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Chemical Engineering

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ENZYME PRETREATMENT OF HARDWOOD CHIPS IN KRAFT PULPING

Bachelor's Thesis 2013

ABSTRACT

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This bachelor's thesis concerns the application of enzymes pretreatment of hardwood chips in Kraft pulping. The purpose of this work is to understand the basic knowledge about enzymes and Kraft pulp, and meanwhile, to find out their effect on hardwood chips in Kraft pulping. Through comprehensive study, the knowledge was accumulated which brought a clear understanding for the enzymes' structure and properties of pulp, together with their working principles for pulp.

In the experiment part, four different cooking types of Kraft pulp were studied: Pulp with auto-hydrolysis treated (Pulp A), pulp with untreated (Pulp B), pulp with cellulase treated (Pulp C) and pulp with xylanase treated (Pulp D). These pulps were obtained after pulping fresh birch chips in liquid circulated batch digester by Kraft pulping process. Screened pulps were beaten in PFI mill to three different revolutions (0, 3000 and 6000). Then the Kappa number, viscosity and fiber length were measured from pulps; Additionally, tensile strength, tear strength and air permeability were measured from hand sheets.

Beating brought significant changes in the fiber properties. Untreated pulp has the highest kappa number, and pulp with xylanase treated has the lowest kappa number. Viscosity values were decreased as the revolutions increasing. Tensile index was rising after each beating. As an important remark, beating had negative effect on the tear strength. Fiber length decreased because of beating, which directly reduces the web strength of paper made from it. Air permeability decreased to a quite low value after beating, which is a required property for paper making.

Key words: Enzyme, Birch, Kraft Pulp, Structure, Properties, Xylanase, Cellulase, Hand Sheets.

CONTENTS

1 INTRODUCTION

Enzymes have been widely used in recent years. The significant advances of enzymes opened up a new world for the paper and forest industry to reduce energy consumption and produce environment friendly, which is a major area of research and development in the paper and forest industry. [1.]

Enzymes, as industrial biocatalysts, are a class of proteins extracted from animals, plants, and microorganisms. It has a board range of applications in different industries such as food, textiles, pharmaceuticals, detergents, paper and pulp, waste management, etc. Modern enzyme industry is high-tech industry, which is characterized with high catalytic efficiency and specificity. The yeast is a single-celled micro-organism. It usually has several thousands of proteins and has cells tissues. The application area is comprehensive, which refers to environmental technologies, biomedical research, fundamental biological research, health-care industries, food/chemical industries and fermentation industries. [2.]

In the theory part, the basic knowledge for enzyme and birch are introduced, whereas more emphasis is given on Kraft pulping, as our entire experiments are based on Kraft pulping method. It includes different kind of pulps and their processes. The following deals with types and action of enzyme pretreatment of birch in Kraft pulping.

The experiments required for this study were carried out in the facilities of Saimaa University of Applied Sciences in Imatra.

2 ENZYMES

Enzymes are giant macromolecules, biological catalysts and they mostly consisted of protein, which are polymers of amino acids and small amount of RNA. The molecular weight of enzyme is from 10,000 to 2,000,000 Da. All enzymes contain four elements C, H, O, N. In the organisms, synthesis and degradation of protein, fat and carbohydrate, as well as many complex chemical changes in the life activities are closely related with the enzyme. [3.]

Enzymes are biological catalysts and therefore they have some basic properties as catalyst, e.g. they speed up the rate of chemical reactions without losing or changing by the reaction. Compared with non-biological catalysts, biocatalyst can react at normal temperature and pressure, and have the high catalytic efficiency. The temperature has effect on the activity of enzymes. Under lower temperatures, the speed of chemical reactions increases by temperature increasing for the enzymatic reaction. However, when the temperature exceeds a certain value, the enzymes denature and lead to decrease of catalytic activity. The optimum temperature for activity of enzymes is different due to different enzymes and the most enzymes have an optimum temperature around 37℃. When substrate, enzyme concentrations and temperature are constant, the range of pH on the reaction rate that enzyme-catalysed is from 5 to 8. [4.]

According to the structure of enzymes, enzymes can be classified as monomer enzyme, oligomeric enzyme, multienzyme system and multi-enzyme complex. On the other hand, all known enzymes are divided into six categories according to their catalysed reaction type. They are oxidoreductases, transferases, hydrolases, lyases, isomerase and ligases. [5.] [6.] [7.]

2.1 Cellulase

Cellulase is produced using a genetically modified strain of Trichoderma reesei.

2.1.1 Description

The main activity is endo-1.4- β -D-glucanase. It is efficient in the modification of cellulosic material and it is especially suitable for treating paper and wood chips. [8.]

Reaction: Hydrolysis of 1.4-beta-D-glycosidic linkages in cellulose, lichenin and cereal beta-D-glucans.

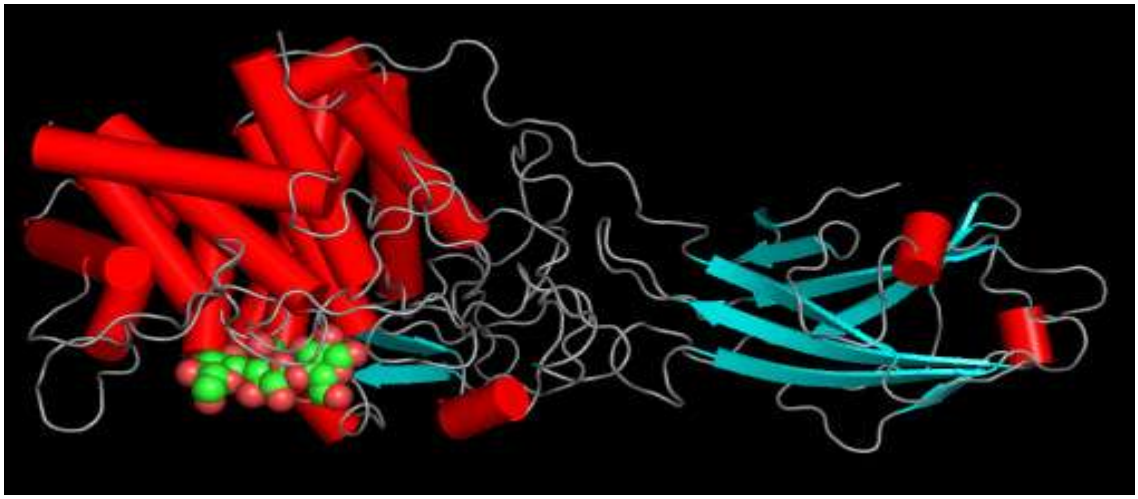


Fig.2.1.1 Model of cellulase enzyme, produced by T. fusca, based on PDB structure 1JS4. [9]

2.1.2 Mechanism

There are three types of reactions catalyzed by cellulases: 1. Breakage of the noncovalent interactions present in the amorphous structure of cellulose (endocellulase) 2. Hydrolysis of chain ends breaks the polymer into smaller sugars (exocellulase) 3. Hydrolysis of disaccharides and tetrasaccharides into glucose (beta-glucosidase).These are shown in figure2.1.2.1. [9.]

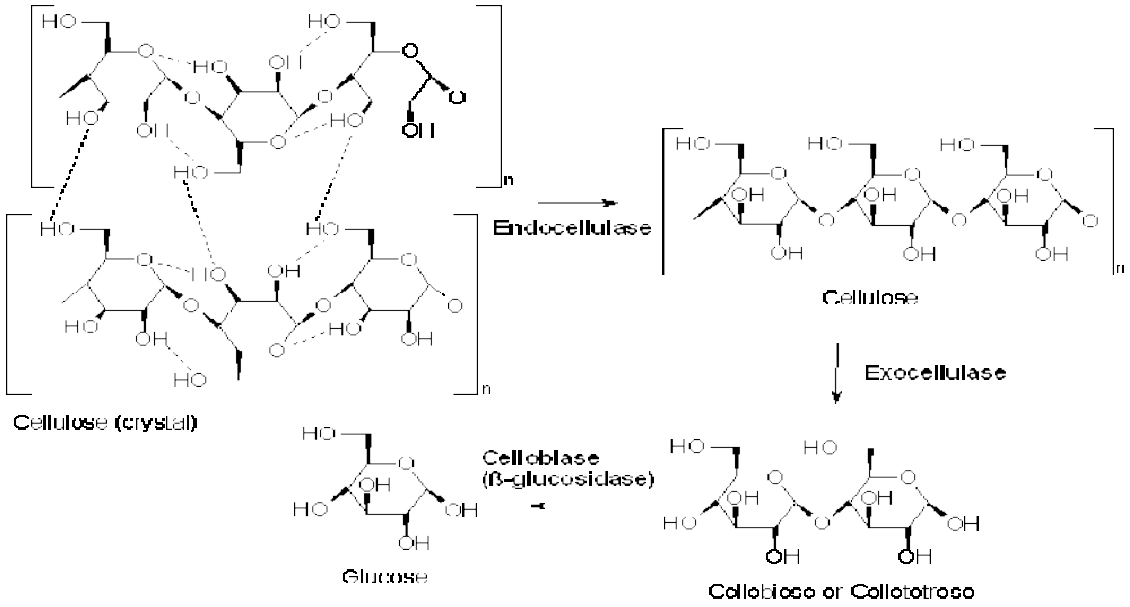
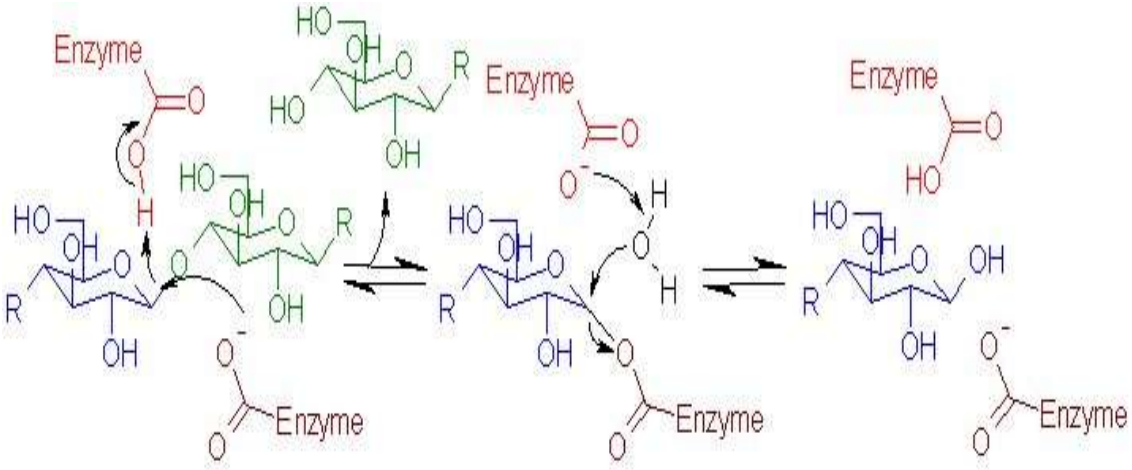


Fig.2.1.2.1 The three types of reactions catalyzed by cellulases



Fig, 2.1.2.2 Mechanistic details of beta-glucosidase activity of cellulose

2.1.3 Properties

Cellulase is a clear, brown aqueous liquid with a density of approximately 1.0-1.1 g/ml [8].

Activity: Cellulase contains a declared minimum activity of 84000CMU/g. The cellulase activity is determined on CMC-substrate at 60℃ and pH 4.8.

2.1.4 Application; Drainage and Refining Enhancement

Cellulase is specially developed for treating paper and wood pulps to enhance drainage and refining. This enzyme can be formulated together with other paper auxiliaries to extend its functionality. [8.]

Cellulase treatment gives several benefits [8] for paper producer:

- Reduced refining energy and/or higher tensile index
- Increased refiner capacity → increased production capacity
- Increased use of recycled pulp in blended furnishes

The preferred process conditions [8] for the product are:

- Enzyme dosage depends on the desired effect, 30 – 100 g/ton of pulp in mill applications (Laboratory tests might require higher dosages, if conditions are not optimal)
- pH of pulp 4.5 – 8.0
- Temperature 30℃ - 60℃
- Treatment time 30 – 60 minutes

2.1.5 Specification

PRODUCT TYPE	CELLULASE
Cellulase activity	≥84,000 CMU/g
Form	Clear brown liquid
Solubility	Miscible with water
pH	4.8 – 5.2
Density	1.0 – 1.1 g/ml
Total viable count	Less than 50,000 CFU/g
Coliforms	Less than 30 CFU/g
Packing	25 kg plastic canisters; 220 kg plastic drums; 1,000 kg plastic container

Table 2.1.5 Specification of cellulase. [8]

Storage: At room temperature the activity of cellulase will not decrease below 90% of the declared activity within 3 months from the date of shipment. Storage at 5 – 10℃ reduce the activity loss and can prolong the maximum storage period. The product should be protected from freezing. [8.]

2.2 Xylanase Enzyme

Xylanase is produced using a strain of none pathogenic fungi. It is used to improve the bleachability of softwood and hardwood Kraft pulps at high temperatures. [8.]

2.2.1 Description

The figure 2.2.1 shows two views of a cartoon of the 3D-structure of the G11 xylanase from Bacillus subtilis (generally known as the xylanase A, or XynA) as determined by x-ray crystallography. The structure is typical of most G11 xylanases and, contains two twisted b-sheets forming a so called "jellyroll" fold which looks remarkably like a right hand, in which the individual b-strands thread back and forth to form the "finger" and "palm" domains (shown as the regions F and P in the diagram on the right). Residues lining the cleft formed between these two domains contribute to the substrate binding and active sites of the protein. An extended loop form the "thumb" domain (shown as T), which can open and close over the active site, so regulating the access of substrate to the catalytic region of the enzyme. [10.]

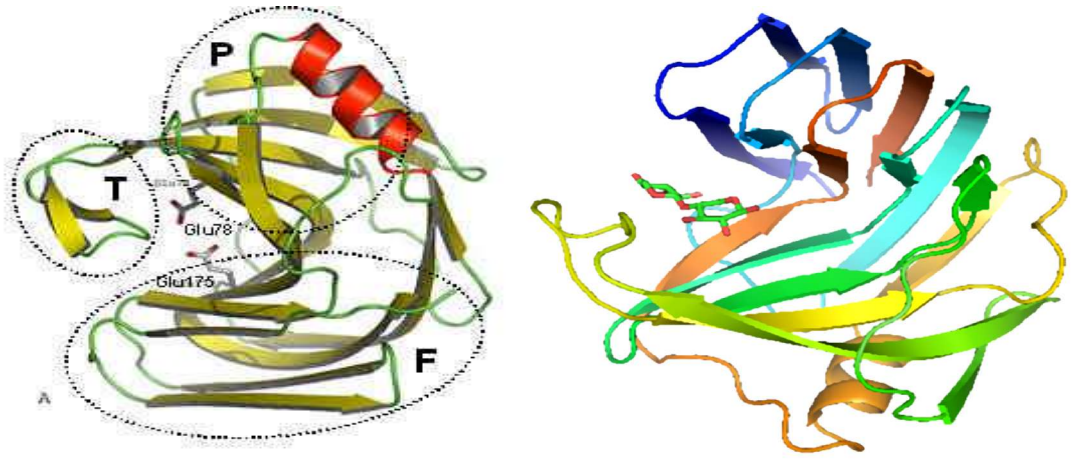


Fig.2.2 1 D-structure of the G11 xylanase

2.2.2 Properties

Xylanase is a clear, light brown aqueous liquid concentrate with a density of approximately 1.00 – 1.05 g/ml [8].

Activity: Xylanase contains a declared minimum activity of 760,000 TXU/g. The Xylanase activity is determined on birch xylan substrate at 70℃ and pH 7.0.

2.2.3 Application

Xylanase is specially developed to improve the bleachability of Kraft pulps. It reduces chemical consumption or achieves higher final brightness in the bleaching by reducing the amount of wood xylan attached on the fiber surface. Xylanase solution is mixed with the unbleached pulp, typically before the brown stock storage tower. It is important to provide efficient mixing of Xylanase into the pulp to achieve an optimal treatment result. [8.]

The preferred process conditions for the product are:

- Enzyme dosage 0.04 – 0.1 l/ton pulp
- pH of pulp 5 – 8
- Temperature 50 – 85 □(122°- 185 □)
- Treatment time 20 – 240 minutes

2.2.4 Specification

PRODUCT TYPE	XYLANASE
Xylanase activity	≥ 760,000 TXU/g
Form	Clear brown liquid
Solubility	Miscible with water
pH	3.4 – 4.5
Density	1.00 – 1.05 g/ml
Dry matter	Not applicable
Total viable count	Less than 50,000 CFU/g
Coliforms	Less than 30 CFU/g
Packing	1000 kg plastic container Bulk

Table 2.2.4 Specification of xylanase. [8.]

Storage: At room temperature the activity of Xylanase will not decrease below 90% of the declared activity within 3 months from the date of shipment. Storage at 5□ - 10□ will reduce activity losses during storage and can prolong the maximum storage period. The product should be protected from freezing. [8]

2.3 Other Enzymes

Some other enzymes like Laccase, Pectinase, Ligninase, Glucose Oxidase and Catalase are also introduced here.

2.3.1 Laccase

Laccases are copper-containing oxidase enzymes that are found in many plants, fungi, and microorganisms. The copper is bound in several sites; Type 1, Type 2, and/or Type 3. The ensemble of types 2 and 3 copper is called a trinuclear cluster. Type 1 copper is available to action of solvents, such as water. It can be displaced by mercury, substituted by cobalt or removed via a

copper complexone. Removal of type 1 copper causes a decrease in laccase activity. Cyanide can remove all copper from the enzyme however re-embedding with type 1 and type 2 copper has been shown to be impossible. Type 3 copper however can be embedded back into the enzyme. Laccases act on phenols and similar molecules, performing a one-electron oxidation, which remains poorly defined. It is proposed that laccases play a role in the formation of lignin by promoting the oxidative coupling of monolignols, a family of naturally occurring phenols. [11.] Laccases can be polymeric, and the enzymatically active form can be a dimer or trimer. Other laccases, such as ones produced by the fungus *leurotus ostreatus*, play a role in the degradation of lignin, and can therefore be included in the broad category of ligninases. [12.]

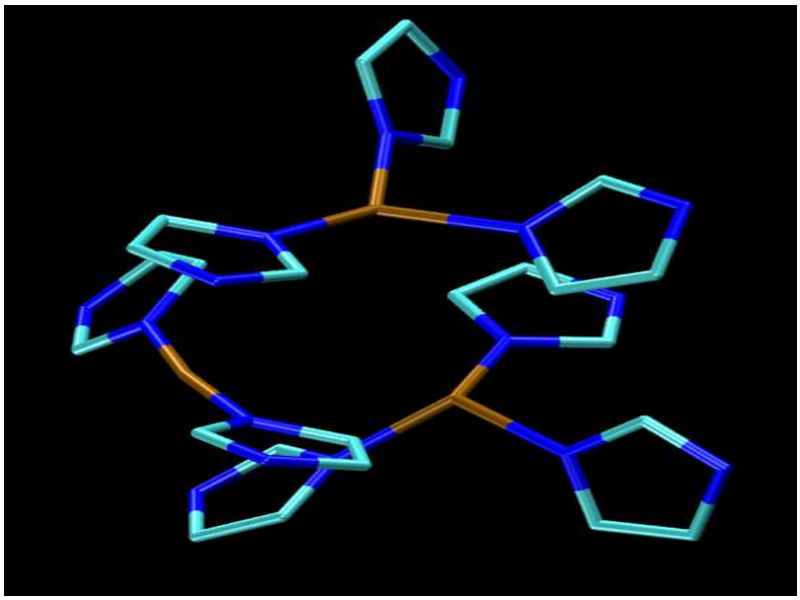


Fig. 2.3.1 The tricopper site found in many laccases, notice that each copper center is bound to the imidazole sidechains of histidine (color code: copper is brown, nitrogen is blue). [13]

Laccases have been examined as the cathode in enzymatic biofuel cells. They can be paired with an electron mediator to facilitate electron transfer to a solid electrode wire. [14] Laccases are some of the few oxidoreductases

commercialized as industrial catalysts. The enzymes can be used for textile dyeing/textile finishing, wine cork making, teeth whitening, and many other industrial, environmental, diagnostic, and synthetic uses. [15.] Laccases can be used in bioremediation. Protein ligand docking can be used to predict the putative pollutants that can be degraded by laccase. [16.]

2.3.2 Pectinase

Pectinase is a general term for enzymes, such as pectolyase, pectozyme and polygalacturonase, commonly referred to in brewing as pectic enzymes. These break down pectin, a polysaccharide substrate that is found in the cell walls of plants. One of the most studied and widely used commercial pectinases is polygalacturonase. It is useful because pectin is the jelly-like matrix which helps cement plant cells together and in which other cell wall components, such as cellulose fibrils, are embedded. Therefore pectinase enzymes are commonly used in processes involving the degradation of plant materials, such as speeding up the extraction of fruit juice from fruit. Pectinases have also been used in wine production since the 1960s. [17.]

Pectinase enzymes are used for extracting juice from purée. This is done when the enzyme pectinase breaks down the substrate pectin and the juice is extracted. The enzyme pectinase lowers the activation energy needed for the juice to be produced and catalyzes the reaction.

2.3.3 Ligninase

Ligninase is the original term encompassing many different types of oxidative, extracellular fungal enzymes which catalyze the breakdown of lignin which is commonly found in the cell walls of plants. Instead of the term ligninase, the term lignin-modifying enzymes (LMEs) should be used, since these enzymes are not hydrolytic but oxidative (electron withdrawing) by their enzymatic

mechanisms. LMEs include peroxidases, such as Lignin peroxidase, Manganese peroxidase and Versatile peroxidase, and many phenol-oxidases of Laccase type. [18]

2.3.4 Glucose Oxidase

The glucose oxidase enzyme (GOX) is an oxido-reductase that catalyses the oxidation of glucose to hydrogen peroxide and D-glucono-δ-lactone. In cells, it aids in breaking the sugar down into its metabolites. [19.]

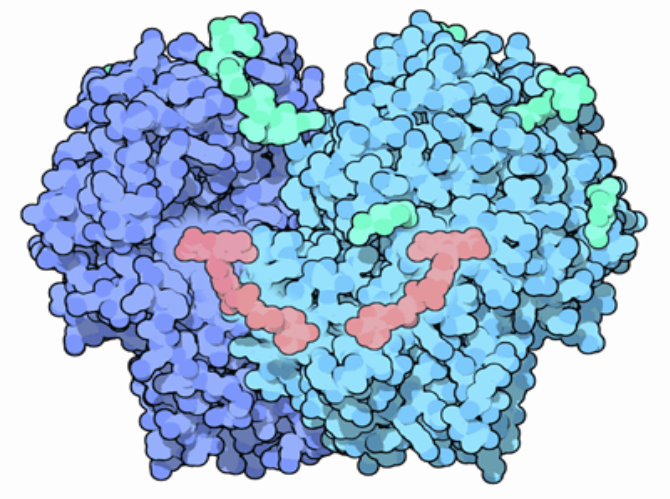


Fig. 2.3.4 Glucose oxidase [19]

Glucose oxidase is widely used, coupled to peroxidase reaction that vizualizes colorimetrically the formed H_2O_2, for the determination of free glucose in blood plasma for diagnostics, using spectrometric assays manually or with automated procedures, and even point of use rapid assays. [20.] [21.] Similar assays allow to monitor glucose levels in fermentation, bioreactors, and to control glucose in vegetal raw material and food products.

2.3.5 Catalase

Catalase is a common enzyme found in nearly all living organisms exposed to

oxygen. It catalyzes the decomposition of hydrogen peroxide to water and oxygen. [22.] It is a very important enzyme in reproductive reactions. Likewise, catalase has one of the highest turnover numbers of all enzymes; one catalase molecule can convert millions of molecules of hydrogen peroxide to water and oxygen each second. [23.]

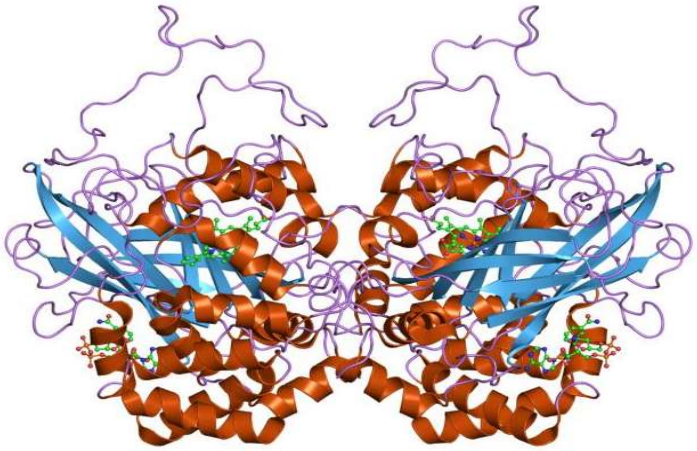


Fig. 2.3.5 Catalase [24]

The reaction of catalase in the decomposition of living tissue:

$$2\ H_2O_2 \rightarrow 2\ H_2O + O_2$$

The presence of catalase in a microbial or tissue sample can be tested by adding a volume of hydrogen peroxide and observing the reaction. The formation of bubbles, oxygen, indicates a positive result. This easy assay, which can be seen with the naked eye, without the aid of instruments, is possible because catalase has a very high specific activity, which produces a detectable response. [24.]

3 HARDWOOD

Hardwood is one of the least utilized forest resources, and for this reason, it has long been considered a primary feed material for biomass processes.

3.1 General

Hardwoods are employed in a large range of applications including: fuel, tools, construction, boat building, furniture making, musical instruments, flooring, cooking, barrels, manufacture of charcoal, etc. Different species of hardwood lend themselves to different end uses or construction processes. This is due to the variety of characteristics apparent in different timbers including density, grain, pore size, growth pattern, wood fiber pattern, flexibility and ability to be steam bent. [25.]

In chemical terms, the difference between hardwood and softwood is reflected in the composition of the constituent lignin. Hardwood lignin is primarily derived from sinapyl alcohol and coniferyl alcohol. Softwood lignin is mainly derived from coniferyl alcohol. [26] The *table* 3.1 indicates, the differences between softwood and hardwood.

Wood	Lignin (%)	Cellulose (%)	Hemicelluloses (%)
Hardwood	18-25	45-55	24-40
Softwood	25-35	45-50	25-35

Table 3.1 Comparing hardwood with softwood in major organic polymers. [27]

Except for the lignocellulose, wood consists of a number of low molecular weight organic compounds, such as terpenes, diterpenes, and fatty acids.

3.2 Birch

Birch is a broadleaved deciduous hardwood tree of the genus Betula [28].

Birch species are generally small to medium-sized trees or shrubs, mostly of temperate climates.

Silver Birch [29]

Wood pulp made from birch gives relatively long and slender fibers for a hardwood. The thin walls cause the fiber to collapse upon drying, giving a paper with low bulk and low opacity. The birch fibers are, however, easily fibrillated and give about 75% of the tensile strength of softwood. [30.] The low opacity makes it suitable for making glassine.

3.3 Chemical Composition of Birch

Cellulose, hemicelluloses and lignin are the main constituents of wood. In different wood species, their relative composition varies greatly. Apart from above mentioned three compounds, wood also contains extractives, such as resin. Extractives are removed, to larger extent, in chemical pulping process. [31.]

Hardwood	Chemical composition
Birch	Cellulose Hemicelluloses Lignin Extractives

Table 3.3 Chemical composition of birch

3.3.1 Cellulose

Cellulose is the main constituent of wood carbohydrates. It is a polysaccharide consisting of glucose units. The cellulose molecule easily forms hydrogen bonds with neighbouring molecules, thus giving xylem cells mechanical support. [32]

Celulose is an organic compound with the formula $(C_6H_{10}O_5)_n$, a polysaccharide consisting of a linear chain of several hundred to over ten thousand β(1→4) linked D-glucose units. [33.] [34.]

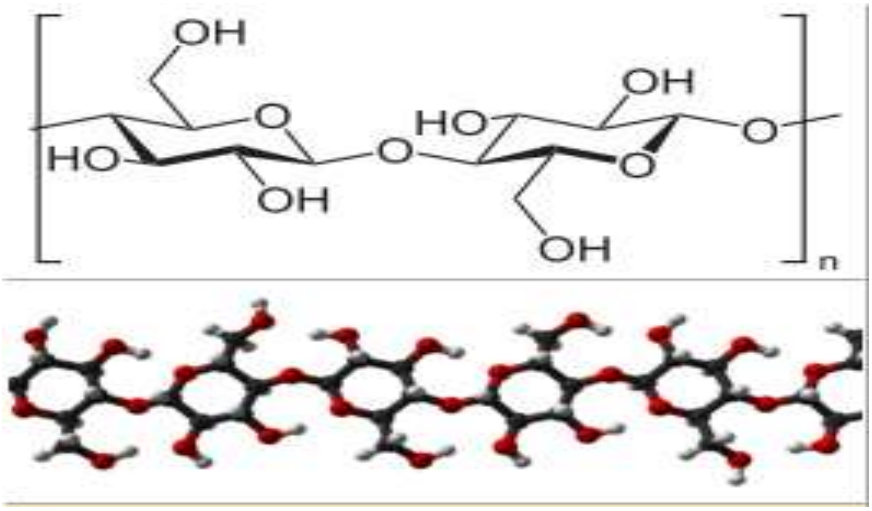


Fig. 3.3.1 the structure of cellulose

Composition[%] / source	Cellulose	Hemicelluloses	Lignin	Extract
Hardwood	43-47	25-35	16-24	2-8
Softwood	40-44	25-29	25-31	1-5
Bagasse	40	30	20	10
Cotton	95	2	1	0.4
Hemp	70	22	6	2
Jute	71	14	13	2
Wheat straw	30	50	15	5

Table 3.3.1 Chemical composition of some typical cellulose-containing materials

As it can be seen from the above, commercial cellulose production concentrates on the harvested source such as wood or on naturally highly pure sources as cotton [11].

Cellulose has no taste, is odorless, is hydrophilic with the contact angle of 20–30, is insoluble in water and most organic solvents, is chiral and is biodegradable. It can be broken down chemically into its glucose units by treating it with concentrated acids at high temperature. [35.]

Many properties of cellulose depend on its chain length or degree of polymerization, the number of glucose units that make up one polymer molecule. Cellulose from wood pulp has typical chain lengths between 300 and 1700 units; cotton and other plant fibers as well as bacterial cellulose have chain lengths ranging from 800 to 10,000 units.[36]

3.3.2 Hemicelluloses

Hemicelluloses include xylan, glucuronoxylan, arabinoxylan, glucomannan, and xyloglucan [37].

While cellulose is crystalline, strong, and resistant to hydrolysis, hemicellulose has a random, amorphous structure with little strength. It is easily hydrolyzed by dilute acid or base as well as myriad hemicellulase enzymes.

As percent content of hemicellulose increases in animal feed, the voluntary feed intake decreases.

Hemicellulose is represented by the difference between neutral detergent fiber (NDF) and acid detergent fiber (ADF) [37].

- Neutral Detergent Fiber (NDF): Neutral Detergent Fiber (NDF) is the most common measure of fiber used for animal feed analysis, but it does not represent a unique class of chemical compounds. NDF measures most of the structural components in plant cells (i.e. lignin, hemicellulose and cellulose), but not pectin. [38][39][40] The process involves a neutral detergent that dissolves plant pectins, proteins, sugars and lipids, thus leaving the fibreous parts behind such as cellulose, lignin and hemicellulose. These parts are not easily digestable, and are often not desired within a feedstuff. [41.]

Acid Detergent Fiber (ADF): The fibrous component represents the least digestible fiber portion of forage or other roughage. This highly indigestible part of forage and includes lignin, cellulose, silica and insoluble forms of nitrogen but not hemicellulose. Forages with higher ADF are lower in digestible energy than forages with lower ADF. That means, as the ADF level increases, digestible energy levels decrease. During laboratory analysis, ADF is the

residue remaining after boiling a forage sample in acid detergent solution. ADF is often used to calculate digestibility, total igestible nutrients (TDN) and/or net energy for lactation (NEl). [42.]

3.3.3 Lignin

Lignin or lignen is a complex chemical compound most commonly derived from wood, and an integral part of the secondary cell walls of plants [43] and some algae [44].

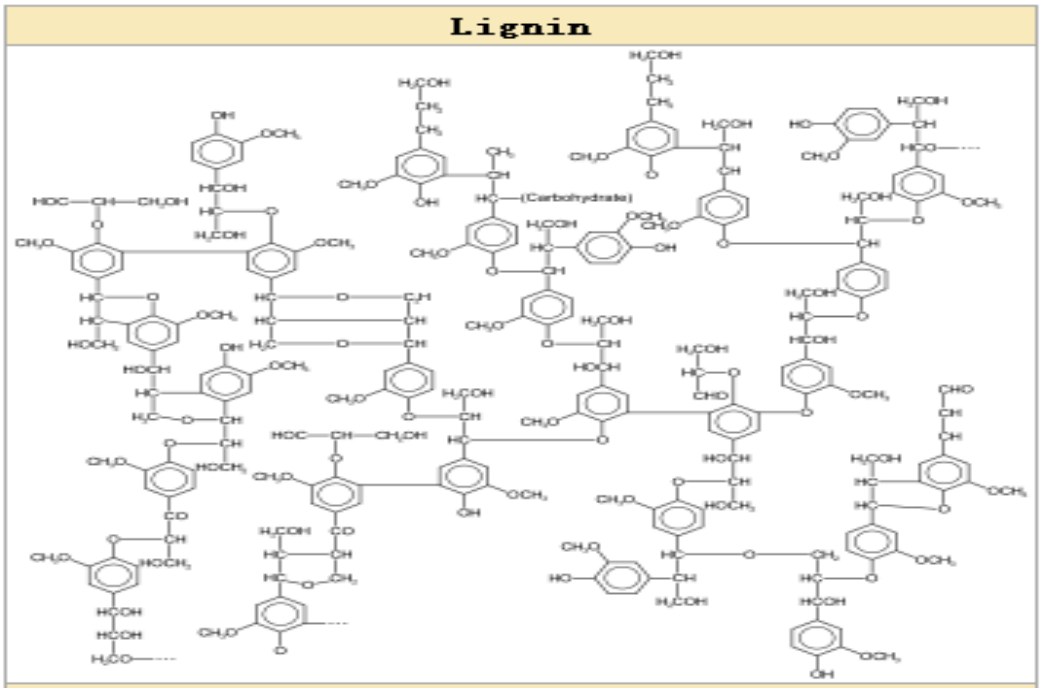


Fig 3.3.3 The structure of lignin. [45]

Lignin fills the spaces in the cell wall between cellulose, hemicellulose, and pectin components, especially in xylem tracheids, vessel elements and sclereid cells. It is covalently linked to hemicellulose and, therefore, crosslinks different plant polysaccharides, conferring mechanical strength to the cell wall and by extension the plant as a whole.[46.] It is particularly abundant in compression wood but scarce in tension wood, which is type of reaction wood [45].

3.3.4 Extractives

In addition to its major structural components, cellulose, hemicelluloses and lignin, wood contains also an exceedingly large number of other low and high molecular weight (organic) compounds, the so-called accessory compounds or extractives. The content of accessory content compounds in the wood of tree from temperate zones amounts approximately 2 to 5 %, but the concentration can be much higher in certain parts of tree, for example, the branches' bases, heartwood and roots. Relatively high amounts (up to 20% of dry matter) of extractives are found in certain tropical and subtropical woods. [47.]

The content and composition of extractives not only vary among the wood species but also with the geographical site and season. This fact is important for the production of pulp as certain extractives in fresh woods may cause yellow discolorations (pitch troubles) or a yellowing of the pulp. In addition, extractives may also influence the strength of refiner pulp, the gluing and finishing of wood as well as the drying behavior. [47]

4 CHEMICAL PULPING

4.1 General

Pulping represents the process by which wood or other lignocellulosic material is reduced to fibrous mass, denoted as pulp. In chemical pulping, lignin is dissolved at elevated temperature (130-170°C), as fibers can be separated without any mechanical defibration only after 90% of the lignin has been removed. Unfortunately, delignification is not a selective process. Parallel to the lignin removal, significant part of hemicelluloses and some cellulose are degraded. The total fibre yield ranges from 45-55% (at a given extend of delignification of about 90%), depending on the wood sources and pulping process applied. In contrast, in mechanical pulping, the lignin bonding the

fibers together is softened by heating the wood material through mechanical stress. Then, the fiber bonds are broken by means of mechanical stress and have an extremely high yield - over 90%, compared to chemical pulping process which is almost double. However, the strength properties of chemical pulps are overwhelmingly superior and can constantly be bleached to an extremely high brightness. In addition, chemical pulp mills that burn wood material dissolved in the process are self-sufficient in regard to electricity and steam power. These are the key reasons for production of pulp predominantly on global scale, by chemical processes. [48.]

Chemically separated fibers are flexible and have a high bonding potential. At the same time they are not much damaged and have kept their length in the separating process. They give strong paper. The main commercial chemical pulping techniques comprise the sulfate or Kraft, the acid sulfite, and the soda process. For example, the chemical pulps accounted for more than 77%of all wood based fibre material worldwide (see Table 4.1). [31.]

Pulp category	Production [M ton]
Chemical	131.2
- Kraft	117.0
- Sulfite	7.0
- Semichemical	7.2
Mechanical	37.8
Nonwood	18.0
Total virgin fibers	187.0
Recovered fibers	147.0
Total pulp	334.0

Table 4.1 Global pulp production by category. [49]

It could be seen from the table above that Kraft pulp production has the highest values among all, no matter if it is compared to mechanical pulp or within chemical pulps.

4.2 Hydrolysis

The aim of the hydrolysis is to cleave the polymers of celluloses and hemicelluloses to monomeric sugars which are able to be fermented to ethanol by microorganisms. The hydrolysis is essential before fermentation to release the fermentable sugars.

In ethanol production, the process of hydrolysis is very sophisticated, depending on several aspects, for example: properties of substrate, acidity, and decomposition rate during hydrolysis process [50]. The hydrolysis can be made either chemically or by a combined chemical and enzymatic treatment. Acids are predominantly applied in chemical hydrolysis and Sulphuric acid is the most frequently used.

4.2.1 Acid Hydrolysis

The solubility of cellulose in acid was detected already in 1815. Concentrated acid hydrolysis technology began in the 1820s, the first concentrated acid hydrolysis process was developed by the Department of Agriculture in the U.S. The required condition, the acid hydrolysis, can be performed by high acid concentration at a low temperature or that of low concentration at a high temperature in contrast. [51.]

The scientific explanation of concentrated acid hydrolysis is described as follows:

The cellulose can be dissolved in the 72% sulfuric acid, 42% hydrochloric acid or 77% and 83% phosphoric acid solution at a lower temperature. [24] Then the cellulose is transformed into monomeric sugars. Within the concentrated

hydrolysis, dimerization reaction will occur in some monosaccharose. The monomeric sugars start to rejoin and form polysaccharide. This reaction is the reverse process of cellulose hydrolysis.

The higher the hydrolyzed monomeric sugars contents and acid concentration, the greater sensitivity is obtained from the dimerization reaction. The monomeric sugars rejoin to generate the glucose disaccharide or three glycans. The hydrolytic solution must be diluted and heated in order to prevent hydrolysis forming polysaccharide. The yield of glucose will increase in the hydrolysis-operative period. [52]

Dilute acid hydrolysis refers to use within 10% acid as a catalyst to hydrolysis of the cellulose and hemicellulose into monomeric sugars. The reaction condition is harder to achieve than in concentrated acid hydrolysis. The required reacting temperature is from 100 ºC to 240 ºC and the pressure is higher than 10 atmospheres in dilute acid hydrolysis process conditions.

The sugar degradation happens at high temperature and highly pressurized environment; the advantages along with some expected problems as disadvantages of the concentrated acid hydrolysis and dilute acid hydrolysis are shown in the table 4.2.1 [53].

Hydrolysis	Advantages	Disadvantages
Concentrated acid process	- Operated at low temperature - High sugar yield	- High acid consumption - High energy consumption for acid recovery - Longer reaction time (e.g. 2-6h) - Equipment corrosion
Dilute acid process	- Low acid consumption - Short residence	- Operated at high temperature - Low sugar yield - Equipment corrosion

Table 4.2.1 Comparison of concentrated acid hydrolysis and dilute acid hydrolysis

The monosaccharose will break down into formic acid further which results in lower sugar yield and inhibition of the fermentation. But this problem can be solved by a two stage process, in which the hemicellulose is mainly hydrolysed in the initial step at temperature of 150 ºC to 190ºC and the remaining cellulose subsequently hydrolysed at more severe conditions at minimally 90 to 230ºC. [54.]

However, the concentrated sulfuric acid hydrolysis is still the most commonly concentrated acid hydrolysis method although obvious disadvantages exist.

4.2.2 Enzymatic Hydrolysis

The degradation of cellulose to monomer sugars in enzymatic hydrolysis is catalyzed by specific cellulolytic enzymes which are called cellulases.

Cellulases are produced from both bacteria and fungi, which can decompose cellulosic material. [55.]

The enzymatic hydrolysis of cellulose is a complex process. There are three different chemical reactions which take place at the same time. [56.]

1. Residual (not yet solubilized) solid-phase cellulose changes chemically and physically.
2. Release of soluble intermediates from the surface of reacting cellulose molecules (primary hydrolysis).
3. Hydrolysis of soluble intermediates to lower molecular weight intermediates and finally to glucose (secondary hydrolysis).

Generally, degradation of cellulose by enzymatic hydrolysis is characterized by a rapid initial phase, and then a slow secondary phase follows. Enzymatic hydrolysis can occur under milder conditions (typically 40-50℃ and pH 4.5-5), which give rise to two advantages of the process; low utility cost since there are few corrosion problems and low toxicity of the hydrolysates. In addition, it is also an environmental friendly process. [57.]

Enzymatic hydrolysis differs from the Acidic hydrolysis. The difference in functional environment is shown in the table 4.2.2.

Acid	Enzyme
Non-specific catalyst therefore will delignify material as well as hydrolyze cellulose	Specific macromolecule catalyst, therefore extensive physical and chemical pretreatment is necessary to make cellulose available for degradation
Decomposition of hemicellulose to inhibitory compounds	Production of clear sugar syrup ready for subsequent anaerobic fermentation
Harsh reaction condition therefore necessary increased costs for heat and corrosion resistant equipment	Run under mild conditions (50□, atmospheric pressure, pH 4.8)
Relatively low yield of glucose	High glucose yield

Table 4.2.2 Comparison of acid and enzymatic hydrolysis

4.3 Kraft Process

The principal method is the Kraft process (strongly alkaline, ~ pH14), which can be used with all kinds of wood. German chemist Carl F. Dahl invented the sulphate process in 1879. The process was called Kraft process, based on German and Swedish word for strength, as it produced stronger pulp at high yield. Kraft pulping has developed as the principle cooking process, accounting 89% of the chemical pulps and for over 62% of all virgin fiber material. In comparison, only 5.3% of the world's chemical pulp production is obtained by the sulfite process. [58.]

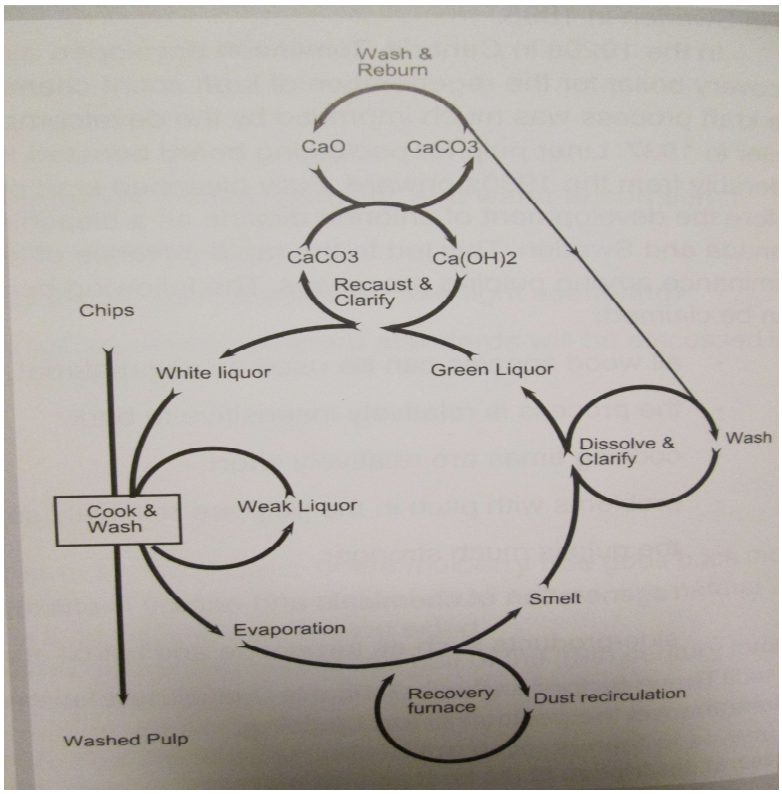


Figure 4.2 Simplified diagram of Kraft pulping's chemical recirculation loop. [48]

The main active chemical agents in the Kraft process are hydroxide and hydrosulfide anions which are present in Kraft cooking liquor, as aqueous solution of caustic sodium hydroxide and sodium sulfide, denoted as white liquor. Other than these, white liquor also contains small amounts of Na2CO3, Na2SO4, Na2S2O2, NaCl and CaCO3 plus other accumulated salts and nonprocess elements. The hydro-sulfide ion plays an important role in Kraft pulping by accelerating delignification and rendering non-selective soda cooking into a selective delignification process. Delignification can be divided into three phases, namely the initial, bulk and residual or final phases. In the bulk delignification phase the main part of the lignin is removed while at the same time only minor carbohydrate losses occur. The point at which cooking is stopped depends on the pulp type being produced. In the production of unbleached pulp the final point is close to the defibration point. However, with continuous delignification, the dissolution of carbohydrates extensively

increases. In order to maintain high yields and to preserve a sufficiently high quality of the pulp, delignification is limited to a certain degree of delignification, targeting kappa number of about 25-30 for softwood Kraft pulps. [48.] [31.]

The advantages of Kraft process are:

- Produces high strength pulp
- Handles wide variety of species
- Tolerates barks in the pulping process
- Cooking time is relatively short compared to other processes
- Regeneration of chemicals and energy is efficient
- Side-products such as turpentine and tall-oil are valuable

These factors, substantial technical development overtime and economical feasibility have further strengthened the position of Kraft pulping.

The main reaction variables in the alkaline cooking are wood species (i.e., their main chemical components), chips' dimensions, temperature, time, and the concentration of cooking chemicals. Some of the fiber strength differences are inherent in the wood species and their growing conditions, whereas other items are chemical and mechanical in nature. Most Kraft digesters are controlled by pulping to a constant H-factor. H-factor which indicates relative speed of lignin dissolution depends on cooking time and temperature. H-factor's dependency on temperature is very strong due to delignification temperature dependency. Even a difference of a couple of degrees in cooking temperature can make a big difference in pulp quality. H-factor has been defined so that 1 hour in 100 °C is equivalent with H-factor 1. As a rough rule of thumb, one can assume that the rate of reaction in Kraft pulping doubles with every 10°C increase in temperature. This pulping parameter is essentially a measure of thermal energy of the pulping process. A second aspect of this is the temperature profile of the cook. How fast the pulping process is brought to

the target cooking temperature and how long the temperature is held is integrated into H-factor and pulping strategy. In addition to H-factor, the maximum cooking temperature and the alkali level of cooking liquor have a significant influence on fiber strength and the inherent bonding potential of the pulp. Most Kraft pulping operators have a target for the level of residual lignin (Kappa number) in the fibers exiting the digester. The variability in kappa number is a measure of Kraft pulping uniformity. [48] [31] [49]

The strength-bearing components of wood fibers are the cellulose molecules that aggregated into fibrils and fibril-aggregates with crystalline and amorphous regions. During chemical pulping, the fiber strength increases with the celluloses content up to certain level, after which cellulose degradation reactions become too severe, which in turn leads to a decrease in fiber strength.

5 EXPERIMENTAL PART

In this experimental part, I designed the whole laboratory work and made many kinds of tests.

5.1 Experimental Design and Methods Used

Four different birch Kraft pulps were pulped in laboratory scale using a liquid circulation batch process. The initial plan was to achieve four different pulps, one with auto-hydrolysis, the other untreated, another with cellulase and the fourth one with xylanase, they were beaten to three different revolution degrees in PFI mill. Different pulp properties were measured from each beaten pulp. The parameters of the experimental setup are put together in table 5.1.

	0	3000	6000
Pulp A (Auto-hydrolysis Treated)	A 0	A 3000	A 6000
Pulp B (Untreated)	B 0	B 3000	B 6000
Pulp C (Cellulase Treated)	C 0	C 3000	C 6000
Pulp D (Xylanase Treated)	D 0	D 3000	D 6000

Table 5.1 Parameters of the experimental design.

As shown in the above table, four different cookings were planned to achieve the target. The required pulps were obtained at the same parameters which affect the cooking process, such as H- factor, amount of active alkali [gNaOH/l], temperature profile of cooking and duration of cooking.

5.2 Raw Material

Fresh birch chips were fetched from the Stora Enso, Kaukopää mill, Imatra for all required cookings. I cut the chips into small pieces using a laboratory knife. The moisture content of the chips used in cooking was different in four different cooks. To preserve the moisture content of chips, they were kept in the refrigerator at temperature 5 ºC. An even distribution of chip size improves the quality of the pulp and also improves defibration speed and production, which was the reason why only the chips within 19 mm – 25 mm length were used in the pulping process. The white liquor used in the cooks was also brought from Stora Enso, Kaukopää mill, Imatra.

5.3 Cooking Method and Washing

Cooking was done in a liquid circulated laboratory batch digester of tank size 0.010 m3 = 10 liters). Liquid was circulated between heat exchanger and digester tank continuously increasing the temperature of liquid, as it was heated by heat exchanger which was operated by electricity. The system can reach maximum temperature up to 170 °C and stand up to 9 bars pressure

during operation. For each cooking ~500 g of oven-dry chips were used. The cooking was done in alkali conditions as white liquor was used in cooking process. The amount of white liquor required was calculated, the value of which is 1.83 liter. The effective alkali was 109.5 [gNaOH /l] of white liquor used for the cooking process.

First of all, the chips were fed into the digester tank, and then a measured volume of white liquor (1.83 l) was poured. Required amount of water (1.17 l) was added to maintain wood to liquid ratio, which was 1/4. According to the H-factor calculation, H-factor in heat-up process was 177, and H-factor in cooking was 980, so the total H-factor was 1157. In each cooking, 90 minutes were needed from the heat-up time to top temperature, and 64 minutes were used to raise the temperature of cooking liquor from 100°C to 170°C. The idea was to increase the heat quite slowly (~1°C /min) providing enough time for impregnation, so that the chips get homogeneously cooked. After each cook, ~100 ml of black liquor was collected to analyse residual alkali content. The black liquor inside the tank was let to cool down by switching off the heater and opening the cold water supply to heat exchanger.

Fig 5.3.1 Revolving digester

Fig 5.3.2 Forced circulating digesters

All the pulps were washed three times, temperature reached 100ºC, and 10 minutes per time. The first time Sodium hydroxide and water were used, and the last two times the water was used only. Use of warm water while washing was necessary, so that the pulp quality remained as stable as possible. After washing for 10 minutes inside the tank, cooked chips were taken out and were further washed.

5.4 Disintegration and Screening

As the cooked pulp was like fiber bundles loosely packed, it was necessary to separate them with mechanical treatment. The pulp was refined in a refiner.

Refined pulp was screened in Somerville screen with the slots of diameter 0.30 mm. The accept and reject pulps from the screening were collected separately into two different cotton bags. The bags were centrifuged to remove as much water as possible, so the degradation of fibers during long storage time will slow down. Later the accept pulp was transferred to an air tight container and was kept inside the refrigerator at 5 ºC. Generally, accept pulps were stored for

maximum of 2 weeks while they were being used in the experiment. The moisture content and weight of shives (reject) were measured and then shives were thrown away.

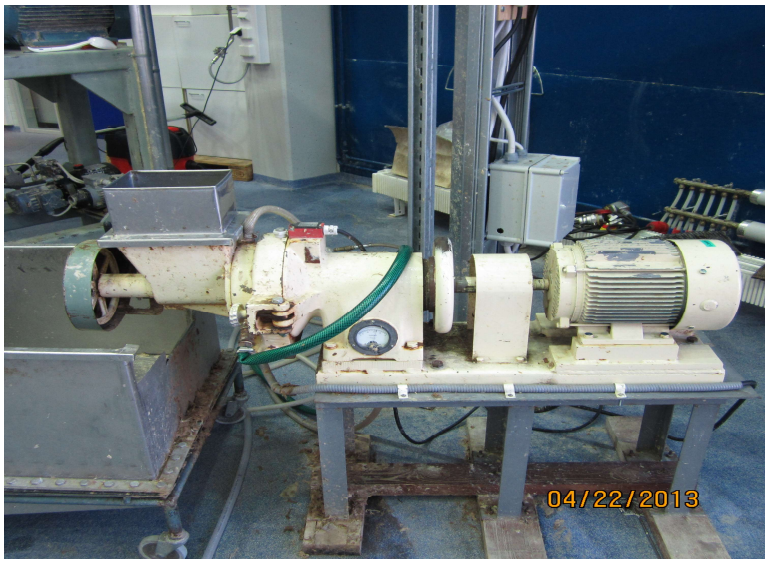


Fig 5.4.1 Refiner

Fig 5.4.2 Screen

5.5 Beating

The accept pulp received after screening was beaten in PFI mill. A measured amount of pulp of specified stock concentration was beaten between a roll with

bar and a smooth beater housing, both rotating in the same direction, but at different peripheral speeds. The main part of the beating energy transfers to the pulp via bar surface not via the edges. In PFI, the beating consistency was high, 10% compared with a normal low consistency beating of about 2%-5% in paper mills.

For beating, 30±0.5 g of oven-dry pulp at 10% consistency was taken. Sample pulps were beaten to 0, 3,000 and 6,000 revolutions. After beating there were 3 different types of beaten pulps from each cooking. The work was done following the standard procedure stated by ISO 5264/2-1979(E).

All the further experiments were continued with these four pulp categories.

Fig 5.5 PFI mill

5.6 Pulp Properties Tests

The kappa number, viscosity and fiber length were measured from each pulp category. The standard procedures followed for tests are listed in appendix 1. The experimental values are listed in appendix 2.

(1) Kappa number

The kappa number is an indication of the lignin content (hardness) or bleachability of pulp. For the analysis, 2.5 g of oven-dry pulp was taken as sample. Two trials were made for each pulp category and kappa number was calculated. An average was taken from calculated trials. Kappa number was measured following the standard procedure stated in ISO 302-1981(E) in Appendix 1. The values of kappa number are given in appendix 2.

(2) Viscosity

The viscosity of a fluid is a measure of its resistance to gradual deformation by shear stressor tensile stress. It was measured following the standard procedure stated in ISO 5351/1-1981(E) in Appendix 1. The values of viscosity are given in appendix 2.

(3) Fiber length

Fiber length was measured using “Kajaani FS 300 Analyzer” to measure the effect of increasing amount of beating on the single fiber. From each pulp category, 2 measurements were taken with same conditions and sample amount and an average of them was taken into account. Fiber length was measured following the standard procedure stated in TAPPI single fiber mode in Appendix 1.The values of fiber length are given in appendix 2. The detailed information of fiber length is given in appendix 3.

5.7 Hand Sheets Preparation

Laboratory hand sheets were prepared using “Rapid-Köthen” sheet former. Hand sheets of basis weight 60g/m2 were made, and the diameter is 0.2m, So the area of one sheet is 0.0314m2, after calculation, we know the weight of each sheet is1.884g, because the pulp consistency is 10%, so weight of the wet pulp what we need is 18.84g for each sheet. Eight sheets from each category were taken, which were within ±3% range of 60g/m2. So we need 150.72g of wet pulp for one category, then mix with 2 L of water, and dilute to 4

L, mixed well. We take a 500 ml sample for each sheet. There were total 96 accepted sheets (8 sheets x 12 categories). These sheets were later used to test different paper properties. The standard procedure followed for hand sheet preparation was ISO 5269-1:1998(E) in appendix 1.

5.8 Hand Sheets Tests

Optical properties and strength properties were measured from the sheets. The following strength properties were measured from sheets.

(1) Tensile strength

Tensile strength is a very important property to describe the general strength of paper. The tensile index value relates strength to the amount of material being loaded. Tensile index therefore has primary use to describe the strength of pulps. Tensile strength was measured using “Testometric Micro 350”. A sample of 15 mm width and 14.1 cm length was used for the tests. Tensile strength was measured following the standard procedure stated in ISO 1924-2(E) in Appendix 1.The values of tensile strength are given in appendix 2.

(2) Tear strength

The tear strength measures the ability of the sheet to resist the propagation of a tear. The tear strength is truly a measure of the amount of energy required to fracture a sample. A rule of thumb is that as tear strength decreases the tensile strength increases. In the experiment, tearing strength was measured using “DIGI-TEAR”, a device produced by Messmer muchel. A sample of 62 mm length and 50 mm width was used for the measurement. Tear strength was measured following the standard procedure stated in ISO 1974(E) in Appendix 1. The values of tear strength are given in appendix 2.

(3) Air permeability

If the air-permeability of the paper is too high, it means that paper is porous. As an effect of beating, paper produced will be less porous and properties such as density, strength, or smoothness will increase to certain extent. Air permeability was measured using the “MBT- Permeance Tester”, a device produced by Messmer instrument limited. Measurements were done using pressure 1.46 Kpa and values are expressed in terms of Bendtsen ml/min. Air permeability was measured following the standard procedure stated in ISO 5636-5(E) in Appendix 1. The values of air permeability are given in appendix 2.

6 RESULTS AND DISCUSSION

Results received from the experiments are illustrated in charts. Explanation below each chart explains the change occurred after each beating. Even though only the key points are explained, a lot more can be analyzed from the chart and in addition to that detail values can be found in appendix 2.

6.1 Kappa Number

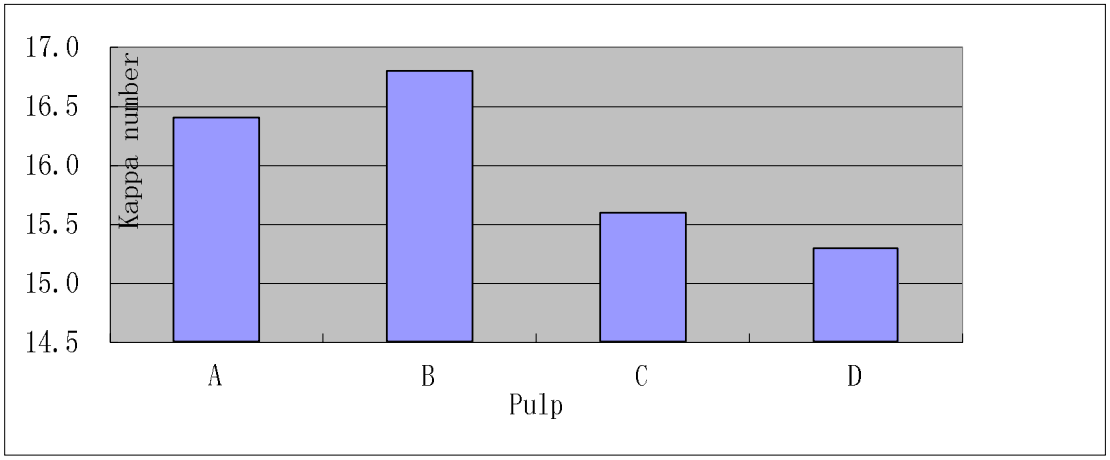


Fig. 6.1 Kappa number

As Fig. 6.1 shows, pulp B (untreated pulp) has the highest kappa number, then

pulp A (auto-hydrolysis), then pulp C (by cellulase) pulp D (by xylanase) has the lowest kappa number, because hemicelluloses and lignin together with lcc, when the hemicelluloses are treated by xylanase, then lignin is also correspondingly reduced.

6.2 Viscosity

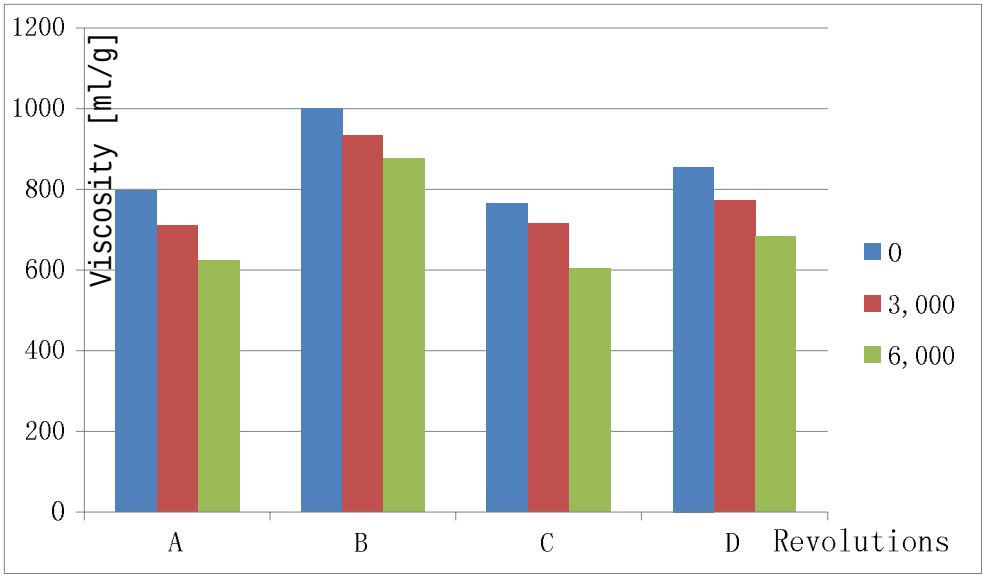


Fig. 6.2 Viscosity

This bar chart shows the viscosity values with four different pulps in three different revolutions. We can see clearly that when the revolutions increase, viscosity of every group pulp decreases, and pulp B (untreated) has the highest viscosity value in every kind of revolution.

6.3 Fiber Length

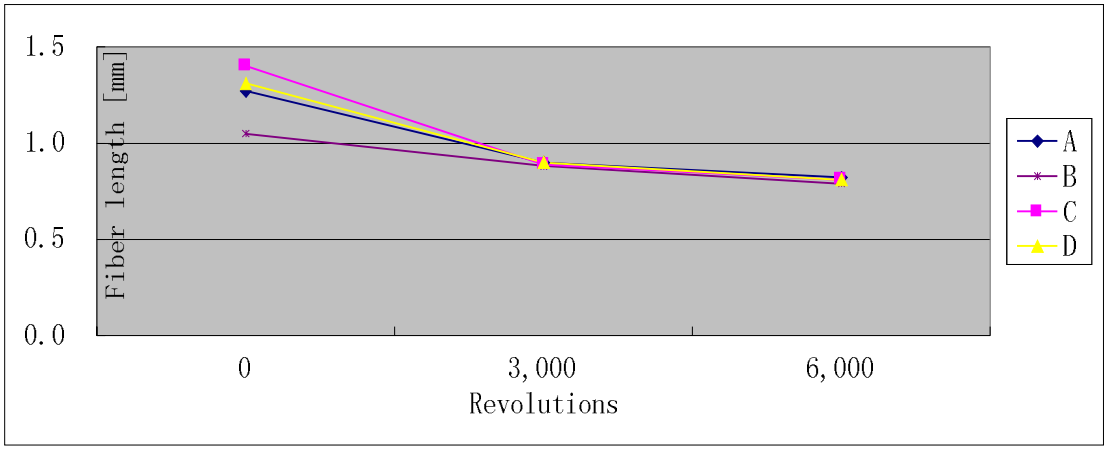


Fig. 6.3 Length-weighted fiber length

Fiber length decreased with the increasing number of revolutions which may be the result of fiber breakage while beating. Although the differences were small, it provides the proof of fibre breaking and creation of secondary fines while performing beating in PFI mill. Firstly, the cellulase pretreatment pulp has the longest fiber, but as the revolutions increase, at last they are go to the same level.

6.4 Tensile Strength

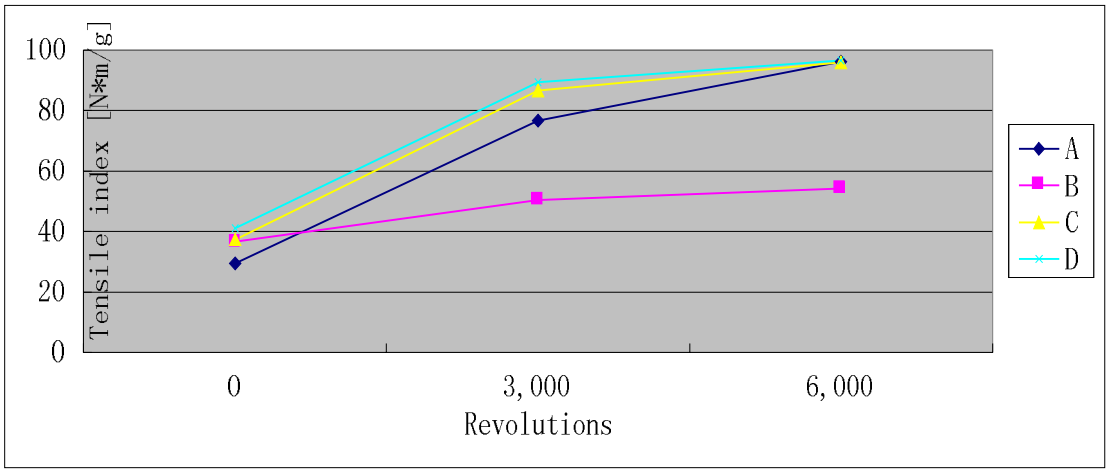


Fig. 6.4 Tensile index

As Fig.6.4 demonstrates, the effect of beating improved paper's tensile

strength properties. The increased amount of beating respectively increased paper's tensile strength. There was a significant increase in paper strength, when comparing beaten fibers to unbeaten fibers.

6.5 Tear Strength

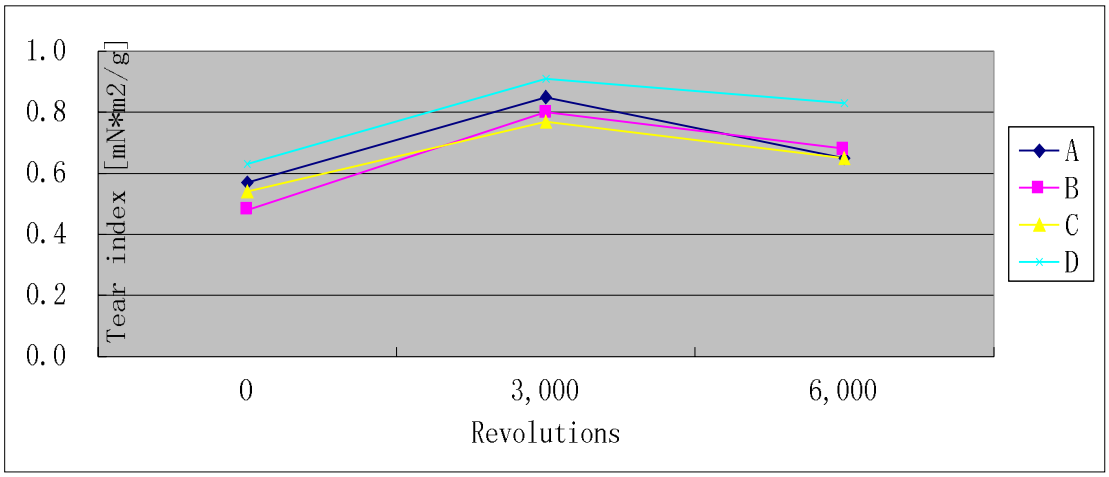


Fig. 6.5 Tear index

The behavior of tear index as we can see from the above chart, increased sharply at the first beating then it gradually decreased. But pulp D decreased more steadily.

6.6 Air Permeability

	0	3,000	6,000
A	4,879 ml/min	30 ml/min	0
B	4,838 ml/min	21 ml/min	0
C	4,912 ml/min	36 ml/min	0
D	4,980 ml/min	51 ml/min	0

Table 6.6 Air permeability

This table shows the air permeability change before and after beatings. As expected, after each beating stage the air permeability decreased to certain level as the paper became less porous. With increasing amount of beating, the

bondability between the fibers enhances and paper density increases which results as dense and smooth paper. High air permeability, more than 2,000 ml/min could be a result of mainly coarse fibers and a relatively low level of primary and secondary fines.

Air permeability was supposed to be higher for high lignin containing pulp. But the high lignin containing pulp had dense formation which directly affected the air permeance. Due to this reason, the air permeance of high kappa pulp (B) was lower than that of low kappa pulp (D).

7 SUMMARY

The aim of this study was to investigate effects of enzyme pretreatment on hardwood chips in Kraft pulping. The four different pulps required for the experiment were cooked in laboratory scale in a batch digester with cooking liquor recirculation. As the result of cooking, pulp with auto-hydrolysis treated (so called Pulp A), pulp with untreated (so called Pulp B), pulp with cellulase treated (so called Pulp C) and pulp with xylanase treated (so called Pulp D) were obtained which were used for the entire experiments. After washing, refining and screening all pulps were beaten with the PFI mill refiner to 0, 3000, 6000 revolutions. Laboratory hand sheets were prepared from all kinds of pulps, then the Kappa number, viscosity and fiber length were measured from pulps; Additionally, tensile strength, tear strength and air permeability were measured from hand sheets.

Some distinct differences in strength properties were observed in the thorough testing of laboratory hand sheets. Beating brought significant changes in the fiber properties. Some of them were desired whereas others were undesired. Untreated pulp has the highest kappa number, and pulp with xylanase treated has the lowest kappa number. Viscosity values were decreased as the

revolutions increasing, and untreated pulp has the highest viscosity value in every kind of revolution too. Tensile indexes were rising after each beating. As an important remark, beating had negative effect on the tearing strength. Fiber length decreased because of beating, which directly reduces the web strength of paper made from it. In addition to that the fiber length with untreated pulp was a little bit small compared to others. This difference in fiber length likely affects the results in paper testing. Air permeability decreased to a quite low value after beating, which is a required property for paper making.

Nowadays, Enzyme has played a vital role in the development of industry. For wood-based industry, application of enzymes decreases the energy consumption and environmental pollution. Wood is mainly composed of three main compounds: cellulose, hemicellulose and lignin. xylanase and cellulase are widely used in the pulp and paper industry for various purposes.

FIGURES

TABLES

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APPENDIX 1

List of standards used at tests:

5.7 Preparation of laboratory sheets for physical testing -- Part 2: Rapid-Köthen method- ISO 5269-1:1998(E)

6.1 Determination of Kappa number of pulp - ISO 302 - 1981(E)

6.2 Determination of limiting viscosity number – ISO 5351/1-1981(E)

6.3 Determination of fiber length - TAPPI single fiber mode

6.4 Determination of tensile strength – ISO 1924-2(E)

6.5 Determination of tear strength - ISO 1974(E)

6.6 Determination of air permeability - ISO 5636-5(E)

APPENDIX 2

List of experimental values:

Pulp	Kappa number
A	16.4
B	16.8
C	15.6
D	15.3

Table 1 Kappa number

	0	3,000	6,000
A	796.0	710.0	624.4
B	999.6	934.2	876.4
C	764.8	716.0	605.2
D	854.8	770.8	683.6

Table 2 Viscosity [ml/g]

	0	3,000	6,000
A	1.27	0.90	0.82
B	1.05	0.88	0.79
C	1.40	0.89	0.81
D	1.31	0.90	0.81

Table 3 Length-weighted fiber length [mm]

	0	3,000	6,000
A	29.39	76.74	96.17
B	36.71	50.49	54.25
C	37.40	86.52	95.96
D	41.08	89.27	96.60

Table 4 Tensile strength index [N*m/g]

	0	3,000	6,000
A	0.57	0.85	0.65
B	0.48	0.80	0.68
C	0.54	0.77	0.65
D	0.63	0.91	0.83

Table 5 Tear strength index [mN*m2/g]

	0	3,000	6,000
A	4,879	30	0
B	4,838	21	0
C	4,912	36	0
D	4,980	51	0

Table 6 Air permeability index [ml/min]

APPENDIX 3

The detailed information of fiber length:

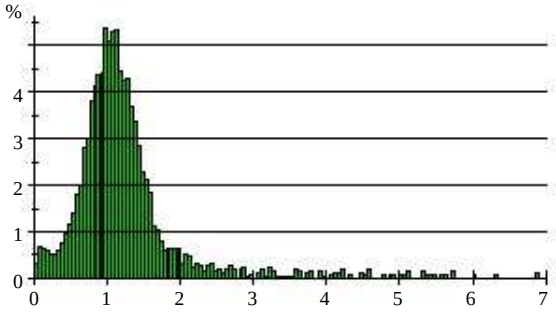
kajaaniFS300

Measured Values

Sample name	Sample date
A -- 0	14-04-2013 09:00

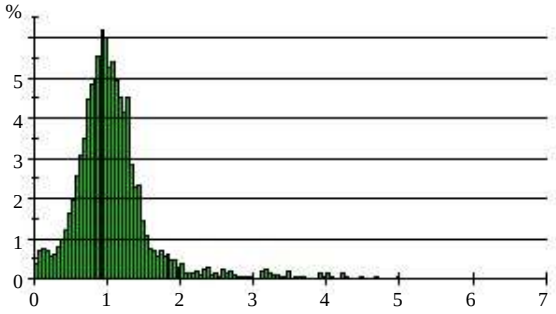
Analysed by	Sample ID
Metso Automation	035 - DD_2013
Analysed date	**Notes**
19/04/2013 16:00	Standard:[TAPPI] Single fiber mode

Fiber length - weighted distribution



Length results:	Cont	Proj	
Range	0.00 - 7.60		mm
L(n)	0.78	0.70	mm
L(l)	1.27	1.07	mm
L(w)	1.90	1.37	mm
Fines(n)	23.73	24.20	%
Fines(l)	2.25	2.54	%
Fibers measured		9040	pcs
Coarseness	0.000	mg/m	
Fibers/mg	0.00	pcs/mg	
Weight	0.000	mg	
Fibers total	14931	pcs	

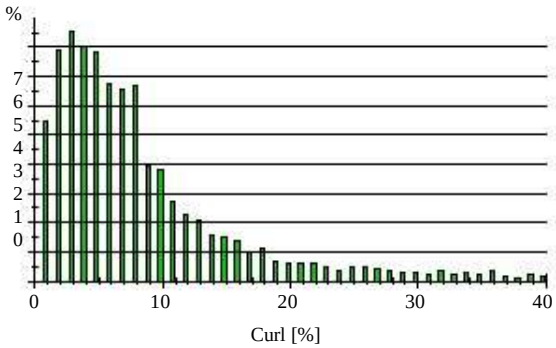
Proj. length - weighted distribution



Fiber curl	10.3	%

Wood species:	<none>
Reference 1:	0.0 %
Reference 2:	0.0 %
Reference 3:	0.0 %

Fiber curl distribution



Custom results:

Y1:	0.00	<none>
Y2:	0.00	<none>
Y3:	0.00	<none>

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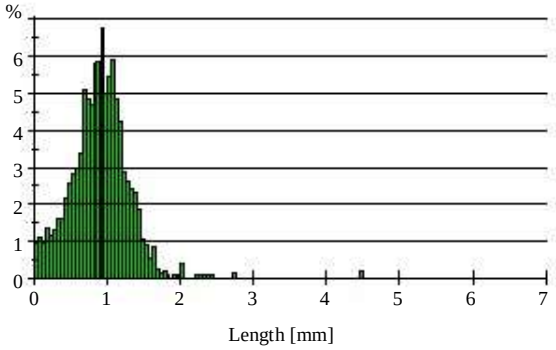
kajaaniFS300

Measured Values

Sample name	Sample date
A -- 3000	14-04-2013 09:00

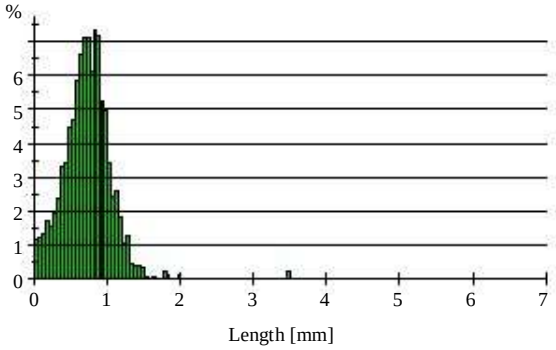
Analysed by	Sample ID
Metso Automation	035 - DD_2013
Analysed date	**Notes**
19/04/2013 16:06	Standard:[TAPPI] Single fiber mode

Fiber length - weighted distribution



Length results:	Cont	Proj	
Range	0.00 - 7.60		mm
L(n)	0.52	0.43	mm
L(l)	0.90	0.72	mm
L(w)	1.09	0.87	mm
Fines(n)	35.47	36.46	%
Fines(l)	4.36	5.45	%
Fibers measured		3955	pcs
Coarseness	0.000	mg/m	
Fibers/mg	0.00	pcs/mg	
Weight	0.000	mg	
Fibers total	7237	pcs	

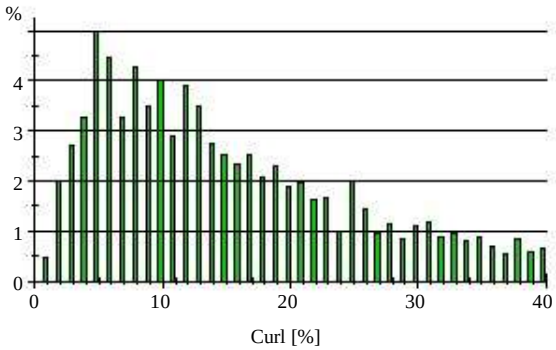
Proj. length - weighted distribution



Fiber curl	21.0	%

Wood species:	<none>	
Reference 1:	0.0	%
Reference 2:	0.0	%
Reference 3:	0.0	%

Fiber curl distribution



Custom results:

Y1:	0.00	<none>
Y2:	0.00	<none>
Y3:	0.00	<none>

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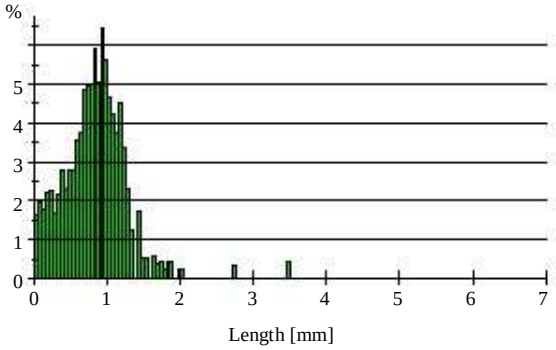
kajaaniFS300

Measured Values

Sample name	Sample date
A -- 6000	14-04-2013 09:00

Analysed by	Sample ID
Metso Automation	035 - DD_2013
Analysed date	**Notes**
19/04/2013 16:12	Standard:[TAPPI] Single fiber mode

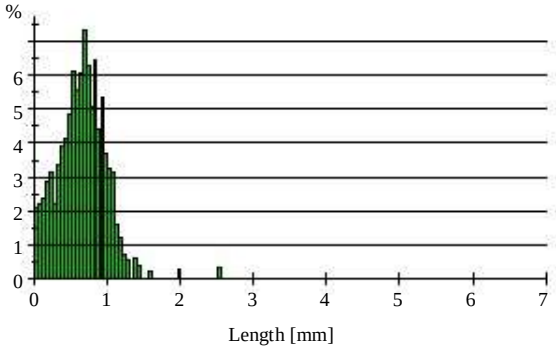
Fiber length - weighted distribution



Length results:	Cont	Proj	
Range	0.00 - 7.60		mm
L(n)	0.40	0.33	mm
L(l)	0.82	0.65	mm
L(w)	1.05	0.82	mm
Fines(n)	47.54	49.03	%
Fines(l)	7.57	9.50	%
Fibers measured		2070	pcs

Coarseness	0.000	mg/m
Fibers/mg	0.00	pcs/mg
Weight	0.000	mg
Fibers total	5367	pcs

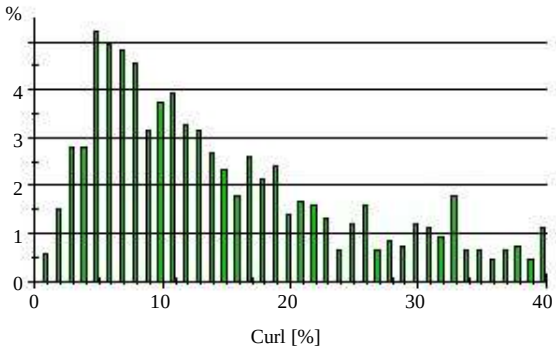
Proj. length - weighted distribution



Fiber curl	21.5	%

Wood species:	<none>	
Reference 1:	0.0	%
Reference 2:	0.0	%
Reference 3:	0.0	%

Fiber curl distribution



Custom results:

Y1:	0.00	<none>
Y2:	0.00	<none>
Y3:	0.00	<none>

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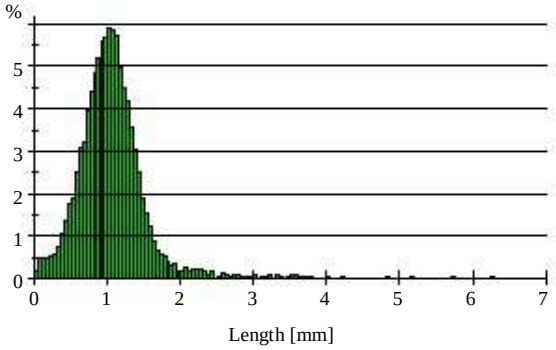
Measured Values

Sample name	Sample date
B - 0	14-04-2013 09:00

Analysed by	Sample ID
Metso Automation	035 - DD_2013
Analysed date	**Notes**
18/04/2013 19:34	Standard:[TAPPI] Single fiber mode

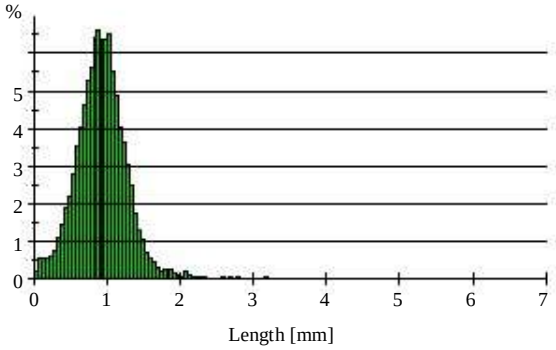
Fiber length - weighted distribution



Length results:	Cont	Proj	
Range	0.00 - 7.60		mm
L(n)	0.77	0.69	mm
L(l)	1.05	0.92	mm
L(w)	1.28	1.07	mm
Fines(n)	15.77	16.17	%
Fines(l)	1.64	1.88	%
Fibers measured		18558	pcs

Coarseness	0.125	mg/m
Fibers/mg	10418.67	pcs/mg
Weight	3.000	mg
Fibers total	31256	pcs

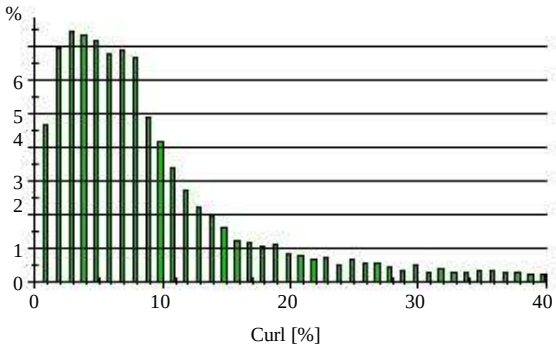
Proj. length - weighted distribution



Fiber curl	10.9	%

Wood species:	<none>
Reference 1:	0.0 %
Reference 2:	0.0 %
Reference 3:	0.0 %

Fiber curl distribution



Custom results:

Y1:	0.00	<none>
Y2:	0.00	<none>
Y3:	0.00	<none>

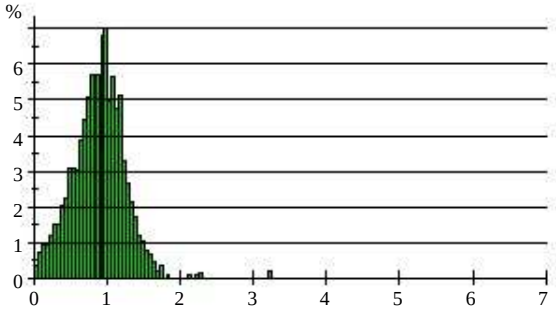
kajaaniFS300

Measured Values

Sample name	Sample date
B -- 3000	14-04-2013 09:00

Analysed by	Sample ID
Metso Automation	035 - DD_2013
Analysed date	**Notes**
19/04/2013 15:20	Standard:[TAPPI] Single fiber mode

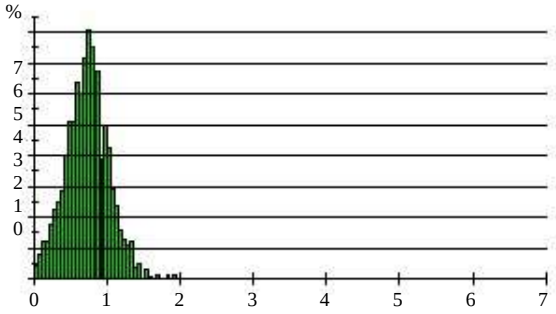
Fiber length - weighted distribution



Length results:	Cont	Proj	
Range	0.00 - 7.60		mm
L(n)	0.61	0.51	mm
L(l)	0.88	0.72	mm
L(w)	1.02	0.84	mm
Fines(n)	22.11	22.98	%
Fines(l)	2.98	3.72	%
Fibers measured		2976	pcs

Coarseness	0.000	mg/m
Fibers/mg	0.00	pcs/mg
Weight	0.000	mg
Fibers total	8122	pcs

Proj. length - weighted distribution

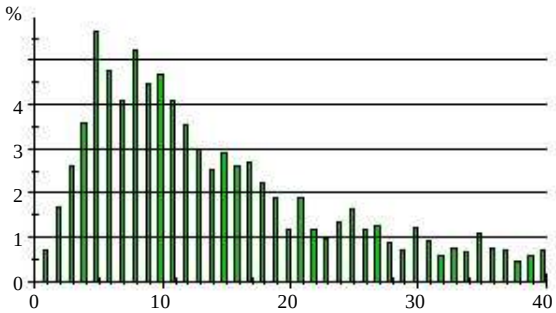


Fiber curl	19.9	%

Wood species:	<none>

Reference 1:	0.0	%
Reference 2:	0.0	%
Reference 3:	0.0	%

Fiber curl distribution



Custom results:

Y1:	0.00	<none>
Y2:	0.00	<none>
Y3:	0.00	<none>

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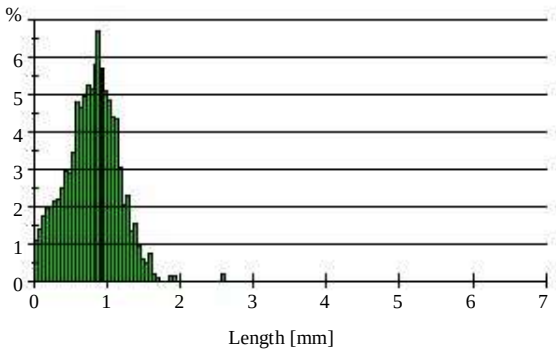
Measured Values

Sample name	Sample date
B -- 6000	14-04-2013 09:00

Analysed by	Sample ID
Metso Automation	035 - DD_2013
Analysed date	**Notes**
19/04/2013 15:47	Standard:[TAPPI] Single fiber mode

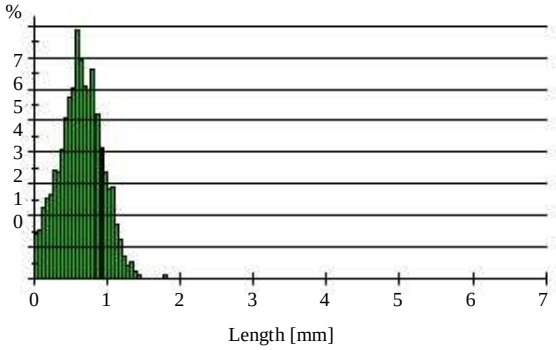
Fiber length - weighted distribution



Length results:	Cont	Proj	
Range	0.00 - 7.60		mm
L(n)	0.45	0.37	mm
L(l)	0.79	0.63	mm
L(w)	0.95	0.77	mm
Fines(n)	39.25	40.66	%
Fines(l)	6.19	7.75	%
Fibers measured		3345	pcs

Coarseness	0.000	mg/m
Fibers/mg	0.00	pcs/mg
Weight	0.000	mg
Fibers total	5797	pcs

Proj. length - weighted distribution

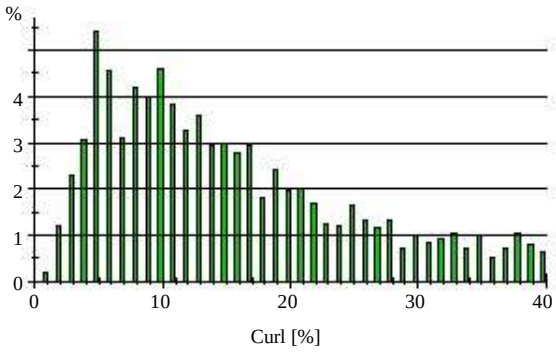


Fiber curl	21.0	%

Wood species:	<none>

Reference 1:	0.0	%
Reference 2:	0.0	%
Reference 3:	0.0	%

Fiber curl distribution



Custom results:

Y1:	0.00	<none>
Y2:	0.00	<none>
Y3:	0.00	<none>

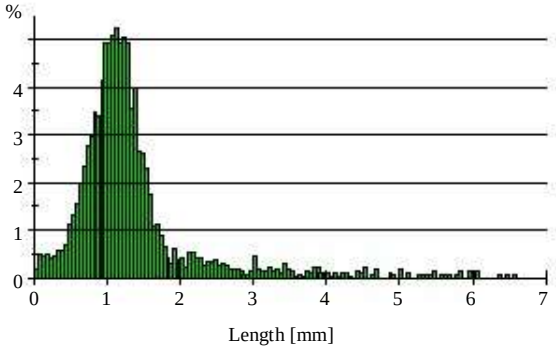
kajaaniFS300

Measured Values

Sample name	Sample date
C -- 0	14-04-2013 09:00

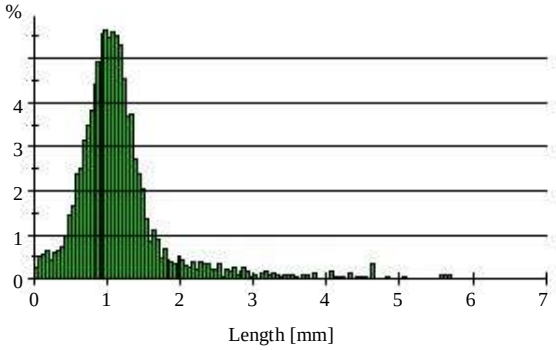
Analysed by	Sample ID
Metso Automation	035 - DD_2013
Analysed date	**Notes**
19/04/2013 16:27	Standard:[TAPPI] Single fiber mode

Fiber length - weighted distribution



Length results:	Cont	Proj	
Range	0.00 - 7.60		mm
L(n)	0.87	0.78	mm
L(l)	1.40	1.16	mm
L(w)	2.16	1.56	mm
Fines(n)	18.75	19.28	%
Fines(l)	1.70	1.95	%
Fibers measured		9068	pcs
Coarseness	0.000	mg/m	
Fibers/mg	0.00	pcs/mg	
Weight	0.000	mg	
Fibers total	11254	pcs	

Proj. length - weighted distribution

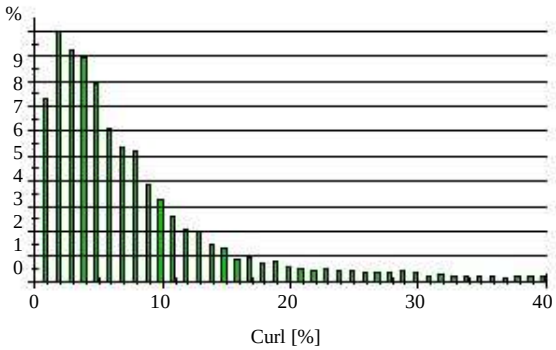


Fiber curl	9.1	%
Wood species:	<none>	
Reference 1:	0.0	%
Reference 2:	0.0	%
Reference 3:	0.0	%

Custom results:

Y1:	0.00	<none>
Y2:	0.00	<none>
Y3:	0.00	<none>

Fiber curl distribution

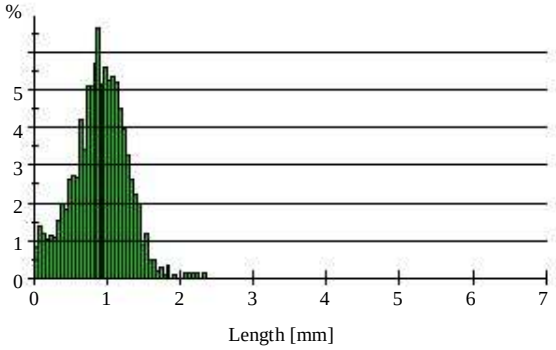


kajaaniFS300

Measured Values

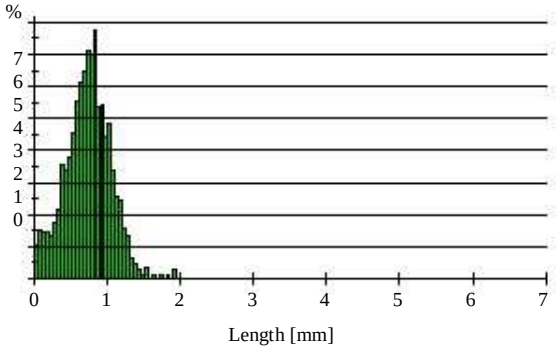
Sample name	Sample date
C-- 3000	14-04-2013 09:00
Analysed by	**Sample ID**
Metso Automation	035 - DD_2013
Analysed date	**Notes**
19/04/2013 16:33	Standard:[TAPPI] Single fiber mode

Fiber length - weighted distribution



Length results:	Cont	Proj	
Range	0.00 - 7.60		mm
L(n)	0.53	0.44	mm
L(l)	0.89	0.73	mm
L(w)	1.04	0.86	mm
Fines(n)	35.62	36.54	%
Fines(l)	4.46	5.49	%
Fibers measured		3161	pcs
Coarseness	0.000	mg/m	
Fibers/mg	0.00	pcs/mg	
Weight	0.000	mg	
Fibers total	5780	pcs	

Proj. length - weighted distribution

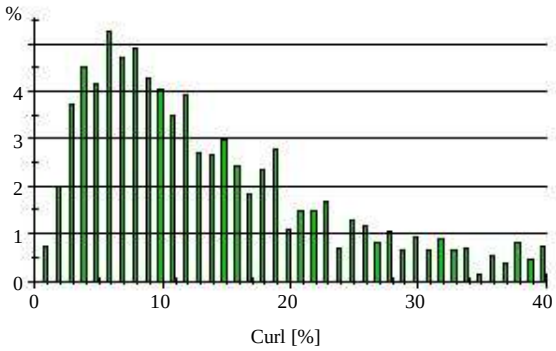


Fiber curl	19.6	%
Wood species:	<none>	
Reference 1:	0.0	%
Reference 2:	0.0	%
Reference 3:	0.0	%

Custom results:

Y1:	0.00	<none>
Y2:	0.00	<none>
Y3:	0.00	<none>

Fiber curl distribution



metso automation

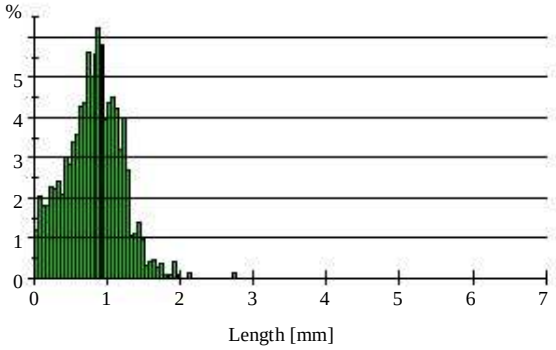
kajaaniFS300

Measured Values

Sample name	Sample date
C -- 6000	14-04-2013 09:00

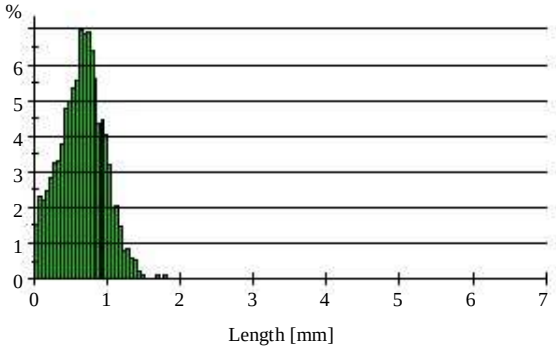
Analysed by	Sample ID
Metso Automation	035 - DD_2013
Analysed date	**Notes**
19/04/2013 16:43	Standard:[TAPPI] Single fiber mode

Fiber length - weighted distribution



Length results:	Cont	Proj	
Range	0.00 - 7.60		mm
L(n)	0.43	0.36	mm
L(l)	0.81	0.65	mm
L(w)	0.99	0.79	mm
Fines(n)	42.91	44.37	%
Fines(l)	6.85	8.56	%
Fibers measured		4302	pcs
Coarseness	0.000	mg/m	
Fibers/mg	0.00	pcs/mg	
Weight	0.000	mg	
Fibers total	9940	pcs	

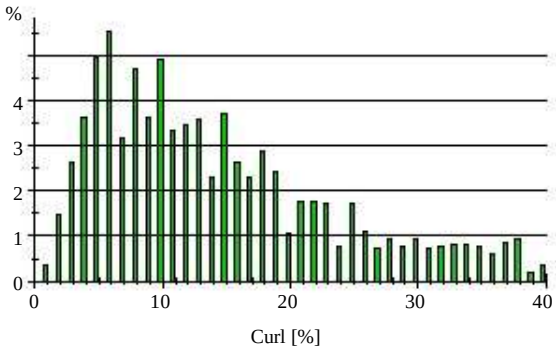
Proj. length - weighted distribution



Fiber curl	19.5	%

Wood species:	<none>	
Reference 1:	0.0	%
Reference 2:	0.0	%
Reference 3:	0.0	%

Fiber curl distribution



Custom results:

Y1:	0.00	<none>
Y2:	0.00	<none>
Y3:	0.00	<none>

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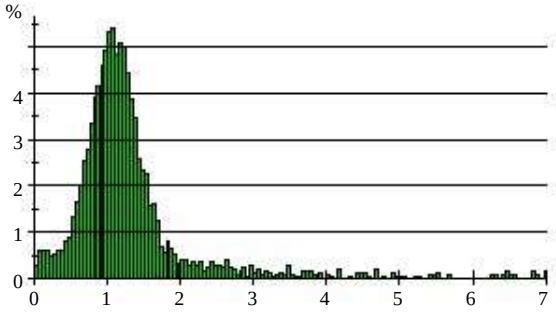
Measured Values

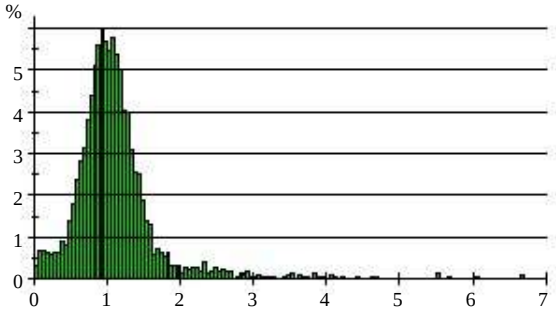
Sample name	Sample date
D -- 0	14-04-2013 09:00
Analysed by	**Sample ID**
Metso Automation	035 - DD_2013
Analysed date	**Notes**
19/04/2013 16:53	Standard:[TAPPI] Single fiber mode

Fiber length - weighted distribution



Length results:	Cont	Proj	
Range	0.00 - 7.60		mm
L(n)	0.81	0.73	mm
L(l)	1.31	1.11	mm
L(w)	1.99	1.47	mm
Fines(n)	22.24	22.56	%
Fines(l)	2.08	2.31	%
Fibers measured		11360	pcs
Coarseness	0.000	mg/m	
Fibers/mg	0.00	pcs/mg	
Weight	0.000	mg	
Fibers total	14813	pcs	

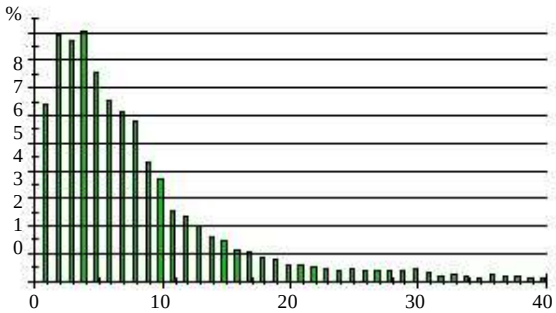
Proj. length - weighted distribution



Fiber curl	9.2	%

Wood species:	<none>
Reference 1:	0.0 %
Reference 2:	0.0 %
Reference 3:	0.0 %

Fiber curl distribution



Custom results:

Y1:	0.00	<none>
Y2:	0.00	<none>
Y3:	0.00	<none>

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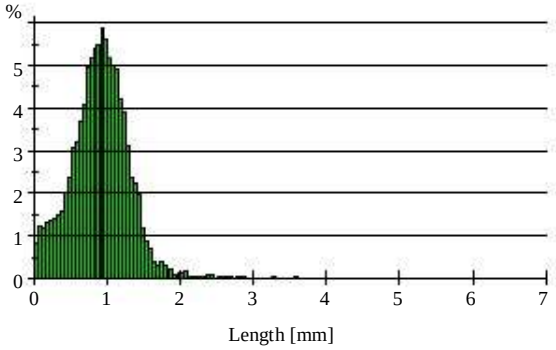
Measured Values

Sample name	Sample date
D -- 3000	14-04-2013 09:00

Analysed by	Sample ID
Metso Automation	035 - DD_2013
Analysed date	**Notes**
19/04/2013 17:04	Standard:[TAPPI] Single fiber mode

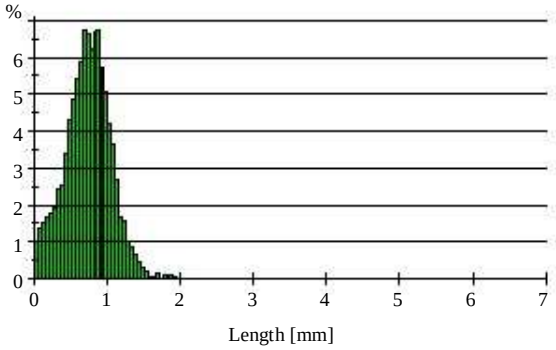
Fiber length - weighted distribution



Length results:	Cont	Proj	
Range	0.00 - 7.60		mm
L(n)	0.53	0.44	mm
L(l)	0.90	0.73	mm
L(w)	1.07	0.86	mm
Fines(n)	35.02	36.09	%
Fines(l)	4.54	5.61	%
Fibers measured		16716	pcs

Coarseness	0.000	mg/m
Fibers/mg	0.00	pcs/mg
Weight	0.000	mg
Fibers total	36927	pcs

Proj. length - weighted distribution

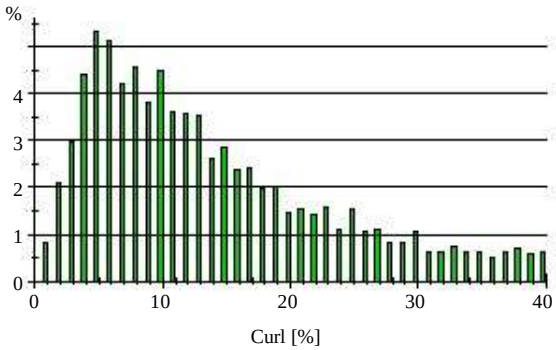


Fiber curl	19.1	%

Wood species:	<none>

Reference 1:	0.0	%
Reference 2:	0.0	%
Reference 3:	0.0	%

Fiber curl distribution



Custom results:

Y1:	0.00	<none>
Y2:	0.00	<none>
Y3:	0.00	<none>

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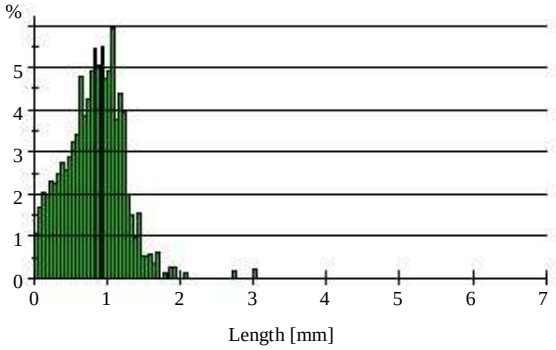
Measured Values

Sample name	Sample date
D -- 6000	14-04-2013 09:00

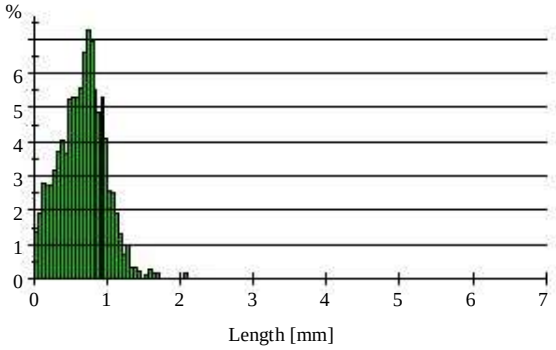
Analysed by	Sample ID
Metso Automation	035 - DD_2013
Analysed date	**Notes**
19/04/2013 17:10	Standard:[TAPPI] Single fiber mode

Fiber length - weighted distribution



Length results:	Cont	Proj	
Range	0.00 - 7.60		mm
L(n)	0.44	0.37	mm
L(l)	0.81	0.65	mm
L(w)	1.01	0.80	mm
Fines(n)	41.25	43.20	%
Fines(l)	6.82	8.79	%
Fibers measured		3178	pcs
Coarseness	0.000	mg/m	
Fibers/mg	0.00	pcs/mg	
Weight	0.000	mg	
Fibers total	5678	pcs	

Proj. length - weighted distribution

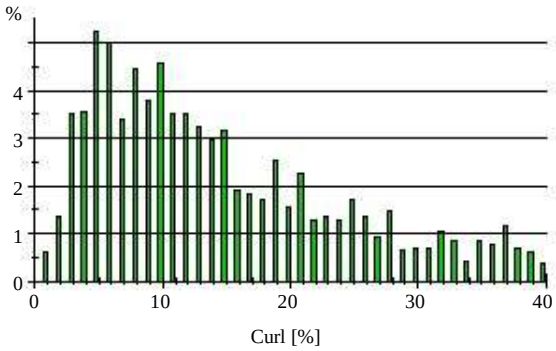


Fiber curl	20.3	%
Wood species:	<none>	
Reference 1:	0.0	%
Reference 2:	0.0	%
Reference 3:	0.0	%

Custom results:

Y1:	0.00	<none>
Y2:	0.00	<none>
Y3:	0.00	<none>

Fiber curl distribution



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