DISSOLVING PULP AND ITS PROPERTIES

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ABSTRACT

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Dissolving pulp is special grade of pulp with high purity that is widely used in textile production industry to get rayon staple for high-quality fabrics. It is also used in the paper production industry as an additive to binders or as a blend with mechanical pulps. Comparing with other types of pulp, dissolving pulp is rarely intended for papermaking.

The aim of this study was to gather theoretical information on the dissolving pulp and its properties. In order to achieve this goal, there were tasks to be solved: to research the production process of dissolving pulp, to figure out important steps of the process, to study dissolving pulp applications and final products, to analyse the world market situation, to test dissolving pulp samples in TAMK laboratory.

The study was done by researching theoretical data. Scientific portals, articles and tutorials were analyzed. In order to handle the experimental part, the Stora Enso company was involved to supply dissolving pulp sheets.

The knowledge of the process of raw wood transformation into the dissolving pulp was obtained. The quality of pulp is influenced by the quality and composition of wood chips fed for cooking. Since the alkaline sulfate cooking is unable to remove sufficient amount of hemicellulose, pre-hydrolisis treatment is significant. World market analysis shows that the demand will continuously grow upward with relatively fair pricing level.

Obtained experimental results show that Stora Enso samples had high levels of dry matter and swelling value. The findings indicate that dissolving of the given pulp sample has occurred in 10% NaOH solution.

Key words: dissolving pulp; cellulose; pulp cooking; pre-hydrolysis; a-cellulose; dry matter content; viscose

CONTENTS

ABBREVIATIONS AND TERMS

TAMK	Tampere University of Applied Sciences
NCG	Non-considerable gas
ECF	Elemental Chlorine Free
PHL	Pre-hydrolysis liquor
WRV	Water retention value

1 INTRODUCTION

Global demand for the dissolving pulp is continuously growing due to the need of the end use products as well as their new development, rapid economic growth in emerging markets and steady growth of the world population. Currently, the global suppliers of he dissolving pulp moved to Asia where the middle class is rapidly growing, thus causing high demand. According to David Fortin, a member of Fiber Economic Analysis team, now world production of cotton is in the stage of stagnation. However, the rising demand for fibres may be ensured by the dissolving pulp manufacturers. (RISI, 2011)

The target of this work was to research and review the dissolving pulp production process and its role in global industry market.

The theoretical part of this thesis starts from information about cellulose which is the main component of cell walls in higher plants. Its existence in the nature, chemical characteristics, general properties and derivatives are described. This part is followed by the detailed dissolving pulp production process starting from raw wood preparation up to the end use. The cooking processes are compared as well. Then, the situation on the world market was analyzed, considering production rate of the dissolving pulp and its consumption overview. The fourth paragraph of this work presents methods to study the properties of the dissolving pulp, such as α-cellulose content, viscosity, degree of polymerization.

Experimental part of the work was carried out with dissolving pulp samples produced by Stora Enso. Origin of the samples, dry matter content, swelling value were tested. Finally, conclusions were made and recommendations for future research were given.

2 GENERAL NOTION ABOUT CELLULOSE AND PULP

Cellulose is an organic compound, polysaccharide, consisting of a linear chain and refers to biopolymers. Pulp is a lignocellulosic fibrous material. It is prepared by chemically or mechanically separating cellulose fibers from wood, fiber crops or waste paper.

2.1 Existence in nature

Cellulose is the main component of cell walls in higher plants. It serves as a carcass bearing main mechanical load. Cellulose can be found mostly in seed fibers of some plants. For example, cotton plant contains 97-98 %, wood - 40-50 % on dry matter; stem fibers, internal layers of plant bark (linenandramie) contain 80-90 % of cellulose, Indian grass - 75 %. Stems of annual plants may contain up to 30-40 % of cellulose, for example, in reed, corn, cereals, and sunflower. Pulp production from natural materials is based on actions of agents destructing or dissolving non cellulosic compounds. The treatment character depends on the composition and structure of the plant. For instance, for naturally soft cotton fiber relatively mild methods of treatment are used. (Terenteva, 2015)

2.2 Chemical characteristics of the pulp

Pulp has complex super molecular structure. Based on X-ray data as well as radiographic and spectroscopic research, pulp is usually assumed to be crystalline polymers. By its chemical nature, pulp is polyatomic alcohol. Pulp reacts with alkaline metals and bases due to presence of hydroxyl groups in macromolecule unit.

Pulp has a wide range of structural modifications. The major are natural pulp and cellulose hydrate. Natural pulp transforms into cellulose hydrate under process of dissolution and further precipitation from the solution, with the action of concentrated alkaline solutions and further decompounding of alkaline cellulose and others. Reverse transformation may be performed through heating of cellulose hydrate in a solvent, which causes its intensive swelling (in glycerin or water). Both structural modifications have various X-ray diagrams and strongly differ in reactivity, solubility (not only cellulose itself, but its esters too), absorbing capacity and other characteristics. Distinctive features of cellulose hydrate preparations are high absorption and higher speed of hydrolysis as well. (Terenteva, 2015)

2.3 General pulp properties

There are three most important parameters that defines the pulp. They are fiber length, brightness and pulping process that was applied. The name of the pulp is given according to these parameters (for example, Northern Soft Wood Bleached Kraft, Southern Hard Wood Unbleached Kraft) and describes whether it is long or short fiber pulp, bleached or not, and cooking method as well.

Appendix 1 includes major pulp properties with the explanation. (KnowPulp, 2015)

2.4 Pulp derivatives

The tendency to modify cellulose materials brought about a range of new pulp derivatives, and in some cases the new grades of pulp derivatives.
Modification of pulp properties and production of new pulp derivatives can be performed with two groups of methods:

- esterification, O-alkylation or transformation of hydroxyl groups into other functional groups (oxidation, nucleophilic substitution using some cellulose esters – nitrates, esters with n-toluene and methane sulfonic acid as original substances);
- graft copolymerization or interaction of cellulose with polyfunctional compounds (cellulose transformation into branched or cross-linked polymer, respectively). (Duan, 2015)

One of the most common methods for pulp derivatives production is nucleophilic substitution. Under this method, cellulose esters with some strong acids (toluene– and methanesulfonic acid, nitric acid and phenylphosphoric acid), as well as cellulose derivatives are used as original substances. Cellulose derivatives are synthesized under the nucleophilic substitution reaction, where hydroxyl groups are substituted with halogens (chlorine, fluorine, iodine), thiocyanogen, nitrile and other groups. Thus, desoxycellulose preparations were synthesized, which contain heterocycles (pyridine and piperidine) as well as cellulose esters with phenols and naphthols and a range of cellulose compound esters (with higher carboxylic acids, α-amino acids, unsaturated acids) were obtained. Intramolecular reaction of nucleophilic substitution (saponification of cellulose tosyl esters) leads to formation of combines polysaccharides containing 2, 3– and 3, 6-anhydrocycles. (Aliev, 2011)

Synthesis of cellulose graft copolymers has the most important practical importance for generation of cellulose materials featuring modern technical advance. The most widely-used methods for synthesis of cellulose graft copolymers include usage of cellulose chain-transfer reaction, radiation-chemical copolymerization and oxidation-reduction systems where cellulose acts as reducer. In the last case, formation of macroradical may occur by means of oxidation of both cellulose hydroxyl groups (oxidation with cerium salts) and functional groups that specially introduced into the macromolecule — aldehyde, amino groups (oxidation with vanadium salts, manganese salts). Also degeneration of diazo compound which forms during diazotization of aromatic amino groups introduced into cellulose. Synthesis of cellulose graft copolymers may sometimes be carried out without generation of homopolymer, which reduces monomer consumption. Cellulose graft copolymers obtained in usual copolymerization conditions consist of a mixture of original cellulose (or its ester to which grafting is made) and graft copolymer (40-60%). Polymerization degree of graft chains ranges from 300 to 28 000, depending on the initiation method and the character of the graft component. (Terenteva, 2015)

3 DISSOLVING PULP

Dissolving pulp is a bleached wood pulp or cotton linters that has high α-cellulose content (> 90%). Special properties of dissolving pulp include high level of brightness and uniform molecular-weight distribution. This grade of pulp is manufactured for uses that require high chemical purity and particularly low hemicellulose content since the chemically similar hemicellulose can disturb following up processes. Dissolving pulp is so called because it does not convert into paper, but dissolves either in a solvent or transformed into a homogeneous solution, which makes it completely chemically accessible and removes any remaining fibrous structure. Once dissolved, it can be turned into textile fibers (viscose or lyocell), or chemically reacted to produce derivatized celluloses. For example, into triacetate cellulose, plastic-like material formed into fibers or films, or cellulose ethers such as methyl cellulose, used as a thickener. (Sirpa, 2015)

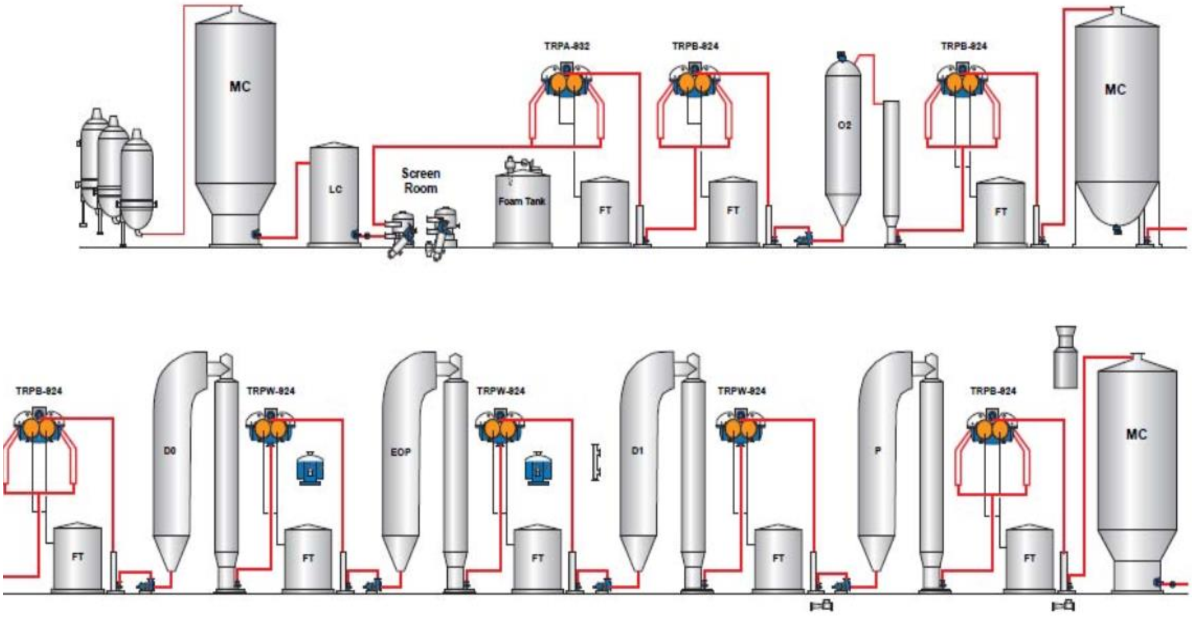
3.1 Raw materials

According to the KnowPulp, all types of wood and cotton are suitable for the production of dissolving pulp. Most of tree species, such as birch, eucalyptus, aspen, pine, spruce are used for the extraction of wood. However, there is also high demand for non-wood fibers like bamboo because they can be used as a raw material as well. Since different trees provide various quality and type of the pulp, the raw material is basically chosen by supposed final product. Thus, hard wood contains less lignin, hemicellulose and extractives than cellulose, and also it gives higher yields. These properties allow hard wood be more competitive for artificial fibers production than soft wood.

Viscose fibers are made out of soft wood and after some time passes, they become yellowish. On the other hand, soft wood suits better for the production of cellulose derivatives because its fiber properties and morphology play a great role when thinking about physical properties of the end product (Berggren, R., 2003).

3.2 Production process

Dissolving pulp is mainly produced chemically from pulpwood in a process that has low yield of the wood (30-35 %). This makes up about 85 – 88 % of the whole production. The process of pulp dissolving can be done by either sulfite or pre-hydrolysis sulfate cooking. In order to achieve the highest quality of the dissolving pulp, it should be derived from fast-grown hardwoods with low non-cellulose content. (Falt, 2004)



PICTURE 1 . Typical dissolving pulp fiberline (Metso, 2011)

Both pre-hydrolysis sulfate and sulfite processes cook the wood in strong chemicals to transform wood chips into cellulose fibers. The modified sulfate process differs from the sulfite process in two ways. It uses an alkaline liquor instead of an acidic one, which protects the machinery from corrosion. Also, usage of sodium sulfide produces a stronger fibers.

Sulfate cooking also known as kraft. The term comes from the German word “strong”. The process was originally developed in Germany in the late 19th century.

While the modified kraft process has become more popular, both processes begin with removing bark from the logs. Then, the logs are chipped and added to a vat with liquor. The mixture is heated to soften the chips, and the residual liquid can be reused in the pulping process. After cooking, the pulp is washed to separate waste from the fibers. (Andersson, 2007).

There are only several companies in Europe which manufacture dissolving sulfite pulp. In general, this process of pulp production is very much similar to production of sulfite pulp intended for paper. The same chemicals are used as in the conventional magnesium-bisulfite process. Therefore, the system of power and chemicals regeneration is the same. Major differences may be observed in parameters of the cooking and bleaching processes. The purpose of cooking during the process of production of dissolving sulfite pulp, lies in achievement of the pre-determined low viscosity, i.e. shorter length of pulp molecular chain and fuller removal of hemicellulose and lignin from the wood (Al-Dajani, 2014).

The detailed step-by step process of the dissolving pulp preparation is described in the next paragraphs.

3.2.1 Raw wood preparation

The process of raw wood preparation includes the following sub processes.

- Wood sawing, where pulp wood is supplied for processing as whole trees, long or short cut woods. Currently, the new barkers have been developed and they cut the woods into the segments of 4.5-6 m.
- Debarking, that may be carried out in two ways. In case of group processing, debarking is done in barkers and in case of individual processing, debarking is done with rotary machines. Barkers are intended for debarking in wet, semi-dry and dry method. All the mentioned methods have advantages and disadvantages. For example, wet debarking method requires plenty of water as the barker is put into a bath and filled with water. In case of semi-dry debarking method, hot water is fed to the closed section of the barker, which creates conditions for defrosting (in wintertime) and bark wetting, thus ensuring appropriate debarking of any wood. Over the last years, dry debarking method in barkers is applied in many mills. Water is used only to wash and defrost timber. Dry debarking method allows lower water content in the bark, thus giving opportunity for energy cost saving at the factory.

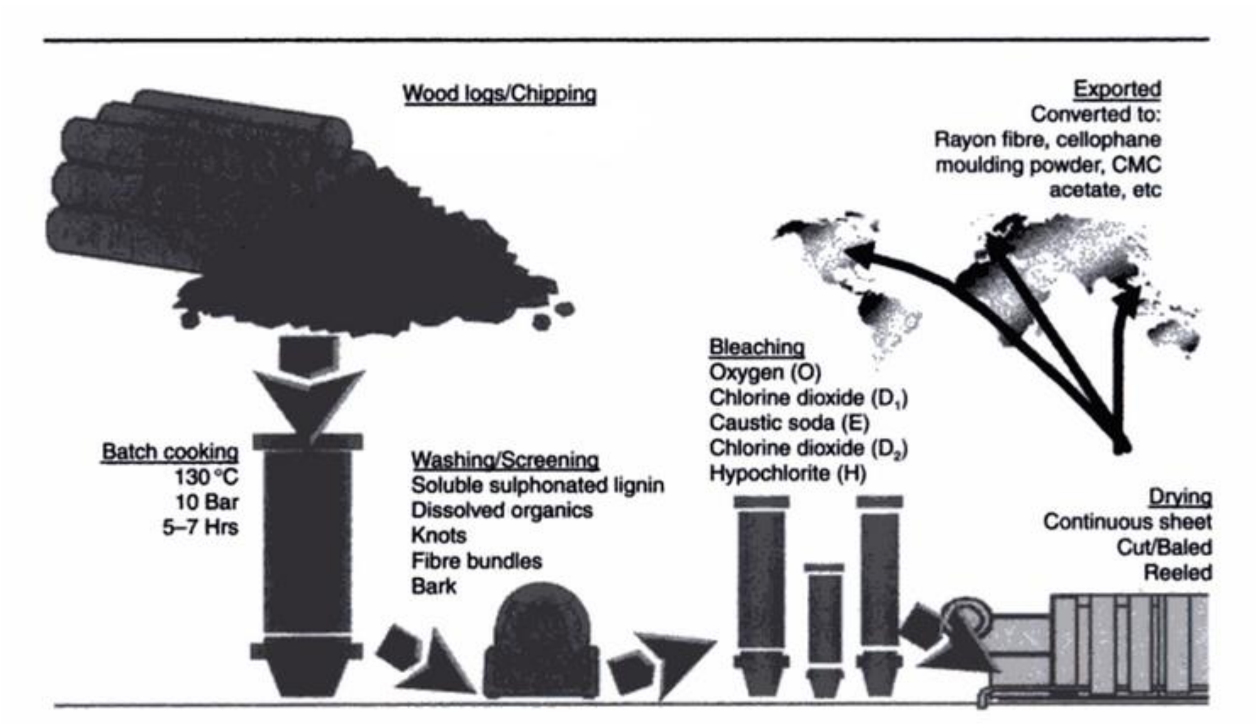
- Wood chipping, in order to obtain pulp. Debarked round wood is chipped with a wood chipper. Nowadays, wood chippers with horizontal feeding and low ejection of chippings are the most widespread. This is determined by the bigger length of wood intended for cutting (up to 4-6 m) and lower loss of wood, as its chipping beats while running up through the blades are excluded.
- Chip classifying, since chips of the same size are important for higher effectiveness of the cooking process and to obtain high quality of pulp as well. Chips are sorted flakes of non-standard size. In order to improve the chips quality, chips are sorted to remove thick pieces and then supplied for the production. Sorting by thickness ensures uniformity of pulp cooking, thus improving its quality and output. (Tian, 2014)

3.2.2 Sulfite cooking

Production of sulfite pulp (picture 2) consists of three main stages:

- production of pulp fiber;
- disposal of sulfite liquors;
- regeneration of chemicals and power, except for cooking with calcium base which prevents regeneration.

However, waste sulfite liquor may be evaporated, and its components may be applied for other purposes. (KnowPulp, 2011)



PICTURE 2. Sulfite pulping operation (Woodings, 2001)

Sulfite cooking is based on application of water solutions of sulfur dioxide (SO_2) and calcium, sodium, magnesium or ammonium base. Cooking is carried out under the pressure at 135-150 °C for 4-12 hours. The cooking solutions have a pH 1,5-2,5. When this method is used, pulp refining should be applied. It removes lignin, hemicellulose, ash, also change chemical and physical properties of the cellulose.

Refined pulp has the following composition (Table 1) :

TABLE 1. Pulp composition after the sulfite cooking.

α- cellulose	95-98%
lignin	0,15-0,25%
pentosanes	1,8-4,0%
resin	0,07-0,14%
ash	0,06-013%

(Aliev, 2011)

3.2.3 Sulfate cooking

The alkaline sulfate cooking is unable to remove sufficient amount of hemicellulose, thus pre-hydrolisis treatment is needed. The wood is cooked in two steps: pre-hydrolisis and then cooking itself.

Pre-hydrolysis can be carried out in two ways:

- treatment with HCl or H_2SO_4. This is acidic hydrolysis. It is relatively rough and requires many time-consuming steps.
- treatment with hot water. This is auto-hydrolysis. Acetyl and formyl groups are removed, organic acids are formed, the pH of the solution is 3.5-4. At the same time, 12-17% of dry wood content is destroyed.

Currently, auto-hydrolysis is the most common way. The yield after acid pre-hydrolysis is lower than after aqueous. So, the yield of unbleached pulp is also lower. Although both methods of pre-hydrolysis make it possible to obtain dissolving pulp of high quality both by the content of a-cellulose and pentosanes.

The quality of pulp is influenced by the quality and composition of wood chips fed for cooking. Large chips and sawdust hamper the cooking process. It is known that cellulose with a high degree of polymerization is considered to be the most suitable for production.

To produce pulp with specified properties and to obtain the required quality it is necessary to adjust the pre-hydrolysis process. Increasing the duration and temperature of hydrolysis leads to a decrease in the yield of pulp and also to a certain content loss of α-cellulose. By increasing the cooking temperature (over 170 ° C) the lignin dissolves, but cellulose destructs as well. By increasing the amount of alkali the pulp viscosity decreases. When sulfidity is increased, the yield is slightly increased, but the viscosity – significally. Increase of the cooking time leads to the pentosans content fall, however, filterability of pulp solutions improves. On the other hand, the yield of pulp decreases and the viscosity decreases. Thus, the technological process of cooking pre-hydrolysis cellulose should be chosen in a way not to get too soft pulp.

Once pre-hydrolysis stage is completed, sulphate cooking is carried out. Sulfate cooking liquor main components are NaOH and Na_2S. During the process, wood is cooked under the pressure at 160-170 °C for 5-6 hours. Specific conditions of cooking depend on the composition of cooking liquor and are determined by the final use of pulp. During sulfate cooking, all wood components react with the cooking agents. As a result the larger part of lignin, some part of carbohydrates and destruction products are released into the solution and form waste (black) liquor.

Table 2 includes composition of the prehydrolyzed sulfate pulp after refining and bleaching .

TABLE 2. Pre-hydrolyzed sulfate pulp composition

α-cellulose	94,5-96,9 %
pentosanes	2-2,5 %
resin	0,01-0,06 %
ash	0,02-0,06 %

3.2.4 Unbleached pulp washing

The stage of washing has multiple purposes. Firstly, to separate as much as possible dissolved minerals and organic substances of black liquor from pulp fibers. Secondly, to increase the degree of cooking chemicals regeneration. Thirdly, to cut down consumption of bleaching chemicals. And finally, to decrease the amount of pollutants from the bleaching unit of drying or paper-making machines.

Efficiency of unbleached pulp washing depends on the number of washing stages as well as efficiency of the applied equipment, concentrations of incoming and washed mass, and consumption of the washing water.

For modern washers, effectiveness of flushing is estimated by the degree of dry substance selection and should be total at least 99 %. Up-to-date washers (diffusors, filters and presses) are designed for flushing with diffusion, squeezing, displacement or combination of these three principles. (Fink, 2004)

3.2.5 Unbleached pulp sorting

The purpose of unbleached pulp sorting is to separate knots, bundles of non-separated fibers, bark, resin and sand from the general flux of conditioned pulp using various sorting equipment.

3.2.6 Oxygen delignification

The purposes of oxygen delignification is to reduce kappa number in pulp before bleaching, to cut down consumption of chemicals for bleaching, to reduce the amount of pollutants to the waste treatment facilities and so to decrease bleaching impact on the environment.

Lignin removal during oxygen delignification is carried out by treating unbleached pulp with oxygen and alkali in reactors at high temperature under extreme pressure. The process of oxygen delignification is carried out in one or two stages. Two-stage delignification ensures 60 - 70 % delignification for softwood pulp, and one-stage delignification - nearly 40 %. Mixed-valence metals may cause destruction of softwood pulp during oxygen-alkali treatment. It can be prevented by adding magnesium compounds into the process (normally $MgSO_4$). (Suchy, Argyropoulos , 2002)

3.2.7 Pulp bleaching

Lignin, extractives and other substances containing chromophore groups, make the pulp dark-colored. Therefore bleaching is intended for final delignification and pulp whitening with minimal mechanical power losses. (Silanpää, 2005)

Bleaching can be divided into Elemental Chlorine Free (without chlorine gas or hypochlorite, but with chlorine dioxide (ClO_2), and Totally Chlorine Free (with oxygen-containing chemicals such as oxygen, hydrogen peroxide and ozone). (KnowPulp, 2011)

Bleaching unit combines a range of separate stages with various chemicals used. Each stage of bleaching is equipped with pulp and chemicals mixer, pulp and steam mixer, bleaching reactor (tower), flushing equipment (to separate waste chemicals, dissolved lignin and other substances from pulp). In order to wash pulp between the bleaching stages, vacuum filters are mostly used.

Chlorine-containing gas emission from the equipment are decontaminated in washer before emitted into the atmosphere. Cooled alkali filtrate or sodium bisulfite solution is used as decontaminating agents. (Silanpää, 2005)

3.2.8 Bleached pulp screening

Upon bleaching, pulp may be sometimes subjected to the final screening. Secondary screening is carried out with the same equipment as for the unbleached pulp. Centricleaners, radiclones (direct and reverse) may be used, especially for hardwood pulp. (Silanpää, 2005)

3.2.9 Pulp drying

Drying machines are used to dehydrate pulp until air-dried condition and to obtain commercial bleached or unbleached pulp. The design of drying machine is similar to paper-making machine.

After process of drying, wet content in pulp should be 8-12 %. Sometimes there will be a need to make dewatering quickly to prevent flocculation of the fibers. Efficiency of this process largely depends on the concentration of pulp mass. In low concentrations provided the lowest resistance to water filtration through a layer of mass on the grid, and therefore, the minimum probability of flocculation.

3.2.10 Finishing processes

Finishing processes include cutting into sheets and then transporting to the further treatment. The shaping of the paper is determined by its final destination. It must have the highest possible mechanical strength, homogeneous structure, uniform weight of 1 m^2 homogeneous surface on both sides and a certain ratio indicators of mechanical strength in the longitudinal and transverse directions.

3.3 Sulfite vs sulfate

Most of the mills that used sulfite method are shouted down in Europe. Despite several advantages of the sulfite cooking, it has been displaced by sulfate process with pre-hydrolysis for significant reasons. Sulfate process brings higher yield from wood, better bleachability and grindability, better optic properties, high whiteness. Therefore, pre-hydrolyzed sulfate pulp may be used unbleached for mass-produced paper (for example, newsprint paper). Also, it releases no NCG into the atmosphere. Thus, pre-hydrolysis sulfate cooking is more environmentally friendly method and PHL includes dissolved hemicellulose, lignin and extractives, which can be recover if needed. (KnowPulp, 2011)

3.4 Dissolving pulp application

The largest user of dissolving pulp is viscose-rayon process. The 90-92 % of cellulose content in sulfite pulps are used mostly to make textiles (like rayon) and cellophane. 96 % of cellulose content in sulfate pulps are used to make rayon yarn for industrial products such as tire cord, rayon staple for high-quality fabrics, and various acetates and other specialty products.(G.A. Smook, 2002)

The dissolving pulp is used in production of regenerated cellulose. In the latter process, the cellulose is converted to cellulose xanthate which dissolves easily in the solution of caustic soda. The resulting viscous liquid can be extruded through spinnerettes and regenerated as man-made fibers. Cellulose can also be dissolved in some organic solvents directly and processed to regenerate the cellulose fibers in different forms.
The lyocell process uses an amine oxide to dissolve cellulose and Tencel is the only

commercial example of this direct-dissolution process, which unlike the viscose process is pollution-free.

As a raw material of cellulose derivatives, dissolving pulp is used in carboxymethyl cellulose (CMC), methyl cellulose (MC), hydroxypropyl cellulose (HPC), hydroxyethyl cellulose(HEC), etc.

Since dissolving pulp is highly refined, product of high whiteness with few impurities, it is making it suitable in specialty paper-related products such as filter paper and vulcanized fiber.

Cellulose powder is dissolving pulp that has undergone acid hydrolysis, been mechanically disintegrated and made into fine powder.This pulp is used as a filler for urea-formaldehyde resins and melamine resin products. (Falt, 2004)

In order to produce some products, dissolving pulp may be added to other pulps. For example, in papermaking, producers blend mechanical pulps with chemically derived dissolving pulp to balance the printability of long fibers with the durability of short fibers. They may also choose not to bleach their pulp in order to create brown paper. While the demand for dissolving pulp shows slow decline from the 1970s to the end of the 1980s, competition from other fibers, such as polyester, increased. Now it stabilized and continues to play an important role in a range of industries. (Andersson, 2007)

The overview of dissolving pulp end use segments is presented at the Figure 1.

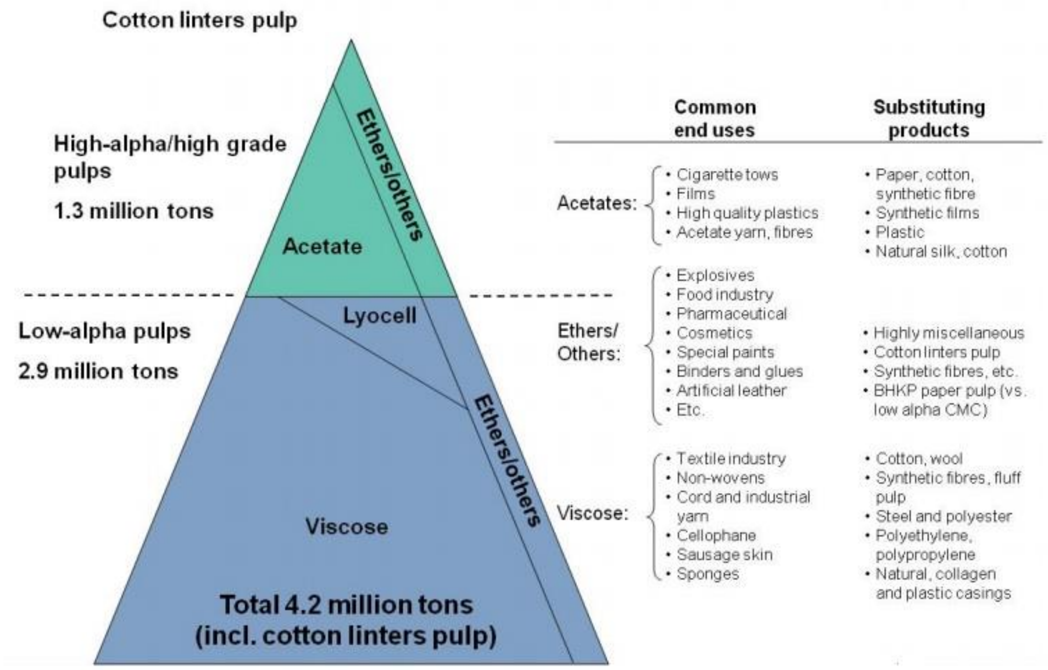


FIGURE 1. End use summary (World Fiber Outlook, Pöyry).

3.5 Analysis of the world market of dissolving pulp

Dissolving pulp features have a wide range of applications, and the demand for it keeps growing up steadily. While the cotton supplies to the world markets tend to be more limited, the textile industry builds up its demand for dissolving wood pulp. (Duan, 2015)

Global dissolving pulp capacity totaled about 7.5 million tons in 2015, mostly distributed in the regions/countries with rich forest resources including North America, South Africa, and Brazil. The world's major dissolving pulp producers are Sappi, Aditya Birla, Lenzing, Sun Paper, Bracell, Rayonier, etc. which produce mainly dissolving wood pulp and altogether hold 57 % share of the global total capacity.

3.5.1 Production rate

The world leader in the production of wood pulp is the US. The United States owns almost a third of world output of wood pulp. The US share of world production in 2013 was 28 %. It is important to note that the US leads by a wide margin from other countries leading in the list of pulp producers. During the 2013, US pulping reached a level of 49 056 tonnes (-2%); almost half of the issue is the production of bleached kraft pulp (Bleached Sulphate Pulp). (Murphy, 2011)

China annually increases volumes of pulp manufacture and uses it solely for the domestic production. During the last decade, the pulp production in China has increased by nearly 2.5 times. In Europe, over the past ten years, some pulp and paper mills have moved their businesses into countries such as Brazil and Indonesia. As a result, figures for the production of paper and paperboard in Indonesia grow. (Duan. 2015)

Top manufacturing countries of dissolving pulp in 2014 are presented at the Figure 2.

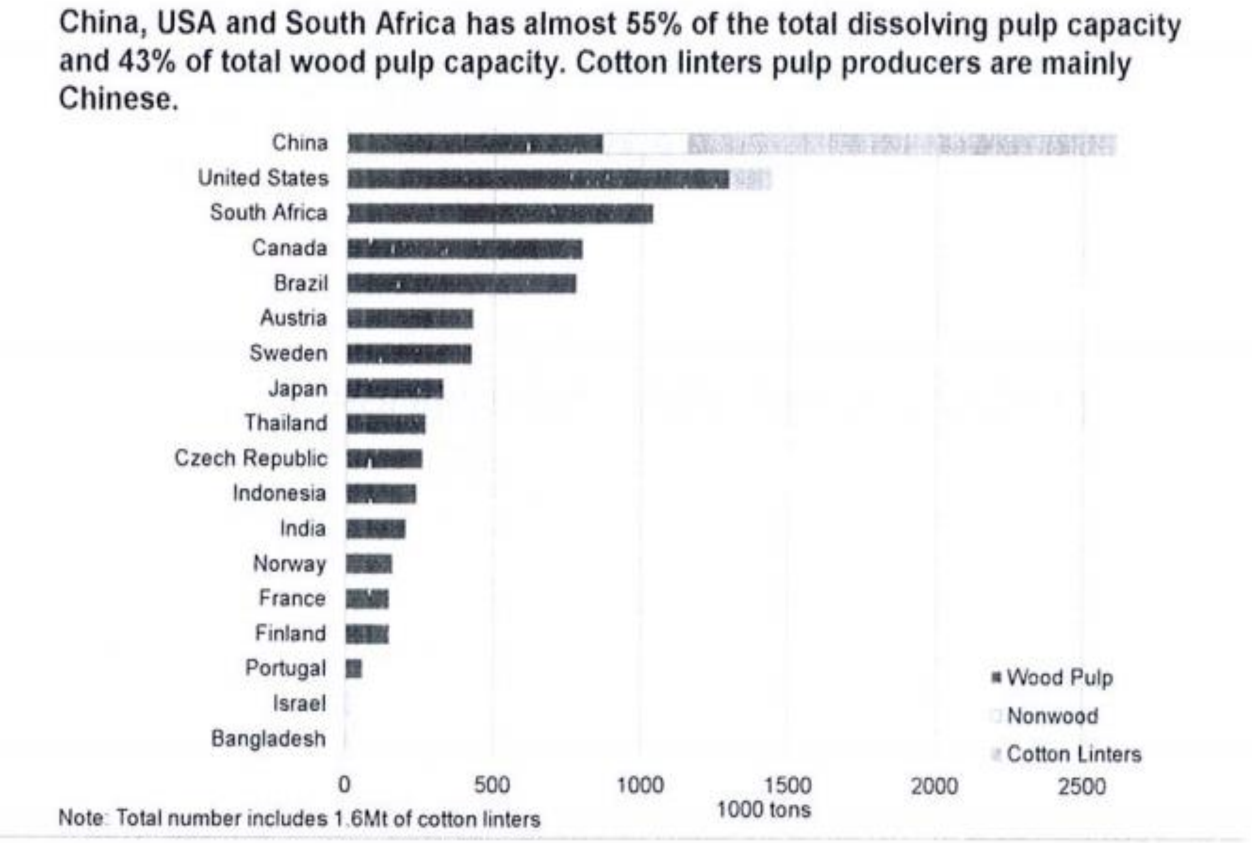


FIGURE 2. Dissolving pulp top manufacturing countries Q2/2014 (Finn fiber – 19.11.2014).

3.5.2 Consumption overview

The RISI, a leading information provider for global forest products study, reports that dissolving pulp is one of the few growing markets in the pulp and paper industry today. A key to the product's success is rapidly growing middle class in China and India, that illustrates high demand for rayon products and clothing. The textile industry, however, is not the only factor driving the dissolving pulp market. Some Canadian companies, such as Quebec's Tembec, have seen tremendous increases after markets surged following an earthquake in Chili and a strike in Sweden that impacted the global paper pulp supply. (Fortress: Speciality Cellulose, 2012).

The world demand for dissolving pulp (Figure 3) is expected to grow from 4.1 million tones a in 2008 to 6.3 million tones by 2025. (Pöyry, 2009)

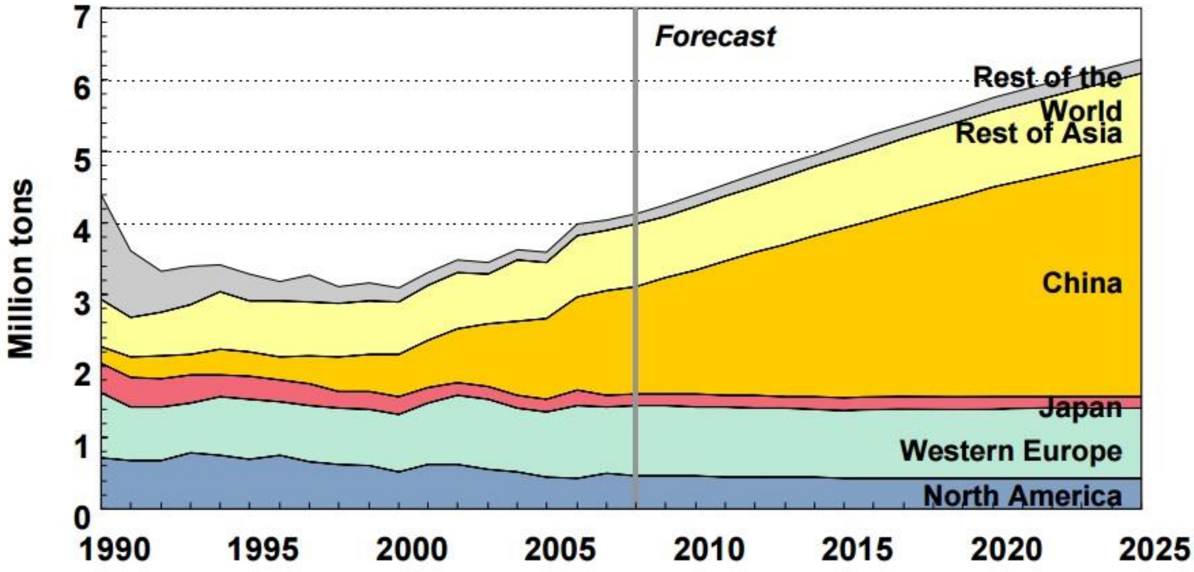
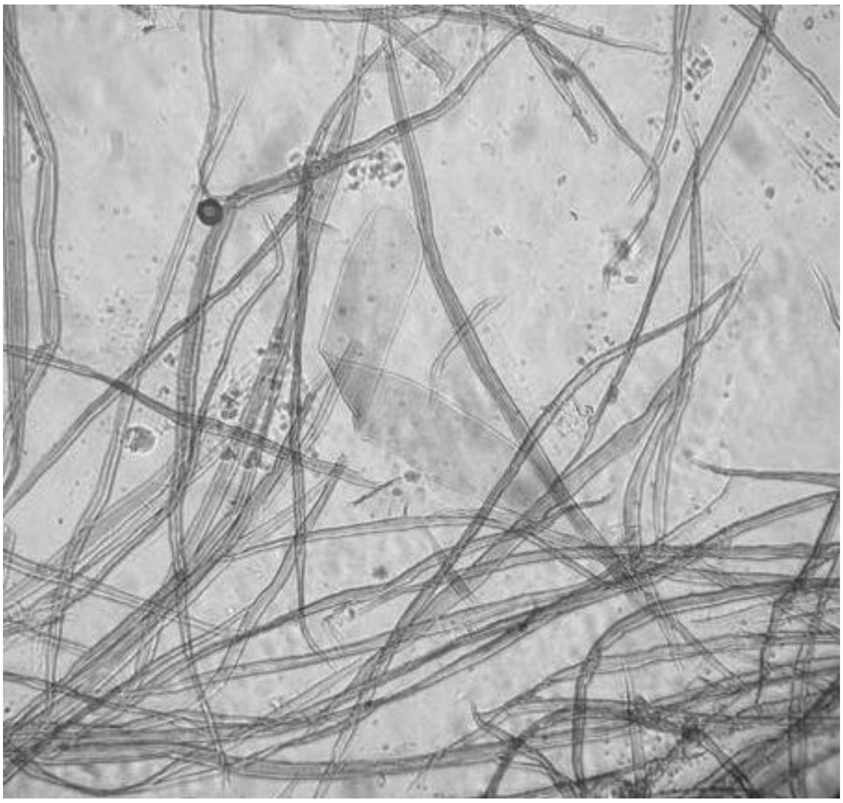


FIGURE 3. Average consumption estimation by region (Pöyry, 2009).

4 MATERIALS, METHODS AND RESULTS

The dissolving pulp samples that were tested through the experimental part of this thesis work were produced by Stora Enso company at the Enocell mill. The product name of the pulp is Pure. Birch (Betula species) and aspen (Populus tremula) were used as raw materials. The company applies modified kraft cooking process and bleach with ECF bleaching sequence. The most common end-use of the Pure is production of staple fibres. Moreover, the product is Anthraquinone-free and makes it suitable for Kosher and Halal food applications. Detailed cellulose characteristics is presented on a datasheet (Appendix 2).

A microscopic photo (picture 3) was taken with Nicon Eclipse E400 and it shows the birch fibres of the sample. More photos are attached in appendix 3.



PICTURE 3. Birch fibers in the Pure dissolving pulp sample

4.1 Dry matter content

The pulp contains a certain amount of moisture, so prior to analyzes handling it is necessary to determine pulp's dry matter content.

The standard ISO-R 638 (SCAN-C 3:78) was used. For that purpose, 5 pieces of the approximate weight 10 g were cut and weighted by using scales SCALTEC CBS32, with accuracy d=0,0001g. Containers and lids were prepared according to the standard, the oven was heated up to 105± 2 ºC. All samples were dried out in the oven for 3 hours and then cooled down for 45 min under the room conditions. The scales were used to weight samples after drying in the oven. The dry matter content for each item was calculated by the formula (1):

$$X = \frac{100(b-c)}{(a-c)} \qquad (1)$$

where

X – dry matter content, %

a – container with lid and sample before drying, g

b – container with lid and sample after drying, g

c – container with lid, g

4.2 Swelling value

Swelling degree is the indicator of pulp quality which characterizes its ability for swelling and is determined in % by growth of pulp specimen weight in 17.5% NaOH solution. Swelling of pulp fibers is important for better accessibility of cellulose macromolecules. Swelling is an increase of volume under the solvent action.

Pulp swelling may be of two types:

1) Intercrystalline (in diluted alkali solutions)
2) Intracrystalline (in concentrated solutions with the concentration over 0 -12 %)

The concentration of sodium hydroxide solution plays an important role for swelling. The swelling degree declines in high concentrated solutions. Concentration of alkali solution, causing maximal swelling, depends on the character of cellulose material and processing temperature.

SCAN-C was used as a method. Ten pieces of the tested air-dried pulp sized 1∗1.5 cm are weighed and placed into crystallizers filled with: one with 25 cm^3 of distilled water, another – with 25 cm^3 of NaOH solution in the concentration of 17.5 %.

Swelling time in water was one hour, in alkali - 10 minutes. Upon expiration of the mentioned time, pulp was carefully taken away with pincers and kept inclined to liquid flow down, the residual drop was carefully wiped with filter paper, then the swollen pulp was weighed on watch glass (preliminary weighed). Ratio of swollen pulp weight to its original weight is the weight swelling value and it is normally expressed in %.

4.3 Alpha-cellulose content

The most important feature of dissolving pulp is alpha cellulose content, because chemical properties of cellulose's molecular structure are significant to the end products. Alpha-cellulose is the fraction of high-molecular cellulose with polymerization degree over 200, but it is not an individual chemical compound. It contains molecules of mannan and xylan, and some residual lignin. An increase in the content of a-cellulose is accompanied by an improvement of the end product quality.

The TAPPI T 203 cm - 09 method is based on pulp treatment with 17.5% sodium hydroxide solution and determination of non-dissolved residue after flushing with 9.5 % alkaline solution and drying.

4.4 Alkali solubility

According to CCA-8:55 (SCAN-C 2:61) , there is a method for the determination of the solubility of pulp in cold sodium hydroxide solutions of different concentrations. This method is intended for the study on bleached pulps. However, it may be used with unbleached pulps as well.

4.5 Viscosity

In general, the solution defines viscosity of a pulp. It gives an understanding of the average degree of polymerization of the cellulose fiber. Thus, the viscosity indicates the relative degradation of cellulose fiber during pulping or bleaching process. Dissolving pulp from wood contains a large content of a- cellulose and gives higher viscosity values.

Under ISO 5351/1 (SCAN-CM 15:88) , the standard procedure of measuring pulp viscosity includes preparation of the 0.5 % cellulose solution, applying 0.5M cuperiethileneaiamine (CED) as a solvent and a device called capillary viscometer. This method is suitable to measure viscosity of bleached cotton and wood pulps. Also, conventional sulfate pulps containing up to 4 % of lignin, may be analyzed using this method.

4.6 Determination of average degree of pulp polymerization

Degree of polymerization is the number of monomer units in polymer macromolecule.

All methods for determination of polymerization degree may be divided into chemical and physicochemical. The simplest device for determination is viscometer. The method is used both for quality characteristics of technical pulp (determination of dynamic viscosity of cellulose solutions in certain reducers), and for determination of average degree of pulp polymerization. Average degree of polymerization should be determined, for pulp–like other polymers is polydisperse, i.e. it consists of molecules of different length. Therefore, average degree of polymerization is a mean value. Alkaline copper reagent is used as solvent. Pulp in alkaline copper solution is very sensitive to air oxidation, and the determined values of viscosity and average degree of polymerization are underestimated. To prevent pulp destruction, air exposure of pulp solution should be reduced maximally, and reducers should be added to the solution.

5 RESULTS

Tests were made in TAMK paper laboratory. Results and conclusions are presented bellow.

5.1 Dry matter content

Detailed results are presented in the table 3:

TABLE 3. Dry matter content of Pure samples.

Before drying, g			After, total, g	Result, %
Container + lid	Sample	Total		
60,387	10,009	70,396	69,896	95
53,333	10,001	63,334	62,853	95,2
56,234	9,999	66,233	65,745	94,2
60,089	9,996	70,085	69,642	95,6
56,765	10,002	66,786	66,092	93,3

The estimated average result is 94,7% and fits to the value range (90-95%) presented in Pure datasheet, even though different methods were used.

5.2 Swelling value

Table 4 shows mass of the sample before and after swelling in water. Swelling value presented as a ratio in %. Average value is 355%.

TABLE 4.Swelling of Pure samples in water

Before, g	After , g	%
0,1524	0,4916	323
0,1268	0,419	330

0,1386	0,447	323
0,1167	0,497	426
0,134	0,501	374

Table 5 shows mass of the sample before and after swelling in concentrated 17,5% NaOH solution. Swelling value presented as a ratio in %. Average calculated as 819% .

TABLE 5. Swelling of Pure samples in concentrated 17,5% NaOH solution.

Before, g	After, g	%
0,1565	1,23635	790
0,136	1,1016	810
0,147	1,24803	849
0,1325	1,0123	764
0,1366	1,20208	880

Also, an attempt to estimate the swelling value of dissolving pulp sample in 10% sodium hydroxide solution was made but failed, since all samples dissolved.

6 CONCLUSION AND RECOMENDATIONS

The whole research work of the topic allows conclude that dissolving pulp production has a good prospective as population and demand for fibers rises.

During the theoretical study, we have acquired knowledge of raw wood transformation into the dissolving pulp. Besides general notion of the topic, pulp derivatives and methods for synthesis of cellulose graft polymers were discovered. The theoretical chapter is significant and it includes processes of wood pulping, comparison between two cooking methods: sulfite and sulfate with pre-hydrolysis . In the sulfate cellulose remains a large number of pentosans that are difficult to be hydrolyzed. So, the content of a-cellulose is not sufficient for cellulose defined to chemical fibers production. This reason for pre-hydrolisis step is very significant during the production process. Analyzing the economical situation it could be summarized so that apparent consumption fell by 2,5% as high-cost paper machines were closed permanently and pulp capacity was converted to value-added grades of dissolving pulp in particular , because it generates lower outputs due to its highly refined nature.

Methods used to study the properties of pulp were researched, studied and mastered. Obtained experimental data shows that all samples provided by Stora Enso had high levels of dry matter and swelling value. Useful practical skills during the independent work were obtained.

Recommendations for the future production were inspired during the research work about world market situation. Global demand for the dissolving pulp continues to grow, so the development of new end uses is needed. Future study abut undesirable properties of pulp fibers such as flammability, defective elasticity and easy destruction over time could be researched to figure out new areas for future development.

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APPENDICES

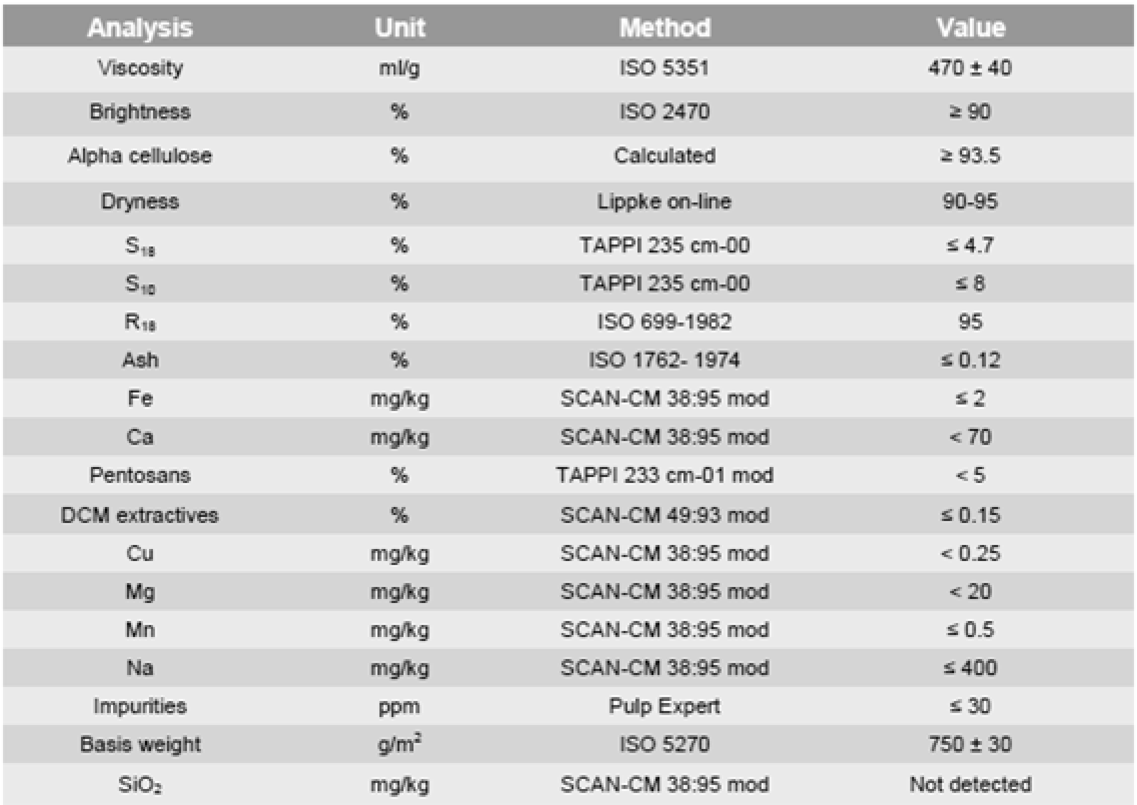
Appendix 1. Basic pulp properties

TABLE 5.Description of the basic pulp properties

Properties	Description
Dry pulp content	The term used to describe solid content of pulp during pulp processing is consistency. Its value might be roughly divided into low (less than 5%), medium (5 - 15%), high (over 15%).
Fiber length	Pulp strength depends on the fiber length and defines its final use. A blend of long and short fiber pulp is efficient since it helps to optimize on fiber cost, strength and formation of paper.
Brightness	It is significant since it defines paper brightness that would be made out of the pulp.
Hemicellulose content	It indicates the chemical differences originating with the tree. It is affected by the pulping process used.
Kappa number	Describes the amount of lignin remained in a pulp.
Viscosity	It indicates the relative degradation of cellulose fiber during pulping /bleaching process.
Coarseness	A measure of the average weight of fiber per unit length, often reported in units of mg/m.
Dirt of pulp	Mostly refers to the recycled pulp and defines the suitability to make fine paper.
Conductivity	Determined by the presence of metal ion (mostly iron ion).
Tensile strength	A maximum strength of randomly oriented

	pulp fiber when formed in a sheet.

Appendix 2. Pure by Stora Enso data sheet

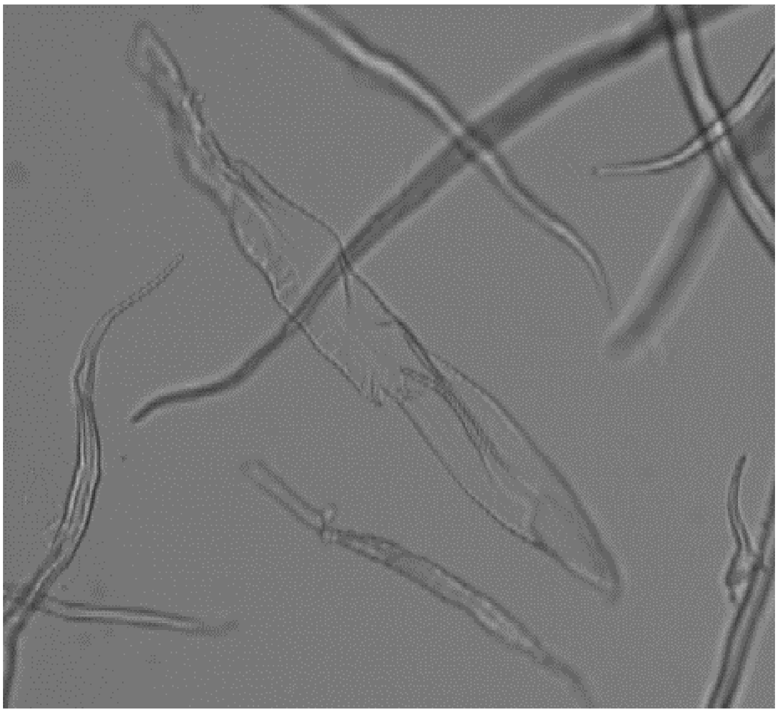


Analysis	Unit	Method	Value
Viscosity	ml/g	ISO 5351	470 ± 40
Brightness	%	ISO 2470	≥ 90
Alpha cellulose	%	Calculated	≥ 93.5
Dryness	%	Lippke on-line	90-95
S_{18}	%	TAPPI 235 cm-00	≤ 4.7
S_{10}	%	TAPPI 235 cm-00	≤ 8
R_{18}	%	ISO 699-1982	95
Ash	%	ISO 1762- 1974	≤ 0.12
Fe	mg/kg	SCAN-CM 38:95 mod	≤ 2
Ca	mg/kg	SCAN-CM 38:95 mod	< 70
Pentosans	%	TAPPI 233 cm-01 mod	< 5
DCM extractives	%	SCAN-CM 49:93 mod	≤ 0.15
Cu	mg/kg	SCAN-CM 38:95 mod	< 0.25
Mg	mg/kg	SCAN-CM 38:95 mod	< 20
Mn	mg/kg	SCAN-CM 38:95 mod	≤ 0.5
Na	mg/kg	SCAN-CM 38:95 mod	≤ 400
Impurities	ppm	Pulp Expert	≤ 30
Basis weight	g/m^2	ISO 5270	750 ± 30
SiO_2	mg/kg	SCAN-CM 38:95 mod	Not detected

FIGURE 4. Cellulose characteristics

Appendix 3. Photos from the microscope

PICTURE 4. Birch fibers in the Pure dissolving pulp sample



PICTURE 5. Birch fibers in the Pure dissolving pulp sample