissolved. For example, under 140°C all of Galactoglucamannan is dissolved alongside with dissolution of Xylan. The hemicellulose degradation is slowed down when delignification enters the bulk phase. It is important to note that hemicellulose degradation produces acid groups that consume alkali. Thus, almost all of the alkali is consumed at the beginning of delignification. (Tikka, 2008)

## 2.4.3  Cellulose reactions

Kraft process and chemical pulping, in general, is great at removing a large amount of lignin but still, some degradation of the cellulose also occurs. During alkaline cooking, about 10-15 % of cellulose is degraded. This degradation mainly takes place in the initial delignification phase and residual delignification lignin phase. It is manifested as pulp yield loss later in delignification and as a reduction in the degree of polymerization of the polysaccharides.  If the cooking is not stopped at the optimal point, the residual delignification will lead to fiber weakening. (Tikka, 2008)

## 2.5  Washing

Pulp washing is a very important operation placed either after initial cooking or in between individual bleaching stages. Often used term in this thesis from now on will be consistency. **Consistency** expresses how much dry matter is suspended in the pulp suspension. Thus, consistency can be formulated as follows:

$$Consistency\ [\%] = \frac{dry\ weight\ of\ sample\ [g]}{total\ weight\ of\ sample\ [g]} \cdot 100 \qquad (2.1)$$

The goal of pulp washing is separation dissolved organic materials and spent inorganic chemicals from pulp fibers. On top of that, pulp washing has two main purposes:

- recovery of dissolved substances from which valuable cooking chemicals are regenerated,
- cleaning pulp of contaminants and preparation for further processing to minimalize liquid effluents which lead to pollution.

These requirements are contradictory because the demand for pulp purity leads to high amounts of water used for washing, while recovery of chemicals demands minimal dilution of

the spent liquor. Environmental protection also calls for the elimination of liquid spills. So, the potential damage to the environment and the cost of treating effluents to be suitable for polluting regulations are big factors that force plants to maximize recovery of used materials in pulp washing. (Tikka, 2008)

There are three basic principles of washing. The first and easiest one can be done by diluting the fiber suspension with water or liquid cleaner than the original cooking or bleaching liquid (washing filtrate) followed by mixing and drainage the washing liquid from the suspension. A second principle is a free liquor in the fibers, concentrated in a pulp mat or layer, displaced with water or cleaner liquid. The last principle uses pressure to push out the original liquor from the fibers in a pressing mechanism. A single operation can never achieve the required purity, so normally there are more washing operations connected in series for maximization of cleanliness and minimize dilution and liquid usage. For example, Figure 12 illustrates counter-current three-stage pulp washing. In each stage pulp and wash liquid has different cleanliness and therefore is achieved optimal usage of wash chemicals. In the next part, among others, the main types of washing devices will be discussed. Although the positives above, the washing cycle can be formed only by one stage. For these washing stages, the same or mix of the following washer can be used (Tikka, 2008).
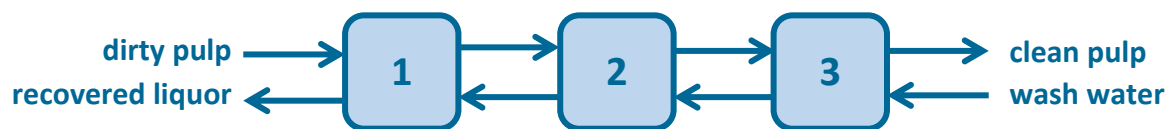


*Figure 12. Three-stage counter-current pulp washing*

## 2.5.1 Drum washers

The drum washer devices use principles based on filtering the liquor from the pulp under pressure, resp. vacuum. These washers can operate with pressure inside lower than atmospheric pressure or with the pressure outside the drum which is higher than atmospheric. Figure 13 describes the function of this device. The operation of the device starts by inletting the pulp from a storage tank. The pulp is diluted to approximately 1-3 % consistency and is winded up on the rotating cylinder where, through the filter, the liquor is extracted. The driving force is a partial vacuum inside the drum. This results in forming a mat on the surface of the drum which is then showered by wash water. This helps to displace the liquid in the pulp mat into the drum. Followed by another extraction zone, the remaining liquid in the mat is drawn in. In the end, the pulp mat is discharged from the drum and continues to repulper where the liquid is squeezed out and forms a more consistent pulp (Ek et al., 2009).
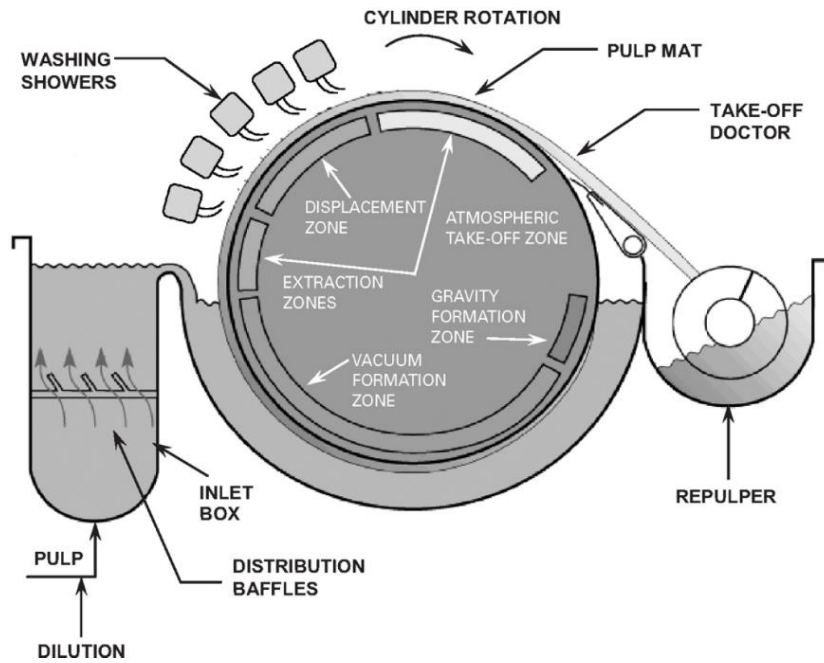
*Figure 13. Principle of drum washer (Ek et al., 2009)*

## 2.5.2  Displacement washers

Displacement washing takes place in devices called diffusers. These devices can work under atmospheric or pressurized conditions. They can be placed either directly on top of the unbleached pulp storage or independently as a close system to which the pulp is pumped. The washing is achieved by pulp traveling axially between concentric screen rings. The liquid in pulp is forced to displace through the screens by the pressure gradient between the wash water at the center and the room of the screen arrangement. The screen assembly is moved together with pulp for approx. 15 cm. The motion of assembly is then stopped, and screens are brought back to their initial position, from which the cycle can start again. When the washing is done, the pulp is removed from the top of the diffuser (ring scraper) and stored in a tank for further processing. (Ek et al., 2009) The diffuser is illustrated in Figure 14.
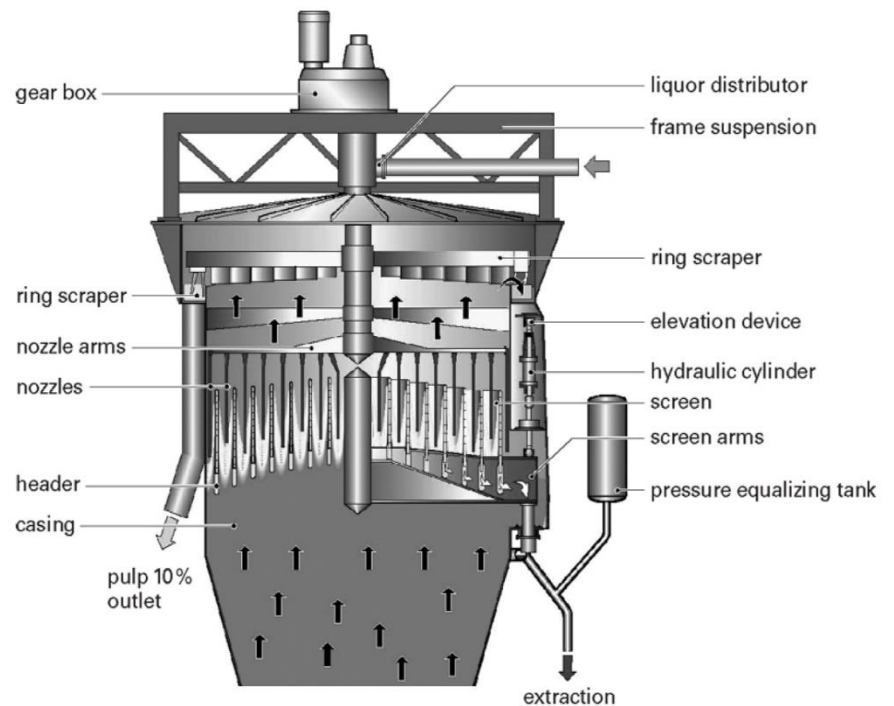


*Figure 14. Description of atmospheric diffuser (Ek et al., 2009)*

### 2.5.3 Horizontal table washers

This type of device is similar to the fourdrinier-type paper machine. In this case, the formed mat is traveling on a synthetic wire and is showered by wash water corresponding to its stage. The washing is done by counter-current flow arrangement as can be seen in Figure 12. Between these washing stages, there is no repulping or redilution. The pressure drop between the mat and boxes underneath is provided either by pressure above the table or slight vacuum in the boxes. This results in displacing the liquor in the mat into the boxes. The effective consistency during this operation is around 10 %. As in Figure 15, usually, there are five to six washing stages on the table to achieve the required purity. At the end of the line, a pulp mat is collected and repulped, meaning squeezing the liquid out and forming a more consistent pulp (Ek et al., 2009).
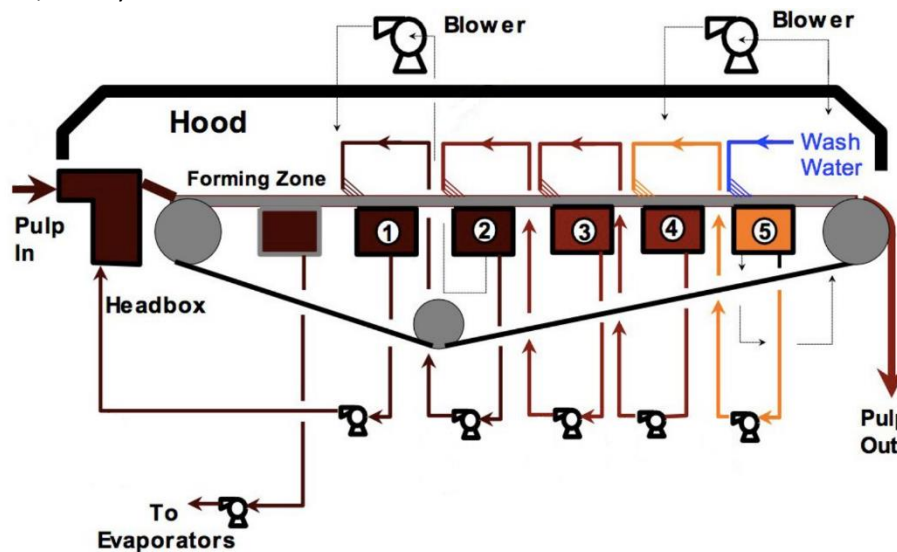


*Figure 15. Diagram of horizontal table washer (*Foam Contol Application*, n.d.)*

### 2.6 Oxygen delignification

Oxygen delignification can be essential as delignifying the continuation of the kraft cooking. This process is placed right after the initial cooking, washing, and screening just before the bleaching plant. The kraft process can remove approximately 97 % of lignin content but the remaining amount of residual lignin is rather resistant under pulping conditions. It is possible, through oxygen delignification, to reduce the residual lignin content of cooked pulp by another 40-75 %, depending on the type of wood used. This results in higher pulp brightness and makes further bleaching easier in a sense of lower demand for bleaching chemicals. Delignification can be done at medium (10-14 %) or high (22-30 %) consistency under alkaline conditions. The idea behind oxygen delignification is to get direct contact between pulp fibers and the oxygen gas, where oxygen reacts with both lignin and carbohydrates. Figure 16 shows reactions of functional groups of lignin during oxygen delignification. Difficulty with the commercialization of oxygen delignification was caused by carbohydrate depolymerization during the process. It was explained by the formation of reactive oxygen-based radicals generated by oxygen attacks on lignin structures. Later was discovered that adding small amounts of magnesium carbonate leads to protecting the carbohydrate from decomposition. (Sixta, 2006)

| Functional group | Relative reactivity to oxygen |
|---|---|
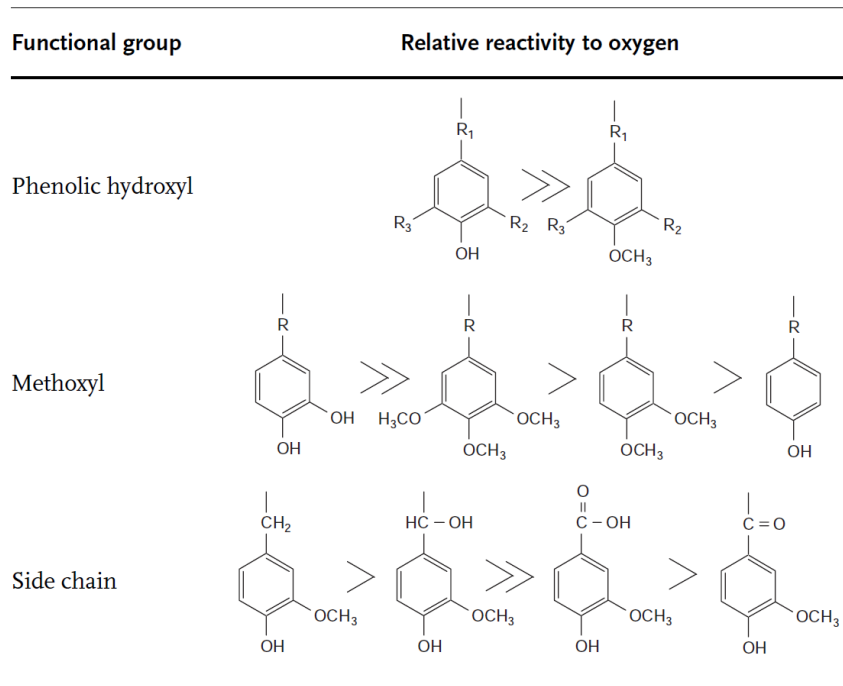
*Figure 16. Reactivity of lignin model compounds with oxygen (Sixta, 2006)*

## 2.6.1  Process description

The oxygen delignification system is shown in Figure 17. Washed and screened pulp is preheated and pumped by a medium consistency pump into the mixer, where pH is adjusted and oxygen is dispersed under pressure into the pulp suspension.  The mixture then continues to upflow reactor, passing through and on the top is discharged to a blow tank, where gases are separated and pulp travels into another washer.  (Tikka, 2008)
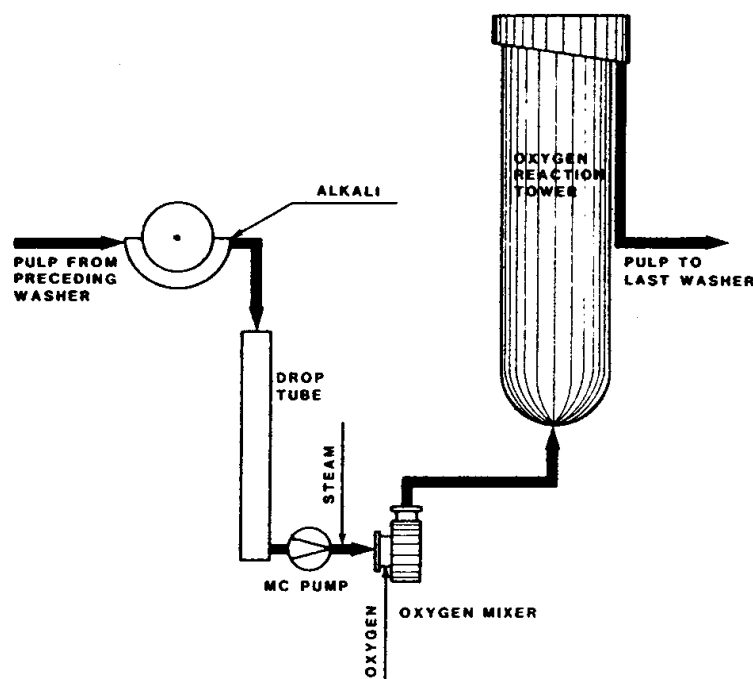


*Figure 17. Oxygen delignification at medium consistency (Smoke, 2016)*

# 3 BLEACHING PROCESS

Pulp after cooking or oxygen delignification still contains small amounts of residual lignin, which results in high colorization of the pulp. On top of that, pulp also contains dirt specks (shives, bark, etc.), resin compounds, and other impurities (carbon particles, rust, grease, sand, etc.) which should be removed by cleaning and screening. These cause problems in further processing of fibers or the use of the products. Further cooking for a purpose of removing these impurities cannot be applied, because it would lead to significant loss of pulp quality due to enhanced cellulose degradation. The purpose of bleaching is thus to chemically reduce the amount of residual lignin and removing the remaining discussed impurities and so increasing the brightness of pulp. Also, bleaching implies modification of optical properties of pulp fibers by changing or removing components capable of absorbing visible light. Bleaching can be also used to modify cellulose polymerization and increasing its content (Sixta, 2006).

## 3.1 Optical properties

The final optical properties of paper made of pulp (sheet such as brightness or opacity) determine its use or further processing. As is shown in Figure 18, the incident light on the paper sheet can be absorbed, reflected, scattered, or transmitted. The goal of bleaching is not changing the mechanical properties of the pulp, therefore, while preserving the scattering effect, the light absorption effect is minimalized instead. (Tikka, 2008) This is in accordance with the Kubelka-Munk theory (3.1), which combines all light effect into a factor known as reflectance:

$$R_\infty = \frac{k}{s} - \sqrt{\left(\frac{k}{s}\right)^2 + 2 \cdot \frac{k}{s}} \qquad (3.1)$$

where    $R_\infty$    is the reflectance of an infinite pile of sheets $[-]$,
         $k$      is the light absorption coefficient $[m^2/g]$,
         $s$      is the light scattering coefficient $[m^2/g]$.
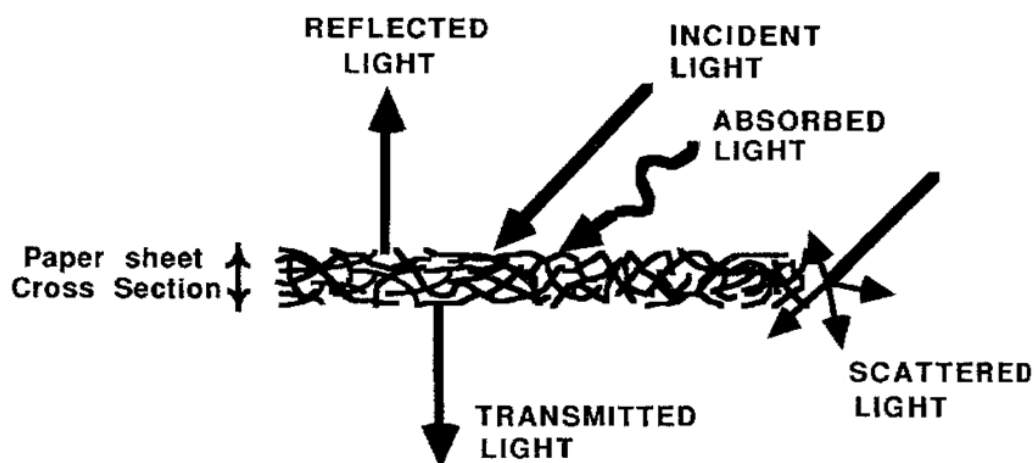


*Figure 18. Physics of light and paper pad (edited) (Tikka, 2008)*

### 3.1.1 Brightness

Brightness (whiteness) is a variable measured after bleaching. The targeted level of brightness is dependent on the use of the pulp for paper production and the requirements of the customer. It is an internationally defined ISO standard as the reflectance of visible blue light (457 nm) from a pad of pulp sheet and can be expressed as a loss of reflectance (Figure 19) according to (3.1). The measuring of the brightness takes place under ISO-defined conditions (ISO 2469, ISO 2470). The ISO brightness of the nonreflecting (black) material is 0 %. On the other hand, perfectly reflective material achieves 100 % of ISO brightness. The brightness levels of unbleached and bleached pulps reach values from 20 % to 95 %. Whereas the light scattering coefficient is not intentionally changed in the bleaching process, the lowering of the light absorption coefficient is done by reducing the number of chromophores, which absorbs light. (Sixta, 2006) Relation between brightness and chromophore concentration expressed as $k/s$ is drawn in Figure 19.
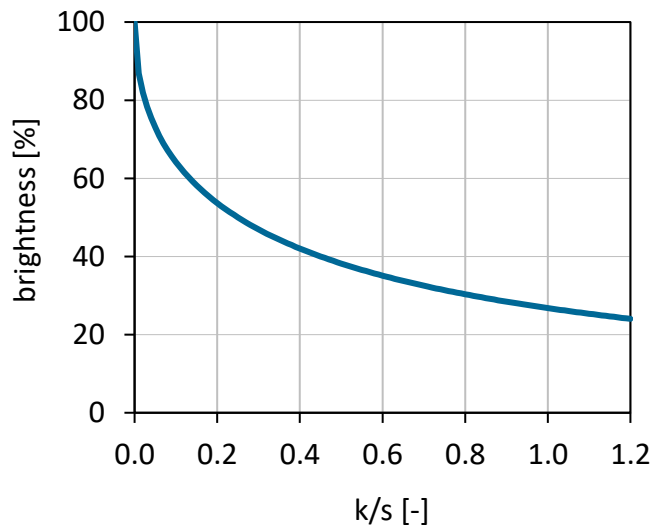


*Figure 19. Brightness and light absorption relation*

## 3.2 Bleaching chemicals

Bleaching reactions are equivalent to oxidation reactions. Various chemicals are used as bleaching oxidants. Their main role is to decompose residual lignin in the pulp and to increase its solubility. Bleaching chemicals can be categorized into three groups according to particular lignin structures they prefer to react with. This concept is presented in Table 1 (Sixta, 2006).

| | Category | | |
|---|---|---|---|
| | **I** | **II** | **III** |
| Bleaching chemicals | $Cl_2$, $O_3$ | $ClO_2$, $O_2$ | $NaOCl$, $H_2O_2$ |
| pH conditions | acid | acid/alkaline | alkaline |
| Reaction sites | aromatic lignin units, phenolic groups, double bonds | free phenolic hydroxyl groups, double bonds | functional lignin groups – carbonyl groups |

*Table 1. Bleaching chemicals reactions classification*

Bleaching chemicals can be also grouped by their particular task. Some chemicals such as oxygen, chlorine, and chlorine dioxide are significant due to their ability to delignify residual lignin. Other chemicals, for example, alkaline hydrogen peroxide, do just a little delignification but they reduce chromophores in lignin. Some are capable of doing both of these jobs (chlorine dioxide, hypochlorite). On top of reactions of bleaching chemicals with residual

lignin, the chemicals also react with extractives in form of barks, knots, pitches, shives, etc. These reactions can be described according to their oxidation potential. The oxidizing power of bleaching chemicals is connected to their capacity to take up electrons and can be expressed as "how many moles of electrons have been transferred during oxidative bleaching" (Tikka, 2008). The name of this unit is Oxidizing Equivalents (OXE). A comparison of oxidizing equivalents of bleaching chemicals is shown in Table 2. For later use, each bleaching chemical is designated with a specific letter. This is essential for the description of bleaching stages in the next chapter.

| | Molar weight [g/mole] | Electrons transferred [mole$^{-1}$] | Equivalent weight [g/mole] | Active chlorine* | Designation |
|---|---|---|---|---|---|
| $Cl_2$ | 71.0 | 2 | 35.5 | 1.00 | C |
| $ClO_2$ | 67.5 | 5 | 13.5 | 2.63 | D |
| $O_2$ | 32.0 | 4 | 8.0 | 4.43 | O |
| $H_2O_2$ | 34.0 | 2 | 17.0 | 2.09 | P |
| NaOCl | 133.0 | 2 | 66.5 | 0.53 | H |
| $O_3$ | 148.0 | 8 | 8.0 | 4.43 | Z |

*oxidizing power in relation to chlorine/mole [kg active chlorine/kg]

*Table 2. Bleaching chemicals with their oxidizing equivalents (Tikka, 2008)*

## 3.3  Sequences

Bleaching is usually done by connecting multiple stages with the same or different treatments. The pulp between individual bleaching stages is often washed to remove dissolved impurities. This leads to improved bleaching efficiency of the bleaching stages. It is also advantageous considering different reactions of bleaching chemicals in Table 1 which provides synergy in bleaching or delignification. In practice, the first bleaching steps are conceived with delignification chemicals, which remove a major amount of residual lignin, while later sequences focus on the elimination of chromophores contained in the pulp. Both principles result in higher brightness levels. (Sixta, 2006) Figure 20 illustrates why it is essential to replace the single bleaching stage with multiple steps. Here, multi-stage bleaching has been done. Under the established convention, which designates these sequences with letters, this sequence can be described as *D/CE$_O$DED*. The explanation is as follows:
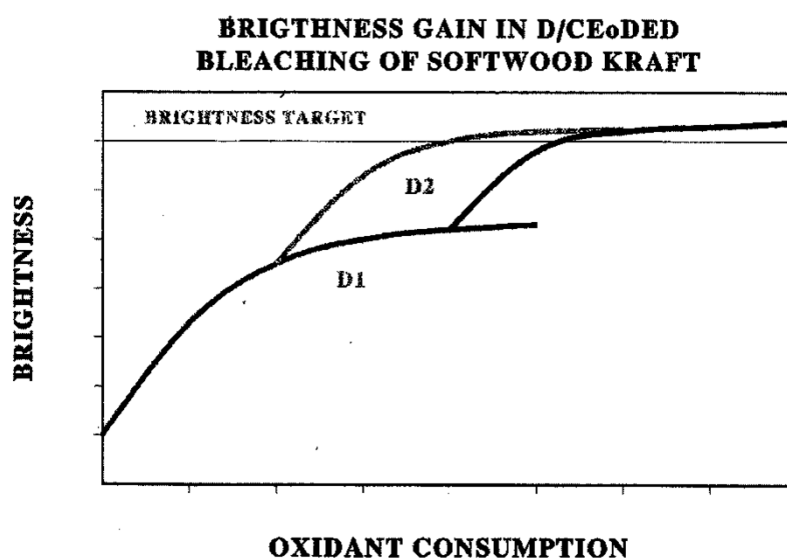


*Figure 20. Brightness development of bleaching sequence (Tikka, 2008)*

- *C* chlorination stage including mixers and washing,
- $C_D$ chlorine dioxide is used in minority, the major chemical used is chlorine,
- *D* chlorine dioxide stage including mixers and washing,
- *(C+D)* chlorine and chlorine dioxide are mixed simultaneously,
- *D/C* chemicals are added in sequence,
- *O* oxygen delignification,
- $E_P$ alkali extraction, where an additional charge of hydrogen peroxide is added,
- *(ED)* no washing between extraction stage and chlorine dioxide stage
- *Q* chelation stage.

As can be seen in Figure 20, with a single chlorine dioxide stage (curve D1), the targeted brightness cannot be achieved. The brightness rising is slowed down after an initial phase due to side reactions with dissolved organic substances. If the bleaching treatment is stopped after the initial phase and the pulp is washed out of the reaction products and then is again introduced to the second bleaching treatment (curves D2), the targeted brightness can be effectively achieved without the need for an extra amount of consumed chemicals. A simple example of the $CE_OHD$ bleaching sequence with mixers and washers is shown in Figure 21. (Tikka, 2008)
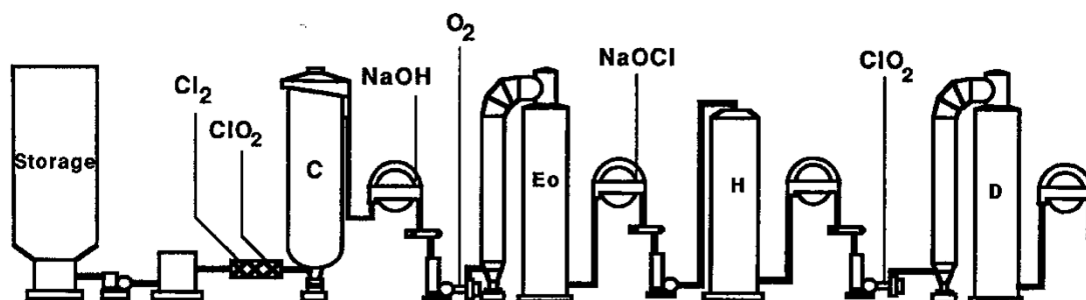


*Figure 21. Block diagram for bleaching sequence (Tikka, 2008)*

## 3.4 Chlorination

In pulp bleaching, chlorine was the most used delignifying chemical. Formerly was chlorine the first choice due to its low price and much better selectivity than other chemicals. Despite its great features, the use of molecular chlorine has been on the decline since the 1980s due to its reactions with pulp constituents and nowadays is prohibited in many countries. The reason is that the use of elemental chlorine results in the formation of chlorinated organic matter which negatively affects the environment and became a real threat. (Tikka, 2008)

Because of strong environmental concerns, pulp-making plants were looking for new technologies that did not use chlorine. The outcome was a transition from chlorine to chlorine dioxide, oxygen, and hydrogen peroxide and a major decrease in chlorinated organic

compounds. Still, in chlorine dioxide bleaching sequences, the formation of small amounts of organically bound chlorine is not avoidable. (Ek et al., 2009)

### 3.4.1 ECF & TCF bleaching

Given the above and pressure from environmental organizations, new efforts have been made to find new ways of bleaching with suppressing the use of elemental chlorine. The new bleaching processes can be divided into two categories: **elemental chlorine-free** (ECF) and **totally chlorine-free** (TCF) bleaching. In the ECF bleaching process, no elemental chlorine is used. As was stated before, chlorine was replaced with chlorine dioxide which is the principal bleaching agent for ECF bleaching. The pulp that has undergone the ECF bleaching is dominating the world market with bleached pulp. For example, 96 % of bleached pulp production in North America is the outcome of ECF technologies. The analyses of wastewater from ECF bleaching confirm that it is virtually free of dioxins and other toxic substances and the chlorine which is not removed from the wastewater has a composition comparable to chlorine occurring in nature and no longer is a significant threat to the environment. The transition to ECF bleaching was reasonably easy for many bleaching plants because they would already have the equipment needed for ECF bleaching and the price increase was no more than 10 %. The ECF type of bleaching is applied in the experimental part of the thesis. (Bajpai, 2018)

The TCF bleaching process is less common than ECF bleaching by 10 times. It is characterized by the usage of chemicals without chlorine in any form. These chemicals are only based on oxygen (hydrogen peroxide, ozone, peroxy acids). Whereas the TCF bleaching does not use chlorine, which is good at removing transition metals, the bleaching process is enhanced by a chelation stage or acid hydrolysis. Extended delignification and oxygen delignification often precedes TCF bleaching.  When the kappa number after delignification is low enough, hydrogen peroxide and oxygen are no longer efficient and ozone, which is a stronger delignifying agent, has to be applied. The drawback of TCF bleaching is that at full brightness it cannot preserve required strength properties (10 times lower than ECF) and compared to ECF, the transfer to TCF bleaching is much more expensive.  The cellulose-degrading mechanism occurring in TCF bleaching could be practically suppressed by decreasing the ozone charge and introducing new bleaching agents that do not have that high negative effect on the cellulose. These new methods are still not available and require further development. (Bajpai, 2018)

## 3.5  Chlorine dioxide bleaching

As was mentioned earlier, chlorine is the driving force of high-efficiency bleaching due to its capability in reducing lignin and making it alkali-soluble. Chlorine dioxide reacts differently from chlorine but is able of doing a similar job. Chlorine dioxide bleaching with subsequent alkaline extraction is able of removing 75-90 % of residual lignin from the pulp. The chlorine dioxide reacts primarily with aromatics and phenolics and is therefore important in brightening the pulp without significant carbohydrate losses. Chlorine-based bleaching is also effective in dissolving transition metals from the pulp because the bleaching takes place in highly acidic conditions (low pH). A negative aspect of bleaching with $ClO_2$ is the formation of

large amounts of chloride ions which leads to the corrosivity of the process liquids. (Tikka, 2008)

Chlorine dioxide is always produced directly in the mill because, in its gas form, it is unstable and therefore hazardous of rapid decomposition to chlorine and oxygen. Chlorine dioxide is generally prepared from sodium chlorite ($NaClO_2$) or sodium chlorate ($NaClO_3$) in strongly acidic conditions. Chlorine dioxide is in the bleaching process reduced through a series of different reactions (Figure 22) producing various intermediates. Some of these (HClO) can form organochlorine compounds as well as molecular chlorine. An example of a complex reaction chain of chlorine dioxide with creosol which is a simple phenolic compound representing structural types that are assumed to be present in residual lignin is shown in Figure 23. (Sixta, 2006)
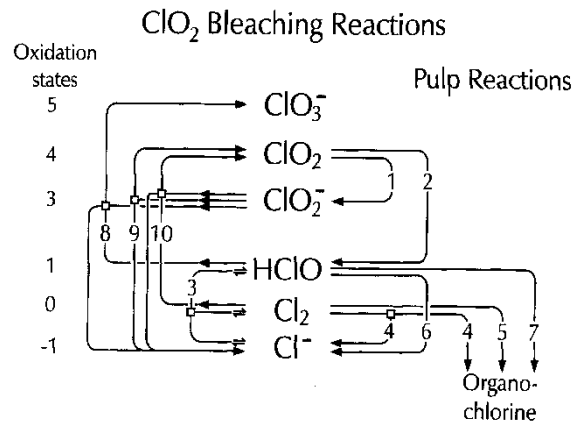


*Figure 22. Illustration of interconnectedness the bleaching reactions of pulp and chlorine dioxide (Tikka, 2008)*
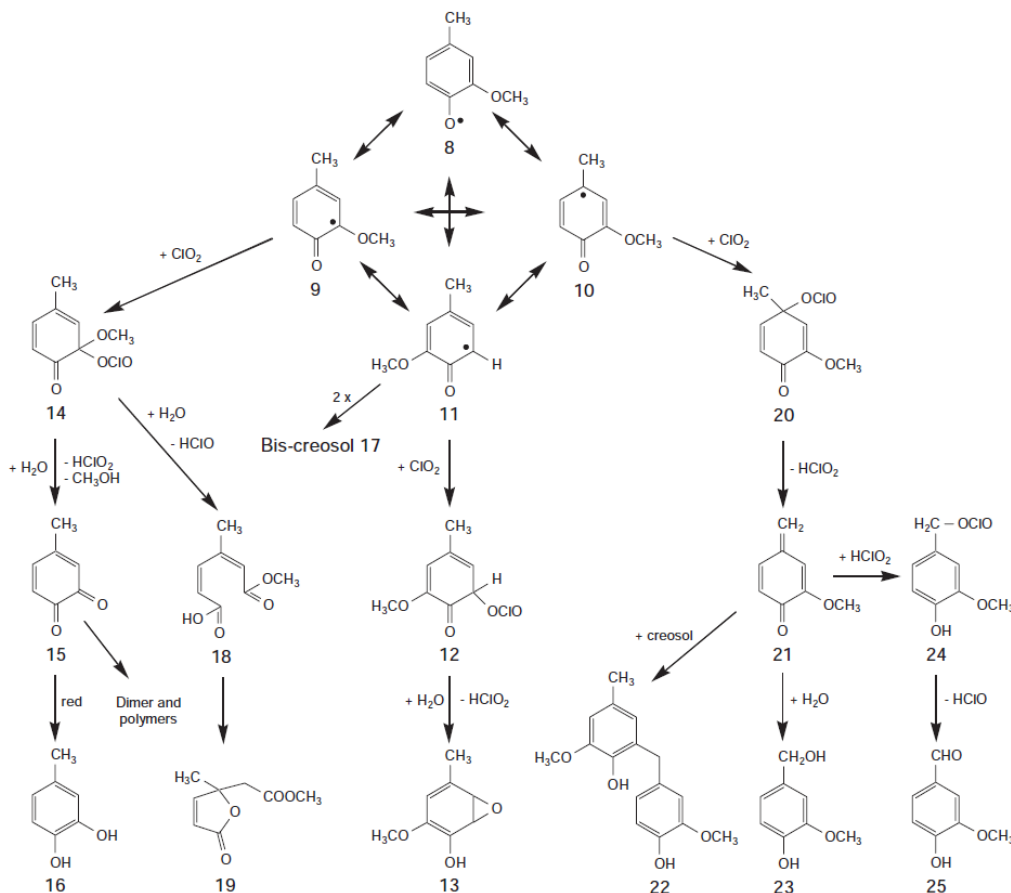


*Figure 23. An example of reactions of chlorine dioxide with creosol (Sixta, 2006)*

### 3.5.1 Bleaching conditions

**Chemical charge**

The pulp brightness development after a charge of chlorine dioxide is added is rapid. After the initial brightness growth, the following increase is gradually slowed down approaching an asymptotic limit. Left over $ClO_2$ is then consumed by secondary reactions or does not react at all as measured residual active chlorine at the end of the bleaching stage. Figure 24 is shown the development of brightness at different charges of $ClO_2$ applied in the third stage. The optimum charge here is around 1 % because the further increase in brightness is minimal. $ClO_2$ bleaching stages are designed to preserve a certain amount of active chlorine at the end of the bleaching to provide an adequate driving force for the bleaching. (Tikka, 2008)
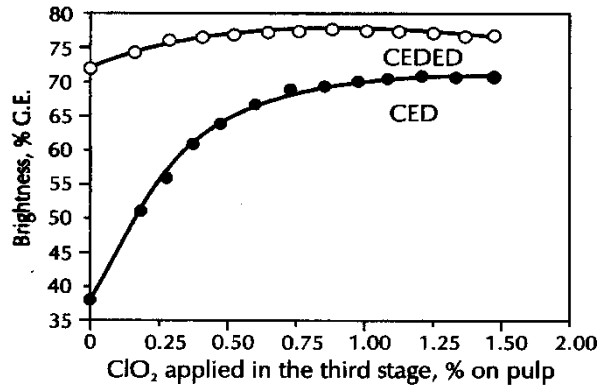


*Figure 24. Chlorine dioxide charge effect of CEDED and CED bleaching sequences (Tikka, 2008)*

**Time, pH, and temperature**

Chloride dioxide bleaching takes place under strongly acidic conditions, where pH is around 2-4. Initially, the brightness and $ClO_2$ consumption are quick. The brightness increase after the initial step is not negligible and continues to rise slowly for hours. Because of this, these stages are meant to retain for a long time. For example, an up-flow reactor can have a retention time of 30 minutes and a down-flow tower up to 2.5 hours. It is common for $ClO_2$ bleaching stages to remain at temperatures of 65-75°C. The bleaching temperature is variable due to adjusting the exit temperature of the chemicals to suit the process. (Tikka, 2008)

**Consistency**

Medium consistency (9-15 %) pulp is usually introduced for chlorine dioxide bleaching. A consistency above 12 % is advised because the $ClO_2$ solution or condensing steam will then dilute the suspension to around 10 %. This is important due to proper suspension flow through the tower and avoiding stock-flow channeling in the tower. (Tikka, 2008)

### 3.6 Hydrogen peroxide bleaching

Hydrogen peroxide ($H_2O_2$) is a bleaching agent widely used in brightening mechanical pulp. It is primarily used for its ability to remove chromophores resulting in higher pulp brightness. For its low price, it is mostly used to enhance the existing bleaching stages resulting in lower consumption of more expensive chemicals. $H_2O_2$ stages can take place as the first stage providing boost for subsequent delignifying stages or during final extraction stages, where it provides pulp brightness stability over time, which would otherwise decay. The reason why hydrogen peroxide came to greater use is environmental danger from the usage of chlorine

and chlorine dioxide, which can cause damage to nature. The environmental trend of diversion from these chemicals contributed also to the use of hydrogen peroxide. (Bajpai, 2015)

Hydrogen peroxide is friendly from an environmental point of view because it only decomposes to oxygen and water (equilibrium (3.2)). In alkaline conditions $H_2O_2$ during bleaching reacts with hydroxyl ion ($OH^-$) forming perhydroxyl anion ($HOO^-$) according to (3.3). (Tikka, 2008)

$$2H_2O_2 \rightarrow O_2 + 2H_2O \tag{3.2}$$

$$H_2O_2 + OH^- \rightarrow HOO^- + H_2O \tag{3.3}$$
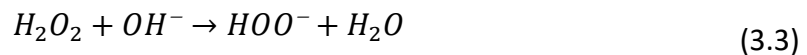
The perhydroxyl anion ($HOO^-$) oxidizes carbonyl chromophores carrying the pulp dark color to colorless carboxylic acids. It is therefore responsible for the majority of the bleaching effect in alkali suspension. It is also important to consider the decomposition of $H_2O_2$. If the bleaching temperature is high, the bleaching is accelerated, but also the undesirable decomposition reactions. The stability of hydrogen peroxide can be severed by transition metals like copper, manganese, and iron. There are three used methods how to avoid this undue effect:

- reducing/removing the metal ions by prior acid stages (chlorine dioxide e.g.),
- deactivating the metal ions using organic chelants,
- stabilizing $H_2O_2$ by adding magnesium sulfate and sodium silicate. (Smoke, 2016)

### 3.6.1 Bleaching conditions

The brightness progress and reactions between pulp and hydrogen peroxide are generally slow. The application of the $H_2O_2$ stage affects the conditions. The conditions can differ if used as a reinforcing oxidizing agent or primary bleaching agent. Reinforcement in the $E_P$ stage (alkaline extraction enhanced by hydrogen peroxide) leads to lower consumption of chlorine dioxide in $D$ stages (chlorine dioxide bleaching stage). Figure 26 shows the time needed for hydrogen peroxide bleaching. Even if the temperatures are higher, the reaction periods are still very long. The charge of peroxide has also an impact on final brightness. Figure 26 demonstrates the brightness progression at different $H_2O_2$ charges. Every example shows the
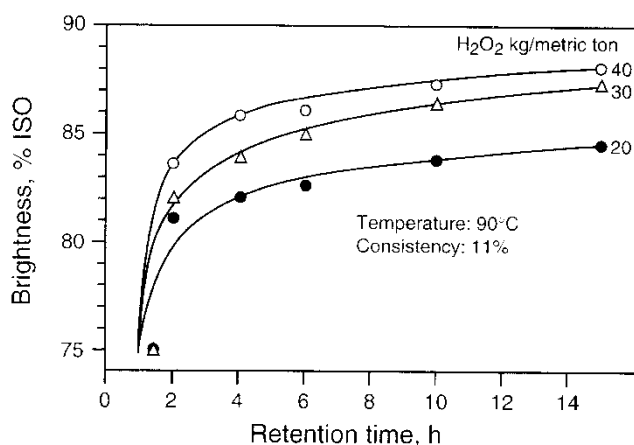


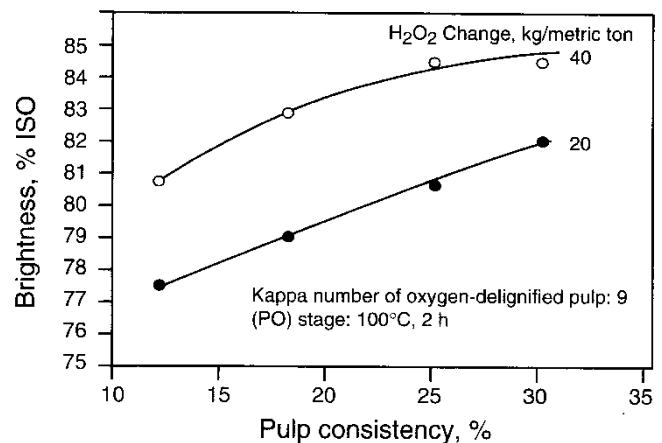*Figure 26. Effect of $H_2O_2$ charge on final brightness (Tikka, 2008)*     same     *Figure 25. Effect of pulp consistency on final brightness (Tikka, 2008)*

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asymptotic trend. The peroxide concentration also contributes to the final results. It follows that the higher the consistency, the higher the brightness will be (Figure 25). (Tikka, 2008)

## 3.7  Alkaline extraction

The purpose of the alkaline extraction stage is to dissolve and removing alkali-soluble compounds. These were formed in the preceding acidic delignification stages (for example chlorine dioxide stage). Usually, there are one or more alkaline stages, and they are significant at brightness growth after acidic stages. The extraction stage can be enhanced by hydrogen peroxide or oxygen. The addition of these enhancements ensures the solubility of lignin in the suspension and makes the extraction easier.

The kappa number of the pulp drops quickly at the beginning of the extraction. After few minutes, it slows down and slowly decreases to an asymptotic level. The extraction can be divided into two substages. The first stage includes the neutralization of organic acids, hydrochloric acids, and carbon dioxide. The second slower stage is related to ionization and slow mass transfer from the fibers into the liquid. Figure 27 shows the effect of temperature using bleaching sequence *CE* (chlorination stage followed by alkaline extraction stage). The efficiency of extraction is positively affected by higher temperatures. This helps the consumption of the chemicals in later stages.

Even small amounts of oxidants can significantly reduce the kappa number after extraction. Whereas the price of oxidants (oxygen, hydrogen peroxide) is much lower than chemicals used in bleaching, the oxidant enhanced extraction is widely used.



*Figure 27. Effect of temperature on extraction (Tikka, 2008)*

For example, the first *D* stage following by the *E* stage can remove 80-90 % residual lignin and makes it soluble. The pulp must go through the washing process, where the dissolved lignin is washed away from the pulp. Otherwise, the lignin fragments carried over from extraction to another bleaching stage could compete for bleaching chemicals with remaining lignin in the fibers. (Tikka, 2008)
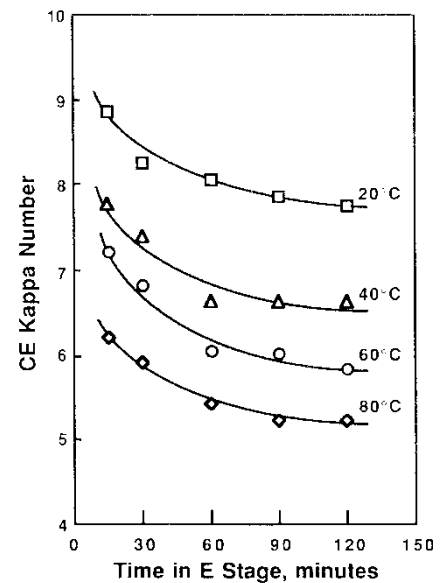
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# 4  LABORATORY EXPERIMENTS

The thesis aims to find optimal conditions and arrangements for the designed sequence intended for bleaching of textile flax pulp. Therefore, in the following part of the thesis, the practical part is carried out to achieve this goal. This is carried out by laboratory experiments at different bleaching conditions. As was described in the theoretical part, the bleaching process has lots of variables. Because the testing of all possible condition adjustments would go beyond the scope of the thesis, five parameters belonging to the ones with the greatest influence on the bleaching process were selected. Variable conditions at which these experiments were performed are following:

- temperature,
- consistency,
- addition rate of chemicals,
- washing degree of the pulp
- and bleaching sequence arrangement.

The thesis motivation is a reduction of economic demands of the bleaching process alongside with necessary adjustment of the current bleaching sequence. This could result in great savings leading to investments in new equipment and the modernization of the bleaching line. Hand in hand, this will lead to increased efficiency of the bleaching process as a whole. This is very important because bleached pulp production from annual plants is economically much more demanding due to more difficult fiber processing and the presence of shives. The idea behind the thesis is also to show the positive effect of more thorough washing of the pulp before introducing it to the bleaching process.

Based on the current arrangement of the bleaching line, the experiments will examine the possibilities of ECF bleaching using two chemicals – hydrogen peroxide and chlorine dioxide. The experiments will be divided into three phases:

1) hydrogen peroxide bleaching trials,
2) chlorine dioxide bleaching trials,
3) finding optimal sequence.

The experiments themselves were carried out in the laboratory of the annual plant pulp line with the use of all the present equipment needed. Analyzing pulp properties and characteristics were performed in the main laboratory of the plant. Pulp characteristics measured in the laboratories are described in the following subchapters.

## 4.1  Pulp characteristics

All measurement of physical and chemical properties of pulp was performed according to published ISO standards. The specifications of every executed laboratory measurement are described below.

### 4.1.1 Kappa number

Kappa number is an indirect indication of residual lignin content after cooking or bleaching stages. It can be said that the Kappa number expresses the bleachability of the pulp. Determination of Kappa number is subject to the ISO 302:2015 standard. The procedure is based on the measurement of the consumption of potassium permanganate ($KMnO_4$) solution which has been added in a precisely defined amount to the pulp suspension. The fiber reaction takes place at 25°C for 10 minutes with constant stirring.

### 4.1.2 Pulp brightness

Method for indication of ISO brightness is described by ISO 2470-1:2016 standard. The measurement was executed at indoor daylight conditions using Elrepho SE 070 spectrophotometer at 457 nm against the MgO standard.

### 4.1.3 Limiting viscosity number

The determination of the limiting viscosity number (LVN) is carried out under ISO 5351:2010 and is the main parameter of pulp strength properties. The method basis is measuring the flow time of pulp diluted in cupri-ethylenediamine (CED) solution. The measuring takes place in a capillary of the viscometer shown in Figure 28. The dissolution of the bleached fibers takes approximately 10 minutes for unbleached pulp and 1.5 hours for bleached pulp.



*Figure 28. Viscometer with water bath (*PMT*, n.d.)*

## 4.2 Bleaching characterization

It is appropriate to provide an evaluation of the bleaching stages. To do this, few parameters characterizing selectivity and efficiency of bleaching and lignin removal will be introduced. Using these, the comparison and classification of individual bleaching stages can be done. Equations are taken over from (Roncero et al., 2003).

### 4.2.1 Residual hydrogen peroxide

For the determination of the hydrogen peroxide residue, internal qualitative method Q40713324 of OP Papírna, s.r.o. the mill was used. The method is based on direct iodometric titration of the iodine released from potassium iodide to a starch indicator in an acid medium using ammonium molybdate as a catalyst.

### 4.2.2 Residual chlorine

Internal qualitative method Q40713325 of OP Papírna, s.r.o. mill for determination of residual chlorine is similar. The principle of this method is direct iodometric titration of the iodine released from potassium iodide to a starch indicator in an acid medium.

### 4.2.3  Lignin removal selectivity

The selectivity of lignin removal is expressed as the ratio of the change in Kappa number to the change in LVN according to the equation:

$$S_L = \frac{\Delta\kappa}{\Delta\eta} \cdot 100 = \frac{\kappa_0 - \kappa_1}{\eta_0 - \eta_1} \cdot 100 \,, \tag{4.1}$$

where      $S_L$    is lignin removal selectivity $[\%]$,
               $\kappa_0$    is initial Kappa number $[-]$,
               $\kappa_1$    is Kappa number after bleaching stage $[-]$,
               $\eta_0$    is initial LVN $[ml/g]$,
               $\eta_1$    is LVN after the bleaching stage $[ml/g]$.

### 4.2.4  Lignin removal efficiency

The efficiency of lignin removal is expressed as the ratio of the change in Kappa number to the potential oxidizing equivalent discussed earlier. The equation is following:

$$E_L = \frac{\Delta\kappa}{OXE} \cdot 100 = \frac{\kappa_0 - \kappa_1}{OXE} \cdot 100 \,, \tag{4.2}$$

where      $E_L$    is lignin removal efficiency $[\%]$,
              $OXE$  is oxidizing equivalent $[kg\ a.c./kg]$.

### 4.2.5  Bleaching selectivity

The selectivity of bleaching is expressed as the ratio of the change in brightness to the change in LVN according to the equation:

$$S_B = \frac{\Delta B}{\Delta\eta} \cdot 100 = \frac{B_1 - B_0}{\eta_0 - \eta_1} \cdot 100 \,, \tag{4.3}$$

where      $S_B$    is bleaching selectivity $[\%]$,
              $B_0$    is initial brightness $[\%]$,
              $B_1$    is brightness after the bleaching stage $[\%]$.

## 4.2.6 Bleaching efficiency

The efficiency of bleaching is expressed as the ratio of the change in brightness to the potential oxidizing equivalent. The formula describing bleaching efficiency is following:

$$E_B = \frac{\Delta B}{OXE} \cdot 100 = \frac{B_1 - B_0}{OXE} \cdot 100 \, , \tag{4.4}$$

where $E_B$ is bleaching efficiency $[\%]$.

## 4.2.7 Breaking length

The breaking length (also known as self-support length) measurement was performed using internal method Q40713007 of OP Papírna, s.r.o. mill. The prepared sheets were cut to 15 mm wide strips and then measured in the laboratory using a tensile testing machine supplied by company Lorentzen & Wettre.

## 4.2.8 Tearing resistance

Determination of tearing resistance was performed according to ISO 1974 standard. Measured values are then used for tear index calculating.

## 4.3 Stage trials

In the following subchapters, a description of the laboratory experiments will be provided. There will be covered methods, how the experiments were carried out, used equipment, description of the procedure, and all calculations necessary for the preparation of the samples. Preparations identical for the following experiments are these:

- measurement of pulp characteristics of the original sample,
- pulp bone dry content detection,
- weighing the required amount of pulp,
- adjustment to the desired consistency,
- pH adjustment of the sample,
- dosing of chemicals into the sample,
- placing the sample in a laboratory water bath of a given temperature.

**Measurement of pulp characteristics of the original sample**

The idea is to compare sample properties after individual bleaching stages with the original unbleached pulp material. Tracking of these properties is essential for adjustment of bleaching conditions because wrong input parameters could eventually lead to cellulose degradation and loss of the strength of the final product. The monitored parameters are Kappa number, limiting viscosity number, and pulp brightness. The photo of material taken from the mill line is shown in Figure 29.



*Figure 29. Example of the original standard washed material →*

**Weighing the required amount of pulp**

This step precedes the detection of the bone-dry content in the pulp which is meant to be bleached. The bone-dry content is needed to be measured before each bleaching stage because even in a closed environment water evaporation can occur to some extent which leads to percentage amount deviations of the dry solids. To find out bone-dry content, a small piece of the sample has to be weighed in the original state and the dry state. The rapid sheet dryer device is used to completely dry out the sample. The calculation is following formula (2.1).

**Sample consistency**

To get desired consistency, an adequate volume of the sample has to be calculated. Here is it necessary to consider the water content in the original sample. Here it assumes the equality of volume and weight of the fluids (i.e., density = 1 g/ml). The corresponding equation of the total volume is following:

$$V = \frac{m_{b.d.}}{cw} \cdot 100 \, , \tag{4.5}$$

where $V$ is the total volume of the sample $[ml]$,
$m_{b.d.}$ is the bone-dry weight of the sample $[g_{bd}]$,
$cw$ is consistency $[\%]$.

The total volume value is then used for filling in the left amount of water after pH and consistency adjustments. It is not possible to add the total volume of the water before pH adjustment, because the amount of chemicals needed for it is at this moment unknown. The value is also considered when dosing the bleaching chemicals into the sample at the final step before putting the sample into the water bath. Therefore, the water volume which has to be added into the sample before dosing bleaching chemicals is expressed as:

$$V_{H_2O} = V - V_{pulp} - V_{chem} - V_{pH} \, ,\qquad(4.6)$$

where      $V_{H_2O}$      is water volume added before dosing chemicals $[ml]$,

               $V_{pulp}$      is a volume of water contained in the pulp $[ml]$,

               $V_{chem}$      is dose volume of chemicals $[ml]$,

               $V_{pH}$      is water and chemicals volume needed to adjust pH $[ml]$.

**pH adjustment**

The adjustment of pH value is carried out by dosing small amounts of sulfuric acid ($H_2SO_4$) by pipette to get the sample to the acidic environment or sodium hydroxide (NaOH) to get it into an alkaline one.

**Addition of the chemicals**

At the final step before putting the sample in the water bath, dosing of the chemicals is performed. The amount of the dose is depending on the addition rate percentage. The addition rate is given as a specific percentage of actual bone-dry content in the sample and the calculation is covered by formula (4.7).

$$m_{chem} = \frac{w}{100} \cdot m_{b.d.} \, ,\qquad(4.7)$$

where      $m_{chem}$      is the dose of a chemical added to the sample $[g]$,

               $w$      is the charge of the chemical $\left[\%_{weight}\right]$.

**Degree of washing**

The washing degree of the sample zero is also necessary to consider. The bleaching trials were performed with two types of original pulp material. The first type was unbleached material after standard washing took directly from the mill line. For the second type, the same material from the line was taken, but on top of that, the sample was provided with additional washing performed in a laboratory using the Büchner funnel and vacuum pump. The efficiency of laboratory washing is 95 %, where the efficiency of standard washing is around 75 %. The degree of washing was determined in the laboratory by the difference in contamination of the filtrate before and after washing using a method based on the chemical consumption of oxygen. The following experiments are executed on both of these samples equally.

      In **Attachment 1** there is provided a more detailed description of the following experiments together with the execution of these calculations for each bleaching experiment and finding optimal sequence.

## 4.3.1 *P* stage trials

The experiments started with trials using hydrogen peroxide as a bleaching agent. With the information from the research part of the thesis and typical bleaching process conditions at the mill taking into account, the conditions for the P stage bleaching experiment performed on standard washed pulp are given in Table 3. There are four sets of experiments each

consisting of 4 individual samples at a different addition rate of hydrogen peroxide, thus there are 16 samples in total at standard washing.

| | | I. | II. | III. | IV. |
|---|---|---|---|---|---|
| $H_2O_2$ charge | [%weight] | 1.0; 2.0; 3.0; 4.0 (4 samples) | 1.0; 2.0; 3.0; 4.0 (4 samples) | 1.0; 2.0; 3.0; 4.0 (4 samples) | 1.0; 2.0; 3.0; 4.0 (4 samples) |
| Initial pH range | [-] | 11.0-11.5 | 11.0-11.5 | 11.0-11.5 | 11.0-11.5 |
| Temperature | [°C] | 55 | 55 | 60 | 60 |
| Retention time | [min] | 150 | 150 | 150 | 150 |
| Consistency | [%] | 5 | 10 | 5 | 10 |

*Table 3. Hydrogen peroxide bleaching conditions at standard washing*

The conditions for hydrogen peroxide bleaching at thorough washing (95 %) are given below. Due to more efficient washing, there is a possibility for a lower charge of $H_2O_2$ in the samples, which could result in similar or even better brightness results. The bleaching conditions at thorough washing are listed in Table 4.

| | | I. | II. | III. | IV. |
|---|---|---|---|---|---|
| $H_2O_2$ charge | [%weight] | 0.5; 1.0; 1.5; 2.0 (4 samples) | 0.5; 1.0; 1.5; 2.0 (4 samples) | 0.5; 1.0; 1.5; 2.0 (4 samples) | 0.5; 1.0; 1.5; 2.0 (4 samples) |
| Initial pH range | [-] | 11.0-11.5 | 11.0-11.5 | 11.0-11.5 | 11.0-11.5 |
| Temperature | [°C] | 55 | 55 | 60 | 60 |
| Retention time | [min] | 150 | 150 | 150 | 150 |
| Consistency | [%] | 5 | 10 | 5 | 10 |

*Table 4. Hydrogen peroxide bleaching conditions at thorough washing*

In the case of hydrogen peroxide bleaching, more detailed preparation of the chemical is needed. Firstly, there had to be found the content of $H_2O_2$ in the solution received from the bleaching line. That was done applying the method of determination residual hydrogen peroxide described earlier in chapter 4.2.1 on a diluted solution to 1:1000. Then, the residual amount of hydrogen peroxide was



*Figure 30. Samples in the water bath during the bleaching process*

transferred to the actual concentration of the received solution. With the use of an online tool (*EVONIK*, n.d.) based on academic literature, the density of the solution was found and used to calculate the solution volume added into the sample. Due to the low amounts of volumes that had to be added, the original solution was diluted 10 times for a purpose of easier dosing of the chemical. The samples during the bleaching process placed in the water bath at 55°C are shown in Figure 30.

## 4.3.2  *D* stage trials

In the next phase, chlorine dioxide was used as a bleaching agent. Given the results of hydrogen peroxide bleaching which are discussed later in the thesis, there were performed two sets of 4 samples on both washing qualities of the pulp. So, for each washing degree, there are 8 samples at different conditions. These conditions are described in Table 5.

| | | III. | IV. |
|---|---|---|---|
| $ClO_2$ charge | [%weight] | 2.0; 2.5; 3.0; 3.5 (4 samples) | 2.0; 2.5; 3.0; 3.5 (4 samples) |
| Initial pH range | [-] | 2.7-3.3 | 2.7-3.3 |
| Temperature | [°C] | 60 | 60 |
| Retention time | [min] | 120 | 120 |
| Consistency | [%] | 5 | 10 |

*Table 5. Chlorine dioxide bleaching conditions at standard washing*

The bleaching conditions applied to thoroughly washed pulp are the same except for the chlorine dioxide addition rate, which is lower for the same reason as in the case of hydrogen peroxide. The conditions are given in:

| | | III. | IV. |
|---|---|---|---|
| $ClO_2$ charge | [%weight] | 1.0; 1.5; 2.0; 2.5 (4 samples) | 1.0; 1.5; 2.0; 2.5 (4 samples) |
| Initial pH range | [-] | 2.7-3.3 | 2.7-3.3 |
| Temperature | [°C] | 60 | 60 |
| Retention time | [min] | 120 | 120 |
| Consistency | [%] | 5 | 10 |

*Table 6. Chlorine dioxide bleaching conditions at thorough washing*

Due to that the chlorine dioxide is generated on-site by reduction of sodium chlorite, the same process had to be applied during the dosing of this bleaching agent. From the mill, hydrochloric acid which serves as a reducing agent, and sodium chlorite were received. These two chemicals are very dangerous when mixed, therefore the dosing had to be performed with caution in the presence of a $ClO_2$ detector. According to operational experience at the mill and considering the concentration of the chemical solutions, the amount of both chemicals dosed is six times the amount of $ClO_2$ dose. Here the assumption that the weight and the volume of the chemicals are equal can be introduced. Thus:

$$V_{HCL,NaClO_2} = \frac{w}{100} \cdot m_{b.d.} \cdot 6 \, , \tag{4.8}$$

where $\quad V_{HCL,NaClO_2} \quad$ is the added volume of HCl, resp. NaClO$_2$ $[ml]$.

### 4.3.3 Optimal sequence trials

The last phase consisted of testing the optimal arrangement for bleaching sequence with the use of available bleaching stages. According to the bleaching results from the previous two phases, the most suitable conditions were chosen. The current bleaching sequence at the mill is *PDE_P*. So, this phase aimed to compare the current sequence with a sequence of different stage arrangements. Also, there is experimented using the current sequence but with the original material being thoroughly washed. There have been three sequences verified in total. The third one was arrangement *DEP*. The purpose of this arrangement was to test out if it is possible to achieve the same or better results of brightness and strength properties with the chlorine dioxide stage being the first, followed by alkaline extraction without hydrogen peroxide enhancement but the hydrogen peroxide bleaching stage being the last one. This could theoretically bring greater saving in chemicals used. In summary, these bleaching sequences will be tested out:

- ***PDE_P*** bleaching of the **standardly** washed sample (Experiment 1),
- ***PDE_P*** bleaching of the **thoroughly** washed sample (Experiment 2),
- ***DEP*** bleaching of the **thoroughly** washed sample (Experiment 3).

The preparation of samples was almost the same as in the case of phases one and two. The only difference was the amount of bone-dry weight. This had to be much higher because, after each stage of bleaching, some amount of the sample had to be withdrawn for measurement of bleached pulp characteristics. The amount of bone-dry weight in the bleached sample also had to be detected. Then, the preparation was repeated for the next bleaching stage. The bleaching conditions for individual stages of the experiments are given below in Table 7.

|  | Stage | Chemical charge | Initial pH | Temperature | Retention time | Consistency |
|---|---|---|---|---|---|---|
|  | [-] | [%weight] | [-] | [°C] | [min] | [%] |
| **Ex. 1** | P | 4 | 11,3 | 60 | 150 | 5 |
|  | D | 4 | 3,5 | 60 | 120 | 4 |
|  | E$_P$ | 0,8 | 11 | 55 | 120 | 5 |
| **Ex. 2** | P | 2 | 11,3 | 60 | 150 | 10 |
|  | D | 2 | 3,5 | 60 | 120 | 5 |
|  | E$_P$ | 0,8 | 11 | 55 | 120 | 10 |
| **Ex. 3** | D | 2 | 3,5 | 60 | 120 | 5 |
|  | E | - | 11 | 55 | 60 | 10 |
|  | P | 2 | 11,3 | 60 | 150 | 10 |

*Table 7. Bleaching conditions for individual stages of tested sequences*

The bleaching conditions given in the table are based on the results of the first two previous phases of bleaching with hydrogen peroxide and chlorine dioxide, which will be in detail described in the next chapter. Here it is necessary to comment on the choice of consistency. According to theoretical assumptions, higher consistency results in higher brightness. It would be then logical to choose the consistency of 10 % for each stage. The problem here was proper mixing. The mixing of the sample and added chemicals was usually carried out by glass rod stirring followed by shaking the bottle with the sample. This was possible in the case of stages with hydrogen peroxide. Due to the immediate reaction of chemicals and chlorine dioxide generation in the case of the *D* stage, the sample had to be closed with the lid immediately after adding the chemicals. This significantly limited the possibilities of mixing only to shaking the bottle. Imperfect mixing led to the deterioration of the results. Therefore, the consistency of 5 % was chosen due to more thorough mixing that could be done by shaking.

### 4.3.4 Measurement preparation

After each bleaching cycle after any bleaching, the preparation of the sample meant for measuring had to be done. The bottles with the bleached samples were taken out of the water bath and then cooled down to attenuate the reactions. Then the liquid in the pulp was squeezed out through a screen to simulate current washing between individual stages, and part of the sample was placed in a vial while the rest was reintroduced to the next bleaching stage. The extract in the vials was used for measuring the pH and the residual amount of chemicals remaining in the samples. The remaining pulp was washed two times in a rapid sheet former device (Figure 31), which was also used for preparing the sheets for measuring the brightness and LVN and formed into a round sheet of the pulp which was folded and placed into a plastic bag. These samples were marked and later measured in the laboratory. An example of prepared samples is shown in Figure 32.



*Figure 31. Rapid sheet former (*M.C. TEC*, n.d.)*

*Figure 32. Samples prepared for pulp properties measurement*

# 5 EXPERIMENT ANALYSIS

The previous chapter described the procedure of the experiment. There were covered the applied calculations and performed measurements. In this chapter, the experiment results are provided. Results of all individual trials will be mentioned and later discussed. The results of performed experiments are present in Excel sheets provided in **Attachment 1**. The most significant results can be seen in trials of whole sequences. Now the results of experimental phases 1 and 2 will be shown.

## 5.1 *P* stage results

Firstly, the brightness bleaching results of standard washed samples are plotted in smoothed line chart in Figure 33 where individual points are measured values.
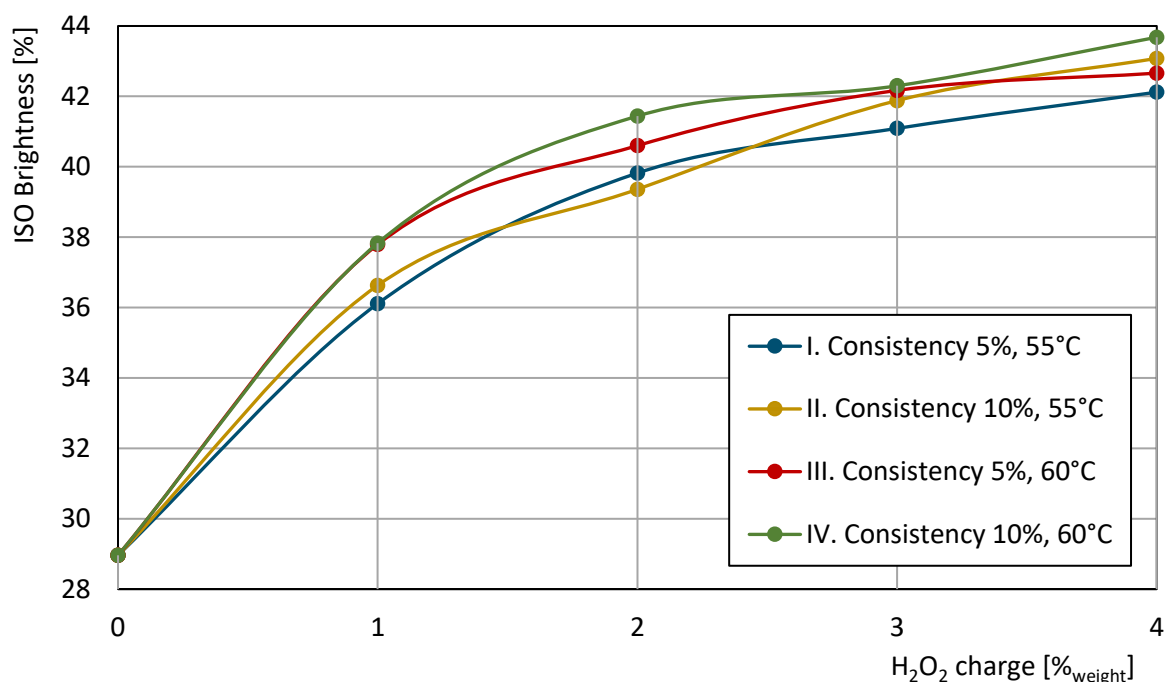


*Figure 33. Brightness gain by hydrogen peroxide bleaching of standardly washed sample*

Here, the brightness development at different $H_2O_2$ charges, temperatures, and consistencies is displayed. In the case of standard washing, these results are not very significant. But for example, at 2 % addition rate, the effect of temperature can be seen quite well. At higher temperature, the brightness difference is approximately 2 %. The effect of consistency is in this case lower – no more than 1 %. A comparison of the final brightness and the effect of different chemical charges is given in Table 8. In the table, there is parameter $\Delta B$. This parameter represents the increase of brightness between individual degrees of chemical addition rates. Equation (5.1) describes the relation.

$$\Delta B = B_{i+1} - B_i \ , \tag{5.1}$$

where      $\Delta B$     is the difference in brightness [%],
             $B_i$      is the brightness of the corresponding sample [%].

| | | Sample no. | H$_2$O$_2$ charge | Brightness | $\Delta B$ |
|---|---|---|---|---|---|
| | | $i$ | [%$_{weight}$] | [%] | [%] |
| 0. | Original sample | 0 | 0.0 | 28.9 | - |
| I. | Consistency 5 % Temperature 55°C | 1 | 1.0 | 36.1 | (7.2) |
| | | 2 | 2.0 | 39.8 | 3.7 |
| | | 3 | 3.0 | 41.1 | 1.3 |
| | | 4 | 4.0 | 42.1 | 1.0 |
| II. | Consistency 10 % Temperature 55°C | 1 | 1.0 | 36.6 | (7.7) |
| | | 2 | 2.0 | 39.4 | 2.7 |
| | | 3 | 3.0 | 41.9 | 2.5 |
| | | 4 | 4.0 | 43.1 | 1.2 |
| III. | Consistency 5 % Temperature 60°C | 1 | 1.0 | 37.8 | (8.8) |
| | | 2 | 2.0 | 40.6 | 2.8 |
| | | 3 | 3.0 | 42.2 | 1.6 |
| | | 4 | 4.0 | 42.7 | 0.5 |
| IV. | Consistency 10 % Temperature 60°C | 1 | 1.0 | 37.8 | (8.9) |
| | | 2 | 2.0 | 41.4 | 3.6 |
| | | 3 | 3.0 | 42.3 | 0.9 |
| | | 4 | 4.0 | 43.7 | 1.4 |

*Table 8. H$_2$O$_2$ bleaching of standardly washed sample - brightness comparison*

If the inspection of the parameter $\Delta B$ is done, it can be said that on average the increase in brightness at values 3 % and 4 % of H$_2$O$_2$ charge is approximately 1 %. In comparison with the H$_2$O$_2$ charge of 1 % and 2 %, where the increase in the case of 1 % charge is calculated from the original sample, therefore, is the default (bracketed) value, the overall largest increase is in the case of 2 % of the H$_2$O$_2$ addition rate. This is the reason, why the amount of hydrogen peroxide added into to sample was reduced during bleaching of the thoroughly washed pulp.

The results of hydrogen peroxide bleaching of the thoroughly washed sample are displayed in Figure 34 below. In the graph, there can be seen that here, in the case of the thoroughly washed sample, the bleaching curves are quite different. The effect of temperature here has a significant impact. The highest brightness i.e., at 4 % charge, is different by more than 5 %. The reactions at higher temperatures are quicker and thoroughgoing and lead to higher levels of brightness. The development of the curves at 55°C (blue and yellow) also shows well the consequence of a lesser amount of hydrogen peroxide. When the brightness reaches approximately 39 %, the progress dramatically slows down, and the retention time needed is prolonged. In Figure 33 there can be seen that the brightness development continues even at 55°C.
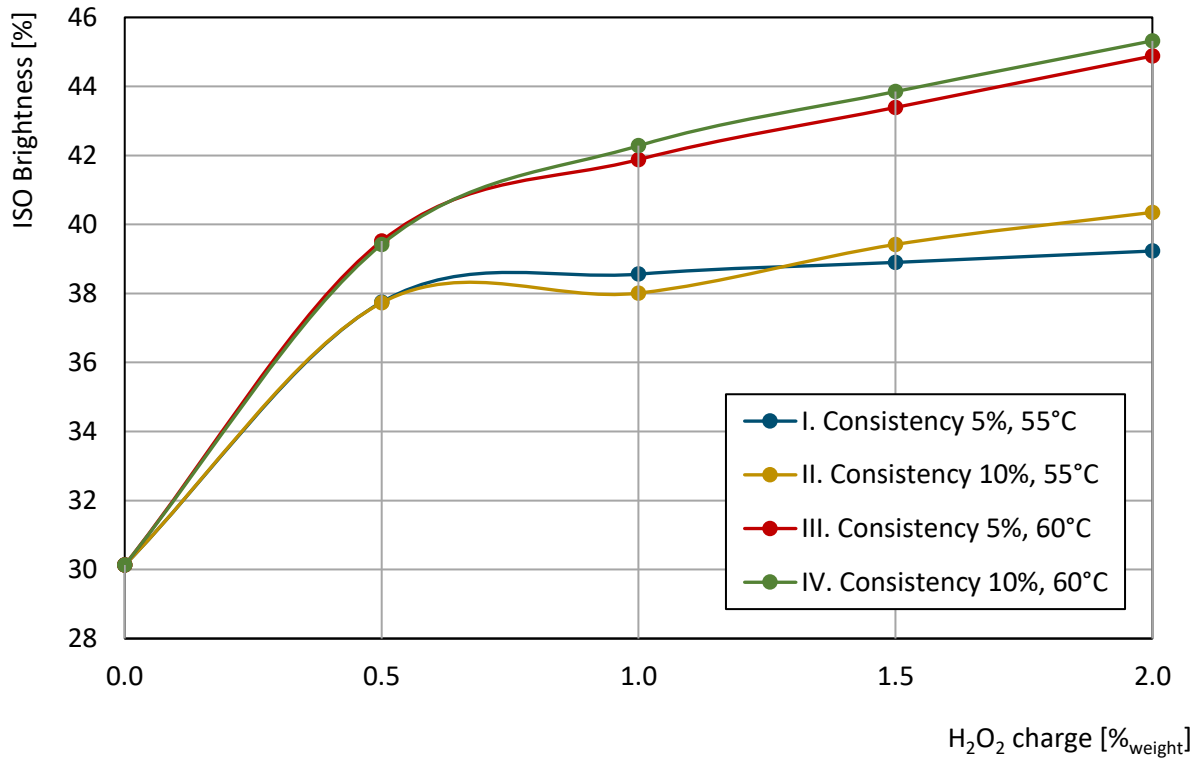
*Figure 34. Brightness gain by hydrogen peroxide bleaching of thoroughly washed sample*

| | | Sample no. | H$_2$O$_2$ charge | Brightness | $\Delta B$ |
|---|---|---|---|---|---|
| | | $i$ | [%$_{weight}$] | [%] | [%] |
| **0.** | **Original sample** | 0 | 0.0 | 30.1 | - |
| **I.** | **Consistency 5 %** **Temperature 55°C** | 1 | 0.5 | 37.8 | (7.6) |
| | | 2 | 1.0 | 38.6 | 0.8 |
| | | 3 | 1.5 | 38.9 | 0.3 |
| | | 4 | 2.0 | 39.2 | 0.3 |
| **II.** | **Consistency 10 %** **Temperature 55°C** | 1 | 0.5 | 37.7 | (7.6) |
| | | 2 | 1.0 | 38.0 | 0.3 |
| | | 3 | 1.5 | 39.4 | 1.4 |
| | | 4 | 2.0 | 40.4 | 0.9 |
| **III.** | **Consistency 5 %** **Temperature 60°C** | 1 | 0.5 | 39.5 | (9.4) |
| | | 2 | 1.0 | 41.9 | 2.4 |
| | | 3 | 1.5 | 43.4 | 1.5 |
| | | 4 | 2.0 | 44.9 | 1.5 |
| **IV.** | **Consistency 10 %** **Temperature 60°C** | 1 | 0.5 | 39.4 | (9.3) |
| | | 2 | 1.0 | 42.3 | 2.9 |
| | | 3 | 1.5 | 43.9 | 1.6 |
| | | 4 | 2.0 | 45.3 | 1.5 |

*Table 9. H$_2$O$_2$ bleaching of thoroughly washed sample - brightness comparison*

The trend of different consistencies also shows that the consistency of 10 % shows slightly better results. The issue of performed experiments was that the hand-operated mixing of the pulp with a consistency of 10 %  is quite challenging. It can be assumed that during machine mixing, the brightness after bleaching would be higher. After inspection of parameter $\Delta B$ here, the differences between individual charges are not that significant compared to the previous case. This means that the charges of less than 2 % are not very effective. This also proves the fact that the amount of residual $H_2O_2$ after bleaching at 60°C is quite smaller compared to other samples.

Therefore, the optimal hydrogen peroxide charge is 2 % or slightly above. This is the reason, why in the final bleaching sequence, the charge of 2 % is selected. The same goes for temperature choice. The temperature of 60°C provides better results and thus is chosen for the final bleaching sequence. Regarding consistency control, 10 % is the choice for the sequence. Though it does not have a great impact on the final brightness due to the reason mentioned above, the consistency of 10 % is industry standard, because overall, this consistency results in higher brightness levels and more effective chemical reactions alongside water savings and will be applied in the later bleaching sequence.

## 5.2   *D* stage results

The experiments using chlorine dioxide as a bleaching agent were performed at 60°C. From the data obtained so far, bleaching at this temperature is more efficient than at 55°C. In the case of standard washed pulp, the addition rate of chlorine dioxide has to be higher than the amount applied to the thoroughly washed pulp. That is because of undesirable chemical reactions with leftover substances from previous cooking. The behavior of bleaching at different charges of $ClO_2$ and consistencies is drawn in Figure 35.
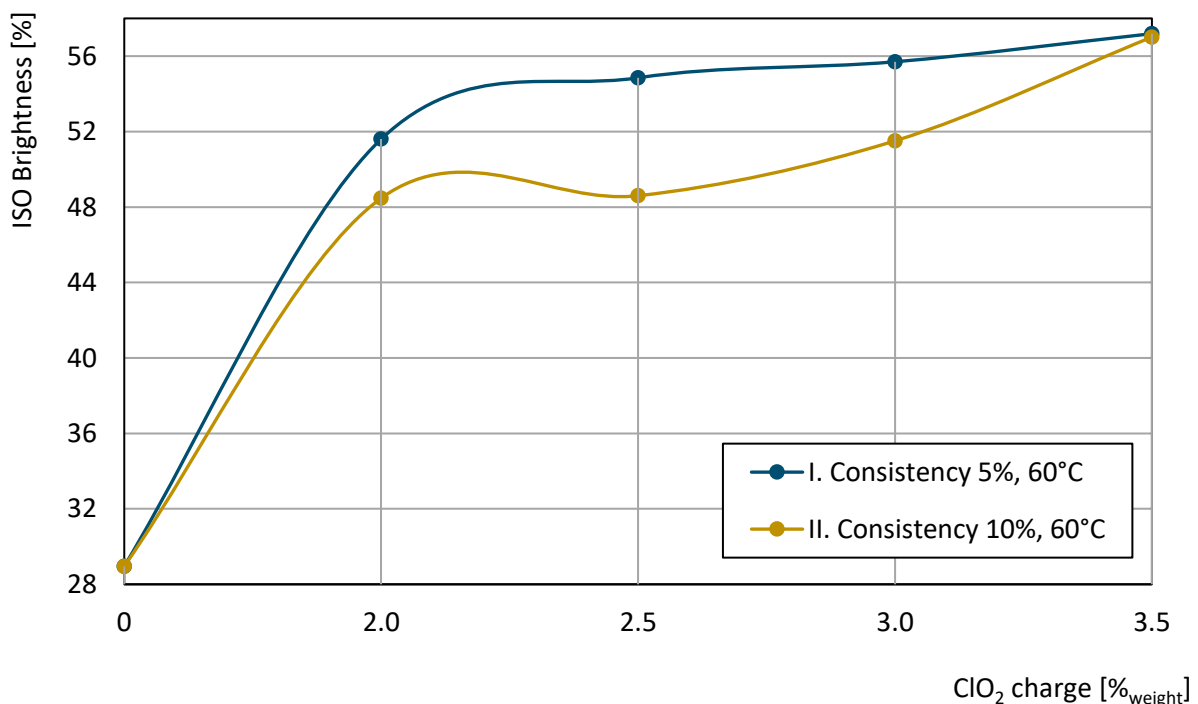


*Figure 35. Brightness gain by chlorine dioxide bleaching of standardly washed sample*

The graph shows the inefficiency of manual mixing. The hazards of manual mixing described earlier prevent thorough mixing of the pulp and chlorine dioxide. This results in inconsistent reactions between the pulp and $ClO_2$, which practically explains the slow development and the jumps (see $\Delta B$ in Table 10) of pulp brightness at 10 % consistency and different addition rates. But the shaking of the sample of 5 % consistency is quite easy and the results show reliable values. As can be seen in the graph, the brightness trend is very fast at lower charges, but rapidly slows down at higher doses. The largest increase can be observed around the charge of 2 %. This is confirmed in Table 10, where at the consistency of 5 %, the largest increase brightness difference is at 2.5 % charge, and at higher charges is relatively small.

| | | Sample no. | $ClO_2$ charge | Brightness | $\Delta B$ |
|---|---|---|---|---|---|
| | | $i$ | [%$_{weight}$] | [%] | [%] |
| 0. | Original sample | 0 | 0.0 | 28.9 | - |
| III. | Consistency 5 % Temperature 60°C | 1 | 2.0 | 51.6 | (22.6) |
| | | 2 | 2.5 | 54.9 | 3.3 |
| | | 3 | 3.0 | 55.7 | 0.9 |
| | | 4 | 3.5 | 57.2 | 1.5 |
| IV. | Consistency 10 % Temperature 60°C | 1 | 2.0 | 48.5 | (19.5) |
| | | 2 | 2.5 | 48.6 | 0.1 |
| | | 3 | 3.0 | 51.5 | 2.9 |
| | | 4 | 3.5 | 57.0 | 5.5 |

*Table 10. Chlorine dioxide bleaching of standardly washed sample - brightness comparison*

In the case of chlorine dioxide bleaching of thoroughly washed pulp, the input charge of the chemicals is lower. Although the brightness development is better matched at the consistency of 10 % - as in the previous case, the more reliable bleaching progress is described by the curve with the consistency of 5 %. These are plotted in Figure 36. From the values given in Table 11 can be said that the biggest increase in brightness is achieved with the $ClO_2$ charge of 1.5 % but subsequent charges are not negligible. These factors combined, the chlorine dioxide charge for the following sequences was also 2 %.

| | | Sample no. | $ClO_2$ charge | Brightness | $\Delta B$ |
|---|---|---|---|---|---|
| | | $i$ | [%$_{weight}$] | [%] | [%] |
| 0. | Original sample | 0 | 0.0 | 30.1 | - |
| III. | Consistency 5 % Temperature 60°C | 1 | 1.0 | 45.3 | (15.2) |
| | | 2 | 1.5 | 53.8 | 8.6 |
| | | 3 | 2.0 | 55.7 | 1.8 |
| | | 4 | 2.5 | 58.0 | 2.3 |
| IV. | Consistency 10 % Temperature 60°C | 1 | 1.0 | 45.6 | (15.5) |
| | | 2 | 1.5 | 51.0 | 5.3 |
| | | 3 | 2.0 | 55.2 | 4.2 |
| | | 4 | 2.5 | 58.9 | 3.7 |

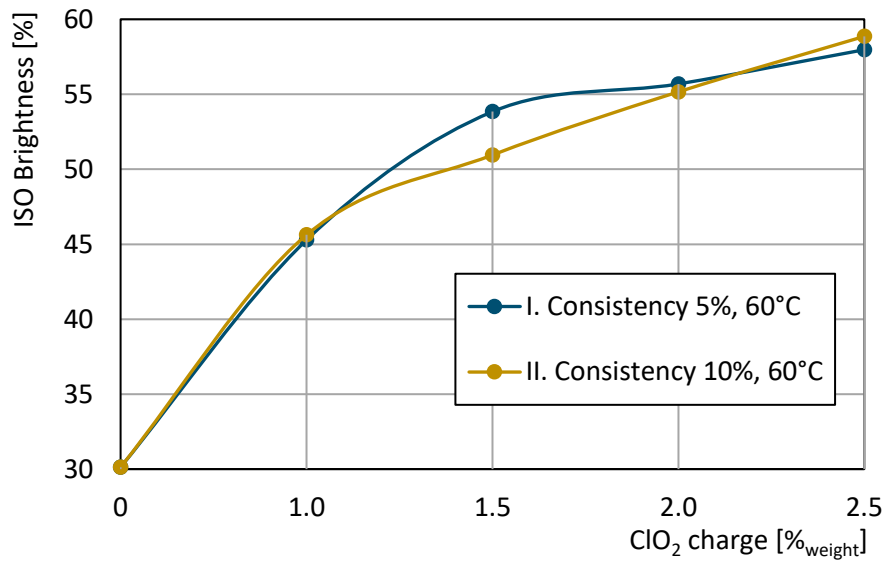*Table 11. Chlorine dioxide bleaching of thoroughly washed sample - brightness comparison*

*Figure 36. Brightness gain by chlorine dioxide bleaching of thoroughly washed sample*

## 5.3 Sequence results

Based on performed experiments with hydrogen peroxide and chlorine dioxide, the optimal conditions for these stages were chosen. These conditions were described earlier in chapter 4.3.3. The conditions for alkaline extraction were not included in the individual experiment, so they are based on the current state at the mill. The conditions for the *E* stage in Experiment 3 are different. The extraction stage is not enhanced by hydrogen peroxide, because the subsequent stage is the hydrogen peroxide bleaching stage, which will bring the desired effect. On top of that, there is no need for the *E* stage to last 120 minutes, so retention time was cut to half i.e., 60 minutes. The brightness curves of the individual stages are displayed in Figure 37.
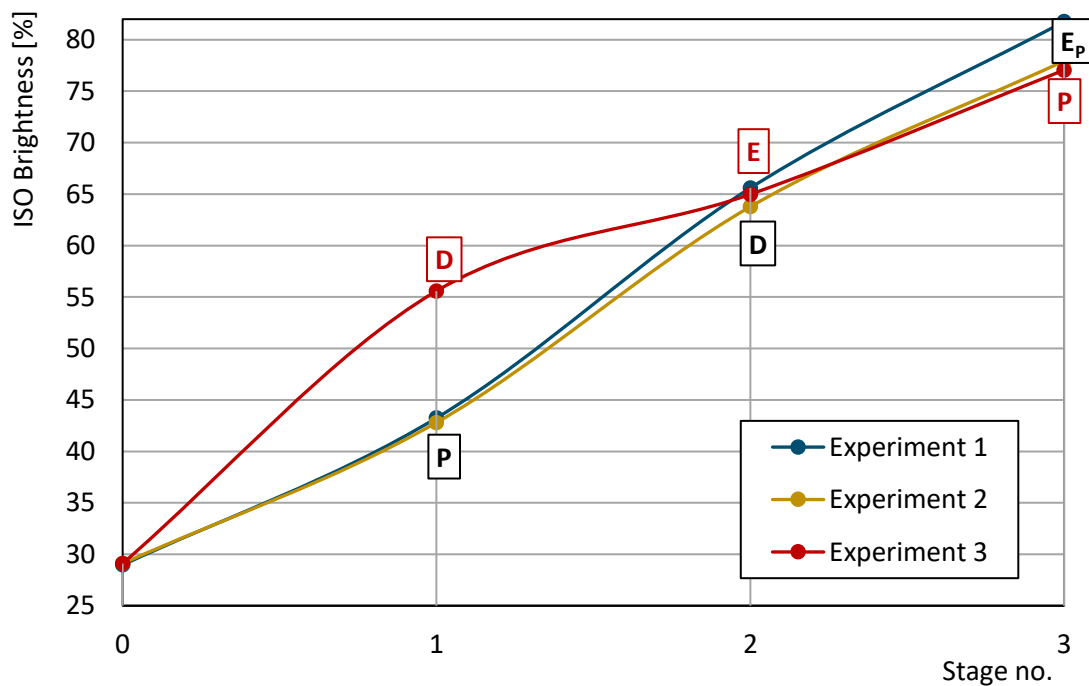


*Figure 37. Brightness development during selected bleaching sequences*

An important indicator of the chemical attack on the cellulose is limiting viscosity number. As a little drop in LVN as possible is desirable. The reduction in LVN is different at each sequence. The curves describing the LVN drops are drawn in Figure 38. Here, the *DEP* sequence (Experiment 3) reaches the best viscosity results, *PDE$_P$* bleaching of thoroughly washed pulp (Experiment 2) follows and the current *PDE$_P$* bleaching of standardly washed pulp (Experiment 1) is characterized by the largest drop in viscosity.
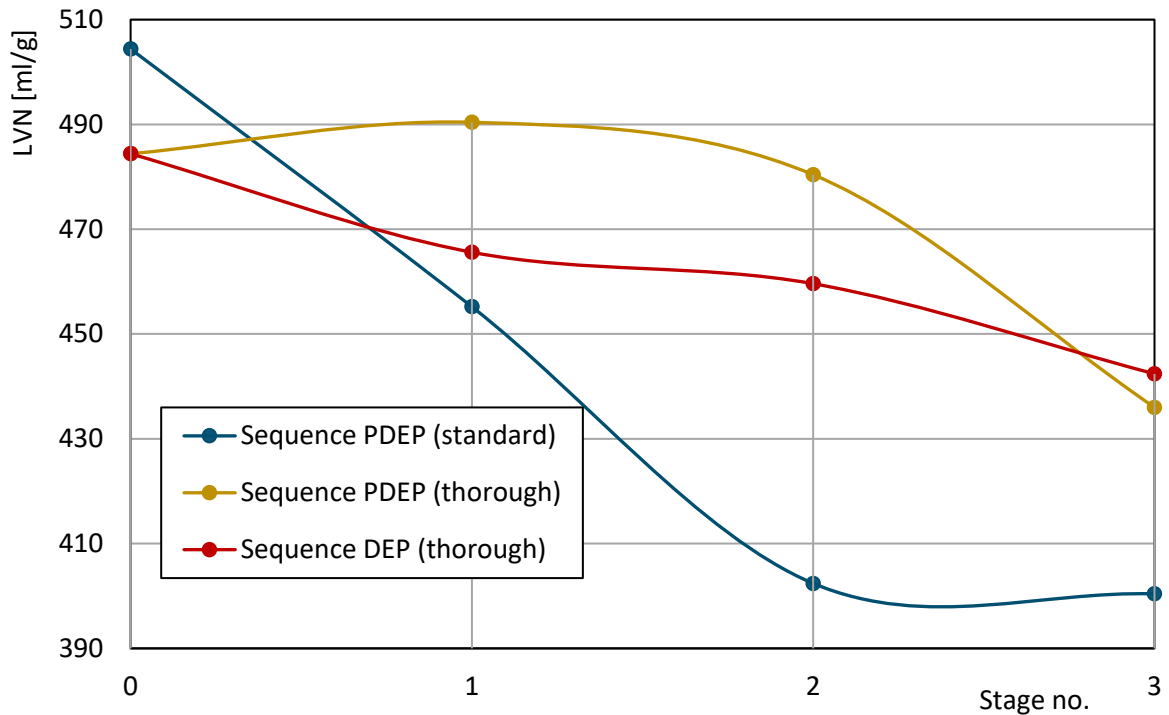


*Figure 38. Viscosity progress at each sequence*

In the following table are listed the results of pulp characteristics after each individual stage of the executed bleaching sequences. These can be compared with the properties of the original unbleached samples listed in Table 13.

| | | Chemical residual | Kappa | LVN | Brightness | Breaking length | Tearing resistance |
|---|---|---|---|---|---|---|---|
| | | [ml/g] | [-] | [ml/g] | [%] | [km] | [mN] |
| Ex. 1 | P | 799.5 | 12.4 | 455.2 | 43.24 | - | - |
| | D | 1,130.0 | 1.6 | 402.4 | 65.59 | - | - |
| | E$_P$ | 37.4 | 0.3 | 400.4 | 81.76 | 2.07 | 213.0 |
| Ex. 2 | P | 629.4 | 12.2 | 490.4 | 42.80 | - | - |
| | D | 0.3 | 3.1 | 480.4 | 63.77 | - | - |
| | E$_P$ | 510.3 | 0.8 | 436.0 | 77.94 | 2.08 | 215.0 |
| Ex. 3 | D | 0.1 | 3.9 | 465.6 | 55.58 | - | - |
| | E | - | 1.1 | 459.6 | 64.98 | - | - |
| | P | 1,479.9 | 0.4 | 442.4 | 77.05 | 2.10 | 237.0 |

*Table 12. Pulp characteristics after each bleaching sequence*

|                                   | Kappa | LVN    | Brightness |
|-----------------------------------|-------|--------|------------|
|                                   | [-]   | [ml/g] | [%]        |
| Standardly washed unbleached pulp | 19.3  | 504.4  | 28.9       |
| Thoroughly washed unbleached pulp | 16.9  | 484.4  | 24.6       |

*Table 13. Properties of the unbleached pulp*

In Figure 39 below, the comparison of the brightness of sheets made after each individual bleaching stage of Experiments 1,2, and 3 in the rapid sheet former is provided. All values listed in Table 12 were measured on these sheets. They are also an important tool for identifying the possibilities of the bleaching stage in bleaching the shives, which is an obstacle to the bleaching of pulp made of annual plants – flax in this case.
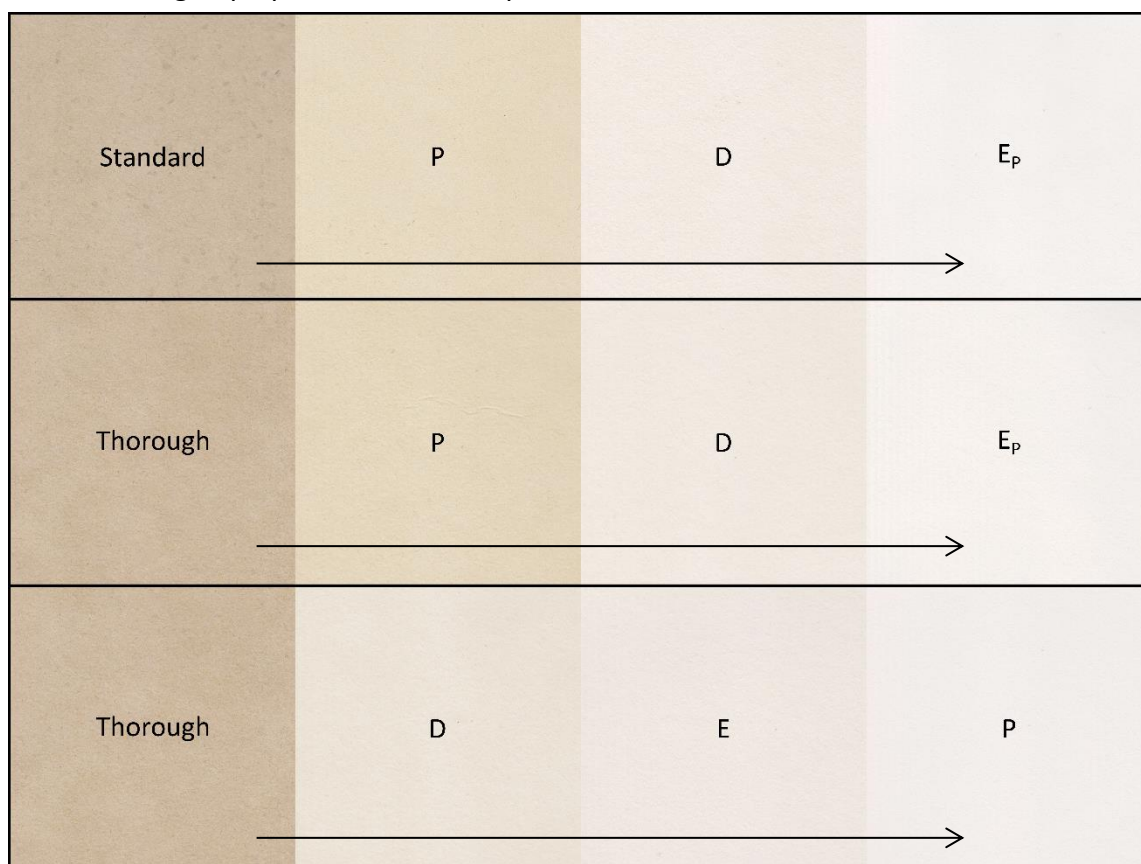


*Figure 39. Brightness comparison of the sheets after each stage of bleaching*

Finally, the comparison of selectivity and efficiency of bleaching and lignin removal was calculated using equations (4.1)-(4.4). The results are presented in Table 14.

|                            |   | Experiment 1 | Experiment 2 | Experiment 3 |
|----------------------------|---|--------------|--------------|--------------|
| Bleaching selectivity      | % | 64.4         | 71.8         | 77.8         |
| Lignin removal selectivity | % | 22.7         | 23.7         | 26.8         |
| Bleaching efficiency       | % | 52.6         | 92.9         | 73.1         |
| Lignin removal efficiency  | % | 18.6         | 30.6         | 46.6         |

*Table 14. Selectivity and efficiency of bleaching and lignin removal*

## 5.4 Results discussion

The most important facts arising from the experiments are discussed in this subchapter. Firstly, the reasoning of the results of the bleaching of hydrogen peroxide and chlorine dioxide will be done. Then the discussion about the results of individual stages will be provided.

Regarding the hydrogen peroxide trials, the important results that need to be considered are the choice of degree of washing, chemical charge, and bleaching temperature. It is clear that by applying more thorough washing, the amount of chemicals that need to be supplied to the sample to achieve the same or even better results in pulp brightness is much lower. The same idea applies to bleaching with the use of chlorine dioxide. Almost half of the dose needed to bleach standardly washed pulp is enough to bleach thoroughly washed pulp to the same or better brightness. According to **Attachment 1**, there are also quite large amounts of residual chemicals present in the sample after bleaching at a higher dosage of the chemicals. Smaller chemical doses at bleaching of the thoroughly washed sample are generally characterized by smaller amounts of residuals, which makes the bleaching process more efficient. Figure 34 is the best pointer to the fact that higher temperature is also essential.

The results of whole bleaching sequences are very significant. The general goal of bleaching the pulp at the mill is 80 % of ISO brightness. Although this is achieved only in Experiment 1, both subsequent experiments are very close to this goal. This is due to more efficient washing of the pulp before introducing it to the bleaching process. The levels of brightness after Experiments 2&3 would not be possible if the number of chemicals would be applied to the pulp which has been through the standard washing at the mill. If the comparison of Experiment 2 and Experiment 3 is done, it can be said, that the difference in final brightness is no more than 1 % which can be neglected. With the use of only half of the dose compared to Experiment 1, these bleaching sequences achieved great results. On top of that, the amount of chemicals needed in Experiment 2 is still more than in Experiment 3. This is due to alkaline extraction enhanced with hydrogen peroxide with a charge of 0.8 %. In the case of Experiment 3, the alkaline extraction stage is free of hydrogen peroxide, so it results in even higher savings. The hydrogen peroxide residual after the final $P$ stage of Experiment 3 also shows that the charge of $H_2O_2$ added into the $P$ stage could be also decreased. Lastly, in addition to this, the alkaline extraction in Experiment 3 takes only one hour compared to the two hours in the case of Experiment 2, which reduces the total retention time required for the bleaching process. After examination of the viscosity and strength properties of the bleached pulp, there are better results in Experiment 2&3 than in Experiment 1 with Experiment 3 leading in this competition. The influence of the alkaline extraction can be also seen in Figure 37. Although the alkaline extraction was not part of the trials, according to chapter 3.7, the dissolving and washing out of the excluded lignin results in great brightness advance. Another positive is that when applied less bleaching chemistry into the pulp, this will result in less water pollution.

With the results in Table 14 can the Experiments be compared from the perspective of efficiency and selectivity. Selectivity, expressing the ratio of attack on lignin or bleaching power to attack carbohydrates, is clearly better in both cases of Experiments 2 and 3. Here can be seen that Experiment 3 also reaches the best results. This is also true in the case of lignin removal efficiency. When comparing bleaching efficiency, Experiments 2 and 3 are much more efficient than Experiment 1. An interesting situation here is that Experiment 2 is more

efficient than Experiment 3. It shows that in the case of Experiment 3, there is still room for further optimization of the chemical charges at stages *D* and *P*, which also proves the big amount of residual hydrogen peroxide in the sample after the *P* stage in Table 12.

## 5.4.1  Possibilities of oxygen delignification

The oxygen delignification stage could be another step to make the bleaching process more effective. Trials of oxygen delignification could not be performed, because required equipment was not available at the mill. Therefore, oxygen delignification experiments were outsourced, and results and possible benefits that could further improve the bleaching sequence are discussed here. Input and output pulp properties after oxygen delignification are listed in Table 15.

|  |  | Input | Output |
|---|---|---|---|
| ISO brightness | % | 29.9 | 38.4 |
| Kappa number | - | 15.6 | 9.6 |
| LVN | ml/g | 584.0 | 548.0 |
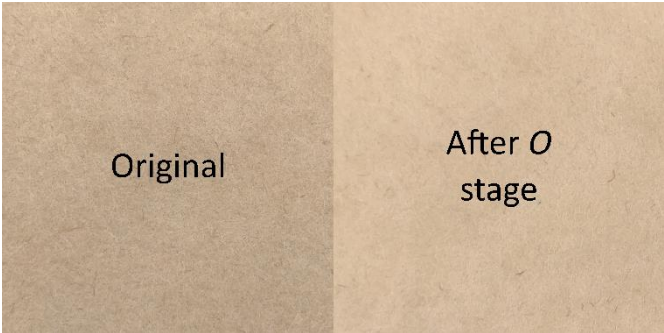


*Table 15. Results of oxygen delignification*

The negative of oxygen delignification is its damage to cellulose. That is why in these experiments, an amount of $MgSO_4$ was used to prevent cellulose degradation and the formation of hydroxyl radicals, which leads to maintaining pulp viscosity. The effect of oxygen delignification has great impacts. The first of them is an almost 10 % brightness increase. Another is a large decrease in Kappa number. Thanks to the dose of $MgSO_4$, the drop in viscosity is not big and is completely acceptable for use in the bleaching process. The main positives of the oxygen delignification are that the preceding cooking can be terminated at higher Kappa numbers because oxygen delignification can take care of the rest, and the bleaching process itself will be open for further reduction in the number of chemicals necessary to reach the required brightness. The amount of shives present in the pulp after oxygen delignification is also smaller compared to the original sample. The reduction of the degree of cooking will result in greater pulp yield and smaller chemical charges in another savings which can justify the investment into this technology.

# 6 TECHNOLOGICAL AND ECONOMIC DESIGN

In this following chapter, the proposed sequence will be checked in terms of material, heat, and economical balance. The bleaching line arrangement is based on the current state at the mill, where the sequence $PDE_P$ is assembled. Before introducing it to the $H_2O_2$ bleaching tower, the pulp is heated in a heat exchanger. In the subsequent stages, the pulp is heated directly by steam and the condensate formed continues in the pipeline, which affects the mass balance and additionally dilutes the pulp suspension. A simplified block diagram that serves as a foundation for the calculations can be seen in Figure 40. The diagram shows the arrangement of the $PDE_P$ sequence. In the case of the $DEP$ sequence proposed earlier, the differences would be the order of bleaching towers, chemical dosing, and arrangement of diluting liquids. After each bleaching tower, there is a washing press device marked as $VXPi$ which displace the filtrate from the suspension. Also, there is a dose of sodium hydroxide at each stage which serves to adjust the pH of the pulp suspension.
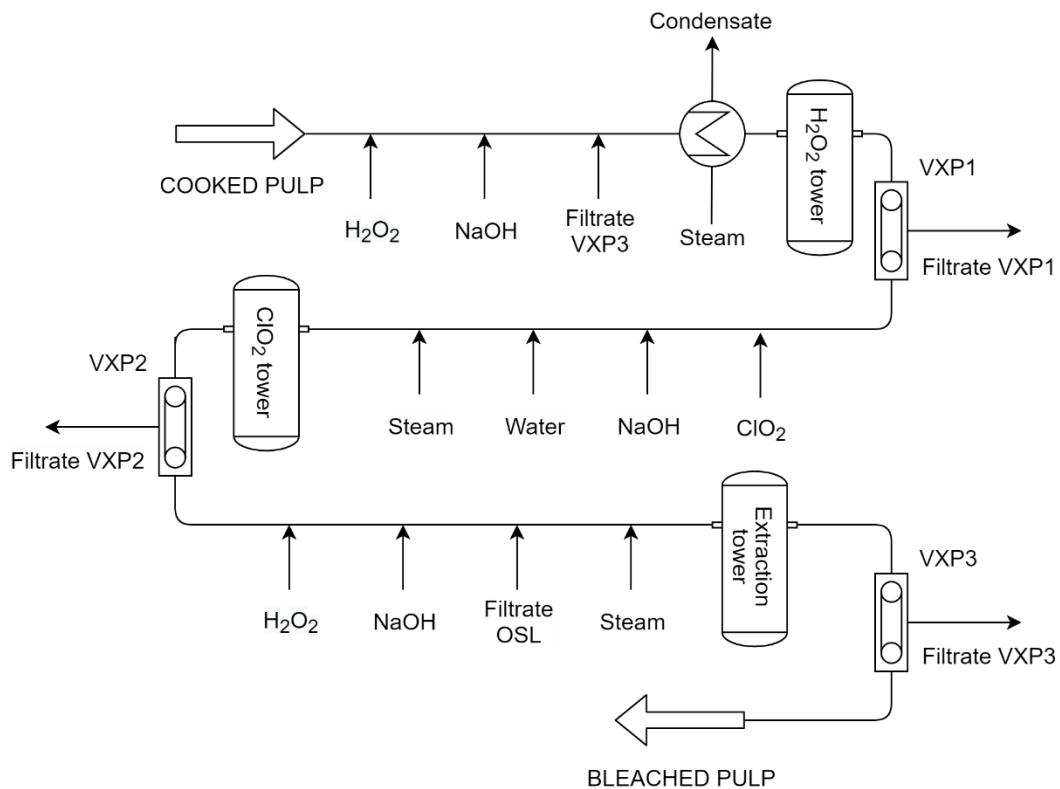


*Figure 40. Block diagram of PDE$_P$ bleaching line*

In order to calculate the mass and heat balance few physical properties of the materials included has to be identified. These parameters are given in Table 16. Whereas the specific heat capacity and density of the filtrates and $ClO_2$ solution are unknown, these values were simplified to be the same as the water values. The specific heat capacity of the pulp corresponds to the average value of cellulose taken from (*Engineering ToolBox*, 2003). The origin of the density of hydrogen peroxide was described earlier in chapter 4.3.1. Specific heat capacity of hydrogen peroxide solution comes from (*USP Technologies*, n.d.).

|  | | Water | Pulp | Filtrate | $H_2O_2$ 37% | $ClO_2$ | NaOH 25% |
|---|---|---|---|---|---|---|---|
| Specific heat capacity | [J/(kg.K)] | 4,184 | 1,400 | 4,184 | 3,475 | 4,184 | 4,184 |
| Density | [kg/m³] | 1,000 | - | 1,000 | 1,141 | 1,000 | 1,200 |

*Table 16. Physical properties of included materials*

## 6.1 Mass and heat balance

The reference production bone dry mass flow, in this case, was chosen as 500 kg_bd/h. This rate approximately corresponds to the mill production. The temperatures necessary for the calculations are also taken from the usual temperatures in the mill bleaching line. The following description of the calculation procedure is corresponding to Experiment 1. The calculation for Experiment 1 and 2 are essentially the same. The whole calculating procedure can be found in **Attachment 2**.

The sequence starts by diluting the pulp and dosing chemicals. This is preparation for the *P* (hydrogen peroxide) stage. At first, the required amount of diluting filtrate in order to reach needed consistency has to be identified. This begins by calculating the total volume required to reach 5 % consistency:

$$V_{total} = \frac{m_{bd}}{cw} \cdot 100 \, , \tag{6.1}$$

where $V_{total}$ is the total volume needed to reach the required consistency $[l/h]$,
$m_{bd}$ is reference production bone dry mass flow $[kg/h]$.

Next, the amount of hydrogen peroxide dose has to be evaluated:

$$V_{H2O2} = \frac{m_{H2O2}}{\rho_{H2O2}} \cdot 10^3 = \frac{w_{H2O2} \cdot m_{bd}}{\rho_{H2O2} \cdot c_{H2O2}} \cdot 10^3 \, , \tag{6.2}$$

where $V_{H2O2}$ is volume charge of hydrogen peroxide $[l/h]$,
$m_{H2O2}$ is the mass charge of hydrogen peroxide $[kg/h]$,
$\rho_{H2O2}$ is the density of hydrogen peroxide solution $[kg/m^3]$,
$w_{H2O2}$ is a percentual charge of hydrogen peroxide $[\%_{weight}]$,
$c_{H2O2}$ is the mass concentration of the hydrogen peroxide solution $[\%]$.

The volume of liquid present in the pulp is calculated as follows:

$$V_{liquid} = \frac{m_{liquid}}{\rho_{liquid}} \cdot 10^3 = \frac{m_{bd} \cdot (100 - cw)}{cw \cdot \rho_{liquid}} \cdot 10^3 \, , \tag{6.3}$$

where $V_{liquid}$ is liquid volume present in the pulp $[l/h]$,
$m_{liquid}$ is liquid mass present in the pulp $[kg/h]$,
$\rho_{liquid}$ is liquid density $[kg/m^3]$.

The volume of the last component – NaOH is estimated based on the current consumption of the mill for all Experiments. It is assumed, that the consumption of sodium hydroxide is slightly lower.

The final volume of diluting filtrate needed is done by subtraction individual volume amounts present:

$$V_{filtrate} = V_{total} - V_{H2O2} - V_{liquid} - V_{NaOH} \, , \tag{6.4}$$

where $V_{filtrate}$    is required amount of diluting filtrate to reach given consistency $[l/h]$,

           $V_{NaOH}$    is the volume of NaOH added to the pulp suspension $[l/h]$.

The last step of mass balance is to calculate displaced filtrate exiting the washing press. This is simply done by subtraction the liquids present in the pulp after the press from the volume of liquids entering the bleaching tower:

$$V_{VXP} = V_{total} - V_{fluid} \, , \tag{6.5}$$

where    $V_{VXP}$    is the volume of filtrate exiting the washing press $[l/h]$,

At this moment, the mass balance of preparation for the P stage is done. The pulp suspension needs to reach a given temperature before introducing it to the bleaching tower. This is done in a heat exchanger using steam of 5 bar. Here, the goal is to find the amount of steam that is needed for adequate heating. The first step is to calculate the heat needed to heat every component present in the pipeline:

$$Q_i = m_i \cdot c_{p_i} \cdot (t_b - t_i) \cdot 10^{-6} \, , \tag{6.6}$$

where    $Q_i$    is heat duty for heating the suspension component $[MJ/h]$,

           $m_i$    is mass flow of the suspension component $[kg/h]$,

           $c_{p_i}$    is the specific heat capacity of the suspension component $[J/(kg \cdot K)]$,

           $t_b$    is the temperature of the bleaching $[°C]$,

           $t_i$    is the temperature of the suspension component $[°C]$.

The total heat duty is found by summation of individual heat duties of the components:

$$Q_{total} = \sum_i Q_i \, , \tag{6.7}$$

where    $Q_{total}$    is total heat duty for heating the pulp suspension $[MJ/h]$.

With the knowledge of the heat duty and state of the condensate formed, it is possible to calculate the amount of steam needed for heating the pulp suspension. This relation is described by equation (6.8).

$$m_{steam} = \frac{Q_{total}}{(h_{steam} - h_{condensate})} \cdot 10^3 \, , \qquad (6.8)$$

where $\quad m_{steam} \quad$ is the amount of steam needed for heating the pulp suspension $[kg/h]$,

$\quad\quad\quad h_{steam} \quad$ is the enthalpy of the heating steam $[kJ/kg]$,

$\quad\quad\quad h_{condenstae}$ is the enthalpy of the condensate $[kJ/kg]$.

Now, the heat and mass balance of preparation for the hydrogen peroxide bleaching stage is completed. The calculating procedure for subsequent stages is similar, so only the main differences will be commented on. The major modification is in the case of heating. In the second and third experiments, it is done by providing hot steam directly to the pulp, which means that formed condensate will dilute the suspension. The issue here is circular reference rising from calculating heat duty, which is based on the amount of diluting water added to the suspension, but the amount of diluting water is decreased by formed condensate. To calculate this, the solver tool present in MS Excel was utilized. However, this tool is not always reliable, therefore manual iteration was done to verify the solver result. The deviation was chosen to be 10⁻³ which is even too accurate for the needs of this model. For clarification, the iteration calculation is drawn in Figure 41.
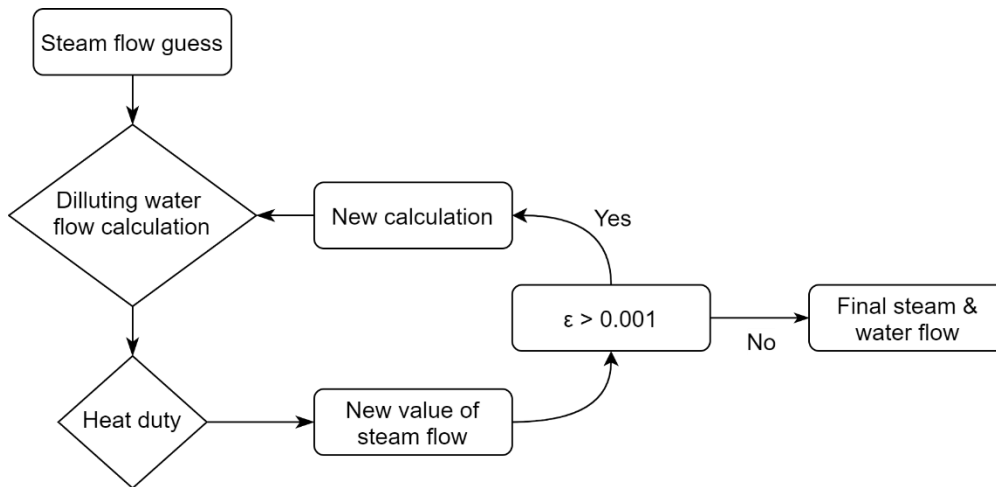


*Figure 41. Steam & water flow calculation procedure*

In the picture, the parameter $\varepsilon$ can be expressed as follows:

$$\varepsilon = abs\big(m_{steam_0} - m_{steam_1}\big) \, , \qquad (6.9)$$

where $\quad \varepsilon \quad$ is difference between old and new value $[-]$,

$\quad\quad\quad m_{steam_0} \quad$ is the old value of steam flow $[kg/h]$,

$\quad\quad\quad m_{steam_1} \quad$ is the new value of steam flow $[kg/h]$.

The next difference is the calculation of the amount of chlorine dioxide dose into the pulp. In this calculation, multiplier 2 presents the amount of HCl and $NaClO_2$ combined and

multiplier 6 represents the surplus needed to form the required amount of ClO₂, which was discussed earlier. This calculation is covered by equation (6.10).

$$V_{ClO2} = \frac{m_{ClO2}}{\rho_{ClO2}} \cdot 10^3 = \frac{2 \cdot w_{ClO2} \cdot m_{bd} \cdot 6}{c_{ClO2} \cdot \rho_{ClO2}} \cdot 10^3 \tag{6.10}$$

where    $V_{ClO2}$    is volume charge of chlorine dioxide $[l/h]$,
         $m_{ClO2}$    is the mass charge of chlorine dioxide $[kg/h]$,
         $\rho_{ClO2}$    is the density of chlorine dioxide solution $[kg/m^3]$,
         $w_{ClO2}$    is the percentual charge of chlorine dioxide $[\%_{weight}]$,
         $c_{ClO2}$    is the mass concentration of the chlorine dioxide solution $[\%]$.

From now on, the calculations for the last stage are very similar – different only in input values for each stage described in the first sheet called "Input data" in **Attachment 2**. The calculation procedure for Experiment 2 is also basically the same. Experiment 3 is different in stage arrangement, but the calculations are also the same. The diluting liquids are also arranged differently. The pulp suspension before the chlorine dioxide bleaching stage is diluted by water. It cannot be diluted by VXP3 filtrate due to hydrogen peroxide contents which would neutralize part of the chlorine dioxide dose. The VXP3 filtrate is here used for dilution of the pulp suspension at the alkaline extraction stage where it does not bring any negative effects, but even positive ones.

## 6.2   Economic balance

The mass and heat balance described in the previous subchapter is the basis for the calculation of economic balance. It is important to note here that for the purpose of the thesis, only the main instruments of the bleaching line that have been part of the performed trials and have a significant impact on the results were considered. The chemical, diluting liquids, and energy consumption of all stages belonging to a given experiment are summed up to give the total amount. These total values of each component are then converted to a ratio of one ton. The following calculation of financial cost for each component is described by equation (6.11).

$$cost_i = \frac{1000}{m_{bd}} \cdot m_i \cdot price_i \ , \tag{6.11}$$

where    $cost_i$    is the cost of the corresponding component per produced ton $[€/t_{bd}]$,
         $m_i$    is the total amount of component used in the sequence $[t] \ or \ [m^3]$,
         $price_i$    is the price of the component $[€/t] \ or \ [€/m^3]$.

In the case of energy costs, the calculation is as follows:

$$cost_E = \frac{1000}{m_{bd}} \cdot \frac{Q_{sequence}}{3600} \cdot price_E \ , \tag{6.12}$$

where    $cost_E$    is the cost of the electrical energy per produced bone-dry ton $[€/t_{bd}]$,
         $Q_{sequence}$   is heat duty of the whole sequence $[MJ/h]$,
         $price_E$    is the price of energy $[€/MWh]$.

The total costs of each experiment were simply calculated by summing up the cost of each component included. These are then the foundation of calculating the percentual saving of Experiment 2 and Experiment 3 concerning Experiment 1:

$$savings_{Exi} = 100 - \frac{cost_{Exi}}{cost_{Ex1}} \cdot 100 \ , \tag{6.13}$$

where      $savings_{Exi}$      are savings of respective experiment against Experiment 1 [%],

$cost_{Exi}$      are costs of respective experiment [€/$t_{bd}$],

$cost_{Ex1}$      are costs of Experiment 1 [€/$t_{bd}$].

## 6.3   Results and discussion

The mass and heat balance results and economical results are presented in Table 17 and Table 18 below.

| | | Experiment 1 | Experiment 2 | Experiment 3 |
|---|---|---|---|---|
| $H_2O_2$ (37%) | kg/h | 64.38 | 37.55 | 26.82 |
| HCl | kg/h | 120.00 | 60.00 | 60.00 |
| $NaClO_2$ | kg/h | 120.00 | 60.00 | 60.00 |
| NaOH (25%) | kg/h | 50.00 | 42.00 | 42.00 |
| Diluting water | m³/h | 9.72 | 7.74 | 3.40 |
| Heat duty | MJ/h | 2,279.65 | 1,353.04 | 1,264.38 |
| Energy per tonne | kWh/$t_{bd}$ | 1,266.47 | 751.69 | 702.43 |

*Table 17. Mass and heat balance results*

| | | Experiment 1 | Experiment 2 | Experiment 3 |
|---|---|---|---|---|
| $H_2O_2$ (37%) | €/ $t_{bd}$ | 31.80 | 18.55 | 13.25 |
| HCl | €/ $t_{bd}$ | 13.92 | 6.96 | 6.96 |
| $NaClO_2$ | €/ $t_{bd}$ | 180.00 | 90.00 | 90.00 |
| NaOH (25%) | €/ $t_{bd}$ | 8.38 | 7.04 | 7.04 |
| Water | €/ $t_{bd}$ | 7.15 | 5.70 | 2.51 |
| Energy | €/ $t_{bd}$ | 33.31 | 19.77 | 18.47 |
| Total costs | €/ $t_{bd}$ | 274.56 | 148.01 | 138.22 |
| Savings | % | - | 46.09 | 49.66 |

*Table 18. Economical balance results*

As can be seen in Table 17, the process requirements of Experiment 2 and 3 in comparison with Experiment 1 are much less demanding. This applies both to chemicals consumption and energy consumption. Experiment 3 is characterized by the best results. The

same goes for process costs. Table 18 shows that Experiments 2 and 3 will bring more than 45 % savings to the economical side of the bleaching line. Experiment 3 reaches even up to 50 % of savings. These results correlate with results that have been already discussed in chapter 5.4. Considering testing basically only different degrees of washing, chemical charge, consistency, and different arrangement, these results are very good and significant and could be the foundations for potential future investments leading to the optimization of the bleaching process.

**Piping system**

From a technological point of view, the switch from the consistency of 5 % to 10 % is accompanied by several changes in the bleaching technology that need to be made. The current piping system mostly contains pipes of DN80, DN100, and DN 125. According to professional consultations with Josef Glawogger, MSc, Senior Manager Corporate Manufacturing at Delfort, and available recommendations and documentations of Andritz company present at the mill, the pipeline was evaluated. The piping design is shown in Table 19 below. The recommended pulp velocity beyond consistency higher than 5 % is less than 0.5 m/s. The data in Table 19 are designed for pulp velocity of 0.3 m/s and consistency of 10 % and are compared at two production rates of 500 and 750 $kg_{bd}$/h.

|  |  | Production rate [$kg_{bd}$/h] | |
| --- | --- | --- | --- |
|  |  | 500 | 750 |
| Pulp suspension flow | l/min | 83.3 | 125.0 |
| Minimal piping DN | mm | 75 | 95 |

*Table 19. Piping design at pulp velocity of 0.3 m/s and consistency of 10 % (*ANDRITZ*, n.d.)*

Considering the minimal DN of the pipes required for the bleaching process and a possible increase in pulp production to 750 $kg_{bd}$/h, the current piping of DN80 is not satisfactory and must preferably be replaced with pipes of DN100. This also includes the replacements of the current pumps. They are meant for maximum consistency of 6 % and therefore must be replaced with medium consistency pumps which are designed up to a consistency of 16 % (*ANDRITZ*, n.d.).

# 7 CONCLUSIONS

In the presented work the issue of wood and annual plant structure, pulp production, and further treatment in form of washing, bleaching, etc. was discussed. In the theoretical part devoted to bleaching, the basic technological principles were explained, and the possibilities of bleaching chemicals were shown. The thesis was focused on the bleaching process in paper production specifically in OP Papírna, s.r.o. mill located in village Olšany in Olomouc region of Czech Republic.

In the following practical part of the thesis, experimental trials to find optimal bleaching conditions were performed. The results of these experiments are very positive. The experiments achieved identifications of optimal conditions relating to temperature, consistency, a charge of chemicals, washing degree of the pulp, and bleaching sequence arrangement. After the experimental part, the design and required calculations containing mass, heat, and economical results were carried out. The results of these calculations showed that the proposed changes in technology are very favorable and will serve the investment plans leading to the optimization of the bleaching process at the mill.

According to achieved results, the following proposal of practical adjustments at the bleaching plants can be made:

- change bleaching arrangement from sequence *PDE$_P$* to *DEP*,
- pulp bleaching consistency switch from 4-5 % to 10 %,
- investment in new washing equipment,
- installing new oxygen delignification stage, thus creating an *O/ODEP* sequence.

These proposals are accompanied by several changes in the bleaching technology that has been already discussed above.

# LITERATURE CITED

*ANDRITZ: ANDRITZ GROUP - ENGINEERED SUCCESS*. Retrieved 2021-05-18, from https://www.andritz.com/group-en

Baillie, C. (2004). *Green Composites - Polymer Composites and the Environment* (1st ed.). Woodhead Publishing.

Bajpai, P. (2015). *Pulp and Paper Industry - Chemicals*. Elsevier.

Bajpai, P. (2018). *Biermann's Handbook of Pulp and Paper - Raw Material and Pulp Making, Volume 1 and 2* (3rd Edition). Elsevier.

Cepi. (2020). *KEY STATISTICS 2019 European pulp & paper industry*. https://www.cepi.org/wp-content/uploads/2020/07/Final-Key-Statistics-2019.pdf

Delfort. *Delfort: OP Papírna, s.r.o.* Retrieved 2021-05-17, from https://www.delfortgroup.com/en/career/czech-republic/op-papirna-sro/

Ek, M., Gellerstedt, G., & Henriksson, G. (eds.). (2009). *Pulp and Paper Chemistry and Technology - Pulping Chemistry and Technology, Volume 2*. De Gruyter.

*Engineering ToolBox: Specific Heat of some common Substances*. (2003). Retrieved 2021-05-11, from https://www.engineeringtoolbox.com/specific-heat-capacity-d_391.html

*EVONIK: HYDROGEN PEROXIDE CALCULATOR*. Retrieved 2021-05-06, from https://active-oxygens.evonik.com/media/misc/h2o2-calculator/

*Foam Contol Application*. StarChem. Retrieved 2021-02-20, from https://starchemglobal.com/foam-control/

Haggith, M., Martin, J. (ed.). (2018). *State Of The Global Paper Industry*. https://environmentalpaper.org/wp-content/uploads/2018/04/StateOfTheGlobalPaperIndustry2018_FullReport-Final-1.pdf

*History of Paper: Paper History - Early Origins, Techniques and Uses*. Retrieved 2021-05-16, from http://www.historyofpaper.net/paper-history/

José, C., Rodríguez, I., & Gutiérrez, A. (2006). Chemical characterization of fibers from herbaceous plants commonly used for manufacturing of high quality paper pulps. *Proceedings of the 9th European Workshop on Lignocellulosics and Pulp*, 109-112. https://digital.csic.es/handle/10261/86412

Kerr, A., & Goring, D. (1974). The Role of Hemicellulose in the Delignification of Wood. *Pulp and Paper Research Institute of Canada and Department of Chemistry, McGill University, Montreal, Quebec*, p. 952-959.

*M.C. TEC: Sheet former Rapid Kothen Manual - M.C TEC B.V.* Retrieved 2021-05-06, from https://www.mctec.nl/en/producten/material-properties/pulp-en/sheet-former-rapid-kothen-manual/

Mathews, S., Ayoub, A., Pawlak, J., & Grunden, A. (2013). *Methods for Facilitating Microbial Growth on Pulp Mill Waste Streams and Characterization of the Biodegradation Potential of Cultured Microbes*. https://www.researchgate.net/publication/259498704_Methods_for_Facilitating_Microbial_Growth_on_Pulp_Mill_Waste_Streams_and_Characterization_of_the_Biodegradation_Potential_of_Cultured_Microbes

Miranda, R., Martin, A., de la Blanca, E., Carrillo, I., & Blanco, A. (2008). Identification of Recalcitrant Stickies and Their Sources in Newsprint Production. *Industrial & Engineering Chemistry Research*, *47*(16). https://www.researchgate.net/publication/50221418_Identification_of_Recalcitrant_Stickies_and_Their_Sources_in_Newsprint_Production

*PMT: TV2000 ASTM D2170 viscosity bath*. Retrieved 2021-05-06, from https://tamson-instruments.com/tv2000-230v-50-60hz-astm-d2170

Roncero, M., Colom, J., & Vidal, T. (2003). Cellulose protection during ozone treatments of oxygen delignified Eucalyptus kraft pulp. *Carbohydrate Polymers*, *51*(3), p. 243-254. https://www.sciencedirect.com/science/article/pii/S0144861702002126

Rouette, H. (2001). *Encyclopedia of Textile Finishing*. Woodhead Publishing.

Sain, M., Faruk, O. (ed.). (2015). *Biofiber Reinforcements in Composite Materials*. Woodhead Publishing.

Simão, L., Hotza, D., Raupp-Pereira, F., Labrincha, J., & Montedo, O. (2018). Wastes from pulp and paper mills - A review of generation and recycling alternatives. *Ceramica*, *64*(371). https://www.researchgate.net/publication/326683862_Wastes_from_pulp_and_paper_mills_-_A_review_of_generation_and_recycling_alternatives

Sixta, H. (ed.). (2006). *Handbook of Pulp* (1st ed.). Wiley-VCH Verlag GmbH &Co. KGaA.

Smoke, G. (2016). *Handbook for Pulp & Paper Technologists* (4th Edition). TAPPI.

Tikka, P. (ed.). (2008). *Volume 6 (Part 1), Chemical Pulping Part 1, Fibre Chemistry and Technology* (1st ed.). TAPPI.

Triantafyllidis, K., Lappas, A., & Stöcker, M. (2013). *Role of Catalysis for the Sustainable Production of Bio-Fuels and Bio-Chemicals*. Elsevier.

U.S. Congress, Office of Technology Assessment. (1989). *Technologies for Reducing Dioxin in the Manufacture of Bleached Wood Pulp*. Washington, DC: U.S. Government Printing Office. https://ota.fas.org/reports/8931.pdf

*USP Technologies: Heat Capacity of H2O2 Solutions*. Retrieved 2021-05-11, from https://www.h2o2.com/technical-library/physical-chemical-properties/thermodynamic-properties/default.aspx?pid=36&name=Heat-Capacity

# LIST OF ABBREVIATIONS

EU                   European Union

ISO                  International Organization for Standardization

OXE                  oxidizing equivalents

ECF                  elemental chlorine-free bleaching

TCF                  totally chlorine-free bleaching

LVN                  limiting viscosity number

$PDE_P$              sequence of hydrogen peroxide stage followed by chlorine dioxide stage finished by alkaline extraction stage enhanced by hydrogen peroxide

DEP                  sequence of chlorine dioxide stage followed by alkaline extraction stage finished by hydrogen peroxide stage

VXP                  washing press subsequent to the bleaching stage

## LIST OF SYMBOLS

| Symbol | Meaning | Unit |
|---|---|---|
| $R_\infty$ | the reflectance of an infinite pile of sheets | $[-]$ |
| $k$ | light absorption coefficient | $[m^2/g]$ |
| $s$ | light scattering coefficient | $[m^2/g]$ |
| $S_L$ | lignin removal selectivity | $[\%]$ |
| $\kappa_0$ | initial Kappa number | $[-]$ |
| $\kappa_1$ | Kappa number after bleaching stage | $[-]$ |
| $\eta_0$ | initial LVN | $[ml/g]$ |
| $\eta_1$ | LVN after bleaching stage | $[ml/g]$ |
| $E_L$ | lignin removal efficiency | $[\%]$ |
| $OXE$ | oxidizing equivalent | $[kg_{a.c.}/kg]$ |
| $S_B$ | bleaching selectivity | $[\%]$ |
| $B_0$ | initial brightness | $[\%]$ |
| $B_1$ | brightness after bleaching stage | $[\%]$ |
| $E_B$ | bleaching efficiency | $[\%]$ |
| $V$ | the total volume of the sample | $[ml]$ |
| $m_{b.d.}$ | bone-dry weight of the sample | $[g_{bd}]$ |
| $cw$ | consistency | $[\%]$ |
| $V_{H_2O}$ | water volume added before dosing chemicals | $[ml]$ |
| $V_{pulp}$ | the volume of water contained in the pulp | $[ml]$ |
| $V_{chem}$ | dose volume of chemicals | $[ml]$ |
| $V_{pH}$ | water and chemicals volume needed to adjust pH | $[ml]$ |
| $m_{chem}$ | dose of a chemical added to the sample | $[g]$ |
| $w$ | charge of the chemical | $[\%_{weight}]$ |
| $V_{HCL,NaClO_2}$ | the added volume of HCl, resp. NaClO$_2$ | $[ml]$ |
| $\Delta B$ | difference in brightness | $[\%]$ |
| $B_i$ | the brightness of the corresponding sample | $[\%]$ |
| $V_{total}$ | total volume needed to reach the required consistency | $[l/h]$ |
| $m_{bd}$ | reference production bone dry mass flow | $[kg/h]$ |
| $V_{H2O2}$ | volume charge of hydrogen peroxide | $[l/h]$ |
| $m_{H2O2}$ | mass charge of hydrogen peroxide | $[kg/h]$ |
| $\rho_{H2O2}$ | the density of hydrogen peroxide solution | $[kg/m^3]$ |
| $w_{H2O2}$ | percentual charge of hydrogen peroxide | $[\%_{weight}]$ |

| | | |
|---|---|---|
| $c_{H2O2}$ | mass concentration of the hydrogen peroxide solution | $[\%]$ |
| $V_{liquid}$ | liquid volume present in the pulp | $[l/h]$ |
| $m_{liquid}$ | liquid mass present in the pulp | $[kg/h]$ |
| $\rho_{liquid}$ | liquid density | $[kg/m^3]$ |
| $V_{filtrate}$ | required amount of diluting filtrate to reach the consistency | $[l/h]$ |
| $V_{NaOH}$ | the volume of NaOH added to the pulp suspension | $[l/h]$ |
| $V_{VXP}$ | the volume of filtrate exiting the washing press | $[l/h]$ |
| $Q_i$ | heat duty for heating the suspension component | $[MJ/h]$ |
| $m_i$ | mass flow of the suspension component | $[kg/h]$ |
| $c_{p_i}$ | specific heat capacity of the suspension component | $[J/(kg \cdot K)]$ |
| $t_b$ | the temperature of the bleaching | $[°C]$ |
| $t_i$ | the temperature of the suspension component | $[°C]$ |
| $Q_{total}$ | total heat duty for heating the pulp suspension | $[MJ/h]$ |
| $m_{steam}$ | amount of steam needed for heating the pulp suspension | $[kg/h]$ |
| $h_{steam}$ | enthalpy of the heating steam | $[kJ/kg]$ |
| $h_{condenstae}$ | enthalpy of the condensate | $[kJ/kg]$ |
| $\varepsilon$ | difference between the old and new value | $[-]$ |
| $m_{steam_0}$ | the old value of steam flow | $[kg/h]$ |
| $m_{steam_1}$ | the new value of steam flow | $[kg/h]$ |
| $V_{ClO2}$ | volume charge of chlorine dioxide | $[l/h]$ |
| $m_{ClO2}$ | mass charge of chlorine dioxide | $[kg/h]$ |
| $\rho_{ClO2}$ | the density of chlorine dioxide solution | $[kg/m^3]$ |
| $w_{ClO2}$ | percentual charge of chlorine dioxide | $[\%_{weight}]$ |
| $c_{ClO2}$ | mass concentration of the chlorine dioxide solution | $[\%]$ |
| $cost_i$ | cost of the corresponding component per produced ton | $[€/t_{bd}]$ |
| $m_i$ | the total amount of component used in the sequence | $[t] [m^3]$ |
| $price_i$ | price of the component | $[€/t] [€/m^3]$ |
| $cost_E$ | cost of the electrical energy per produced bone-dry ton | $[€/t_{bd}]$ |
| $Q_{sequence}$ | heat duty of the whole sequence | $[MJ/h]$ |
| $price_E$ | price of energy | $[€/MWh]$ |
| $savings_{Exi}$ | savings of respective experiment against Experiment 1 | $[\%]$ |
| $cost_{Exi}$ | costs of the respective experiment | $[€/t_{bd}]$ |
| $cost_{Ex1}$ | costs of Experiment 1 | $[€/t_{bd}]$ |

# LIST OF ILLUSTRATIONS

# LIST OF TABLES

# LIST OF ATTACHMENTS

Attachment 1 – Results of experiments in excel sheets
Attachment 2 – Mass, heat, and economical balance in excel sheets