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Enzymatic Approach To Improve Tensile, Freeness And Brightness

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ENZYMATIC APPROACH TO IMPROVE TENSILE, FREENESS AND BRIGHTNESS

by

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Yao Ntifafa
November 4th, 2021

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LIST OF SYMBOLS AND ABBREVIATIONS

AKD	Alkyl Ketene Dimer
BOD	Biological oxygen demand
CaO	Calcium oxide
CBM	Carbohydrate-binding module
CO_2	Carbon dioxide
COD	Chemical oxygen demand
CSF	Canadian Standard Freeness
GPAM	Glyoxalated Polyacrylamide
GWP	Global warming power
H_2S	Hydrogen sulfide
Na_2CO_3	Sodium carbonate
Na_2S	Sodium sulfide
Na_2SO_4	Sodium sulfate
NaOH	Sodium hydroxide
NaSH	Sodium hydrosulfide
NO_x	Nitrogen oxides
PAE	Polyamide epichlorohydrin
PFAS	Per- and poly-fluoroalkyl substances
SBR	Styrene-butadiene rubber
SDS	Safety Data Sheets
SH^-	Hydrogen sulfide ions
SO_x	Sulfur oxides
SR	Schopper Riegler
TAPPI	Technical Association of the Pulp and Paper Industry
VFA	Volatiles Fatty Acids
VOC	Volatile organic compounds

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To my mother Adjo Sedinam Kogble (Eveline),

To Abla Signon,

To Shirley & Will Longstreet

ABSTRACT

Weak tensile strength is usually a source of web breaks on paper machines and converting machines. Web break, in general, is due to poor hydrogen bonding between the fibers. Web break which is ultimately a downtime and a waste can be reduced through enzymatic approach. In order to increase the tensile strength of the paper, it is necessary to determine the amount and the conditions in which the enzymes yield a better sheet strength.

A central composite design approach, using dosage, time, and temperature as factors, was used to study the effects of the enzymes on the sheet strength; the pulp used is 100% recycled bleached kraft. In addition, the effects of the enzymes on the pulp freeness and the brightness of the sheet were also monitored. The results revealed significant improvement of the tensile strength (16.1%) and the freeness (3.9%) with no negative effect on the brightness.

CHAPTER I

INTRODUCTION

A paper machine has two main ends that are the wet end and the dry end. Sheet breaks generally occur in the dry end. And when this happens, the production of the entire machine stops. It takes time and experienced personnel to rethread the machine. The downtime due to sheet breaks can cost up to $ 10,000 per hour [1]. One of the main reasons the web breaks is weak tensile strength. Operators, sometimes, can reduce the speed of the machine or increase the basis weight of the sheet to reduce the frequency of the web breaks. The speed reduction or the increase of the basis weight which can be seen as temporary solutions are themselves classified as wastes.

During the papermaking process, the slurry containing the fibers is dewatered and the wet network of the fibers is pressed and dried. The obtained sheet strength is mainly controlled by the bonds between individual fibers. Possible bonding mechanisms during the process are hydrogen bonds, mechanical interlocking, electrostatic interactions, van der Waals forces, and interdiffusion of cellulose molecules [2,3]. Any way to increase these parameters directly increases the strength of the sheet.

Refining or beating of the pulp is a mechanical treatment to modify the fiber structure. The process not only breaks the intra-fiber bonding and increases the surface area of the fiber but also fibrillates, swells, and makes the fiber more flexible for better hydrogen bonding. The action of the refiner ultimately increases the tensile strength; however, more secondary fines are generated, the drainability is reduced and significant energy is consumed; in addition, many fibers are shortened, curled, and cracked due to the refiner metallic bars [4,5]. It is no doubt that excessive refining, especially for recycled fiber, does not make the fiber sustainable [6,7]. Using an approach that can increase the tensile and at the same time conserve the fibers, so they can be reused or recycled several times, is beneficial for the circular economy.

Enzymes can be used to bring and maintain the sheet tensile within specification ranges. Enzymes are basically selective biological catalysts made of proteins. In the pulping industry, enzymes used to improve the pulp and the sheet properties are mainly produced by various microorganisms such as Clostridium, Ruminococcus, Streptomyces, Cellulomonas, Bacillus, Erwinia, Trichoderma, Penicillium, Fusarium, and Humicola; a combination of enzymes from different strains can be also used to improve the pulp and the sheet properties. [8]

In this study, EcoArt Cellulases NS 51059 supplied by EcoArt PE Technologies Canada Inc. are used to improve the inter-fiber bonding. The enzymes fibrillate the surface of the fibers and also produce short polysaccharide chains which in turn increase the contact areas between the fibers and improve the fibers' density in the sheet [9,10]. As a result of these modifications, the hydrogen bonding sites increase, and the sheet tensile increases. In addition, the modifications give advantages over chemical and physical methods; such advantages are selectivity, lower energy input, recyclability, and reusability [11].

The fines in the recycled pulp can prevent water from draining easily. Cellulases could act preferentially on fines by cleaving the amorphous cellulose on the surface of the fines [12]. The fines are hydrolyzed, and the pulp becomes less hydrophilic and easier to drain. In consequence, the speed of the paper machine can be maintained or increased.

Although the primary goal of this study is to increase the tensile, the brightness is monitored at different dosages to see if the enzymes have negative or positive effects. In general, cellulases in certain conditions can improve the brightness of the pulp [13,14,15]. A reduction in brightness due to the application of the enzymes will not be cost-efficient, but an increase in brightness will be a positive outcome for the pulp quality improvement.

Although cellulases are proven to be good candidates [16] to improve the quality of the pulp and the paper, it is important to determine the amount and the conditions in which better results are obtained. An excess of hydrolysis of the cellulose could severely reduce the strength properties of the pulp [17,18]. Thus, an experimental approach in the lab and an application approach on the paper machine are critical to determining the right dosage to study the tensile, the freeness, and the brightness. The enzymes selection, the dosage, and the appropriate reaction time are known to be among the key factors for pulp quality improvement [19].

Case Study Problem Statement

The main objective of this study is to increase the tensile index equal to or above 42.2 Nm/g. The freeness and the brightness will also be monitored to see if the enzymes have any effects on these critical quality parameters of the pulp and the sheet. The historical tensile index, freeness, and brightness are respectively 38.5 Nm/g, 463 ml, and 82.4.

CHAPTER II

KRAFT PAPERMAKING AND ENZYME - OVERVIEW

The main type of paper involved in this study is recycled Kraft paper, but it would be important to briefly remember the origin of paper. Paper is simply a network of fiber derived from wood, rags, straws, or any fibrous materials felted from a fluid system onto a grid. Archeological sources dated from 400 BC reveal that ancient Egyptians, Greeks, and Romans used to write on scrolls of papyrus; papyrus is obviously not a paper but the first record of papermaking dates from 105 AD; the invention is credited to Ts'ai Lun, a member of the Chinese court. Ts'ai Lun broke barks of trees into fibers and ponded them into sheets; the process was improved by adding rags, hemp, and old fish nets to the pulp [A]. Although the papermaking process was kept secret in China, the knowledge expanded to the East, Korea, and Japan, in the sixth century. The propagation of the papermaking process to the west of China is due to the defeat of the T'ang army by the Ottoman Turks; prisoners from the war taught Arabs the papermaking process and the first paper mill in the Arab world was installed in Baghdad in 793 A.D. Paper making process arrived in the northern Africa and the Southern Europe in the 11th century [20, 21].

Although the first paper mill in the United States was built in 1690, it was not until 1798 that the French inventor Nicholas Louis Robert invented the paper machine to replace the hand-moulding process in papermaking [22, 23]. Different approaches were used to digest wood, rags, straws, and other fibrous materials to recover the fibers and make paper. In 1879, the German chemist Carl F. Dahl [24] invented a new approach known as the Kraft process which became the dominant pulping process in the world today. Dahls' work mainly changed the *chemicals recovery cycle* and the production of the *white liquor* used to cook the wood chips (Figure 2-1).

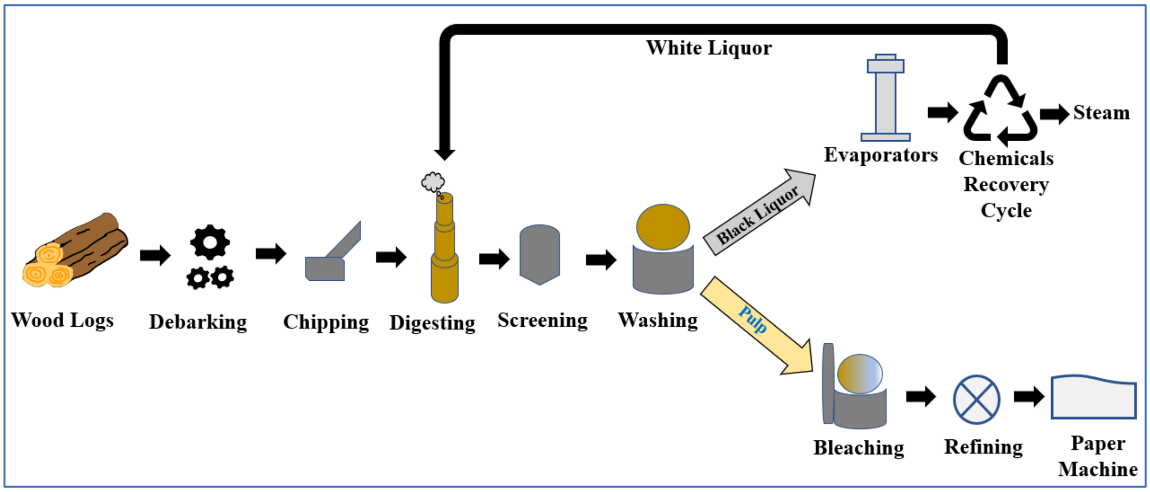


Figure 2-1. Flow diagram of Kraft pulping mill.

The lignin that binds the cellulose in the wood is depolymerized resulting in the production of the cellulose fibers (pulp). The pulp will be eventually used to make paper; The reject (black liquor) which contains mainly digestion chemicals, lignin, and wood extractives will be processed to generate new cooking liquor (white liquor) and steam.

Kraft Papermaking

- **Virgin Pulp and Recycled Pulp**

Dahl used sodium sulfate (Na_2SO_4) instead of soda ash in a pulping recovery system [25, 26]. During the incineration in the recovery system, the sodium sulfate is reduced to sodium sulfide (Na_2S). The liquor produced with the recovered chemicals contains sodium hydroxide (NaOH) and sodium hydrosulfide (NaSH) due to the reaction of the sodium sulfide with water:

$$Na_2S + H_2O \rightarrow NaSH + NaOH \rightarrow Na^+ + SH^- + Na^+ + OH^-$$

Paper made from this liquor, also called white liquor, has superior strength and is named "Kraft paper"; the term "Kraft" means strong in German. The newly invented liquor is more selective and protects cellulose during the digestion process due to the presence of hydrogen sulfide ions (SH^-).

The selectivity of the liquor can be improved by adjusting the sulfidity or the causticity of the liquor. The sulfidity is the percent ratio of the sodium sulfide to the total active alkali while the causticity is the percent ratio of the sodium hydroxide to the total active alkali. A good selective liquor removes the lignin from the wood chips without degrading the carbohydrate components.

$$Sulfidity = \frac{Na_2S}{NaOH+Na_2S}*100 \qquad Causticity = \frac{NaOH}{NaOH+Na_2S}*100$$

The white liquor successfully digests the wood chips by separating lignin, hemicellulose, extractives, and cellulose. The pulp, the main brown solid product left after the digestion, is mainly fiber made of cellulose; The byproduct of the digestion which is viscous, thick, and black, is called black liquor; the black liquor contains mainly leftover reactants (sodium hydroxide and sodium sulfide), dissolved lignin, polysaccharides and dissolved extractives. The black liquor is sent to the recovery boiler to evaporate residual water, burn organic constituents, supply heat for the steam generator, reduce the oxidized sulfur compounds to sulfide, and recover inorganic chemicals from the molten smelt. The recovered chemicals from the black liquor are dissolved to make the green liquor whose main components are sodium sulfide (Na_2S) and sodium carbonate (Na_2CO_3). The green liquor, in turn, is converted to white liquor ($NaOH$ and Na_2S) in the recausticizing plant where calcium oxide (CaO) is added [26, 27]. Figure 2-2 shows the main stages of the chemicals cycle during the Kraft pulping process.

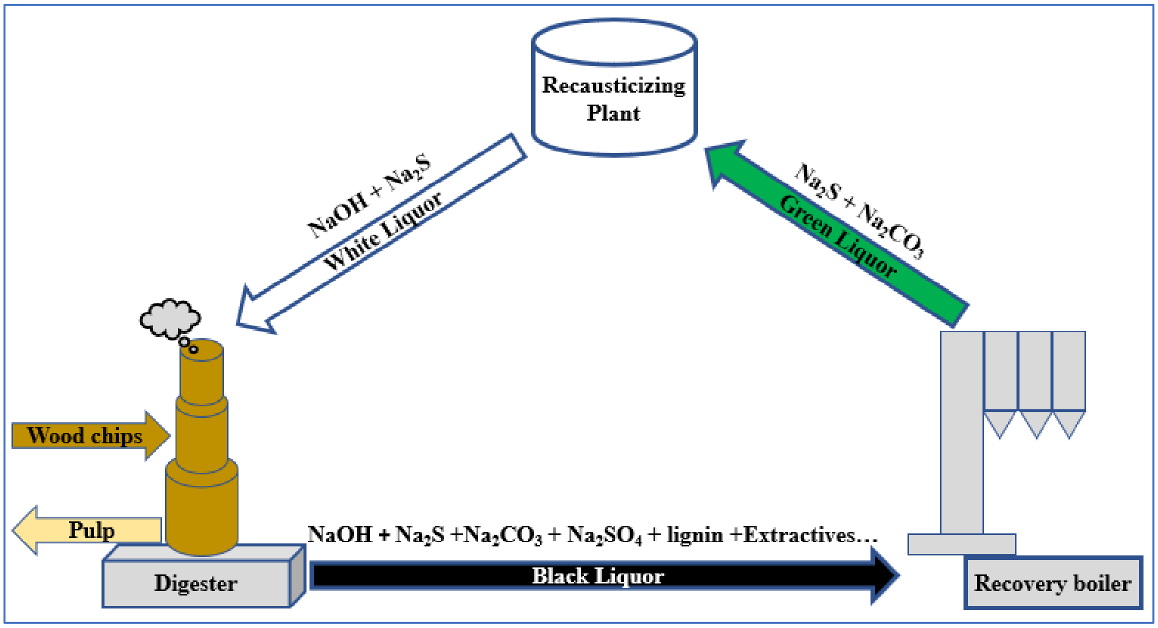


Figure 2-2. Chemicals' recovery cycle during the Kraft pulping process

Although other types of chemical pulping processes such as neutral sulfide (semi-chemical) pulping, sulfide (acid) pulping, and soda pulping exist, the Kraft process accounts more than two-thirds of the world's virgin pulp production and more than 90% of chemical pulp. The market is dominated by Kraft pulp due to the fiber strength, softness, flexibility, and efficient chemical recovery process. Furthermore, Kraft pulp has many advantages compared to mechanical pulp (groundwood pulping, refiner mechanical pulping, and thermal mechanical pulping). The tensile, tear strength, wet web strength, drainage, and density are higher for the Kraft pulp; however, the Kraft pulp is more expensive and has lower bulk, stiffness, and opacity [27, 28, 29].

The pulp obtained after the digestion stage can be washed and used to make paper products or can be bleached and then used to make products. About 5 million tons of newspaper were made in the US in 2018, 6.9 million tons of books, 9.8 million tons of magazines, 4 million tons of office papers, 4 million tons of tissue and paper towels, 1.4 million tons of paper plates and cups, 4.1 million of disposable diapers [30]

The Kraft process has undergone significant improvements throughout the century. Today, Kraft paper is generally made of fiber derived from softwood and hardwood trees. The tree is cut, debarked, chipped, screened, digested, screened again, washed, bleached, refined, formed, dried, reeled and converted. The product after the digestion step is called virgin pulp if wood chips from trees are used and no recycled paper materials are added to the process.

The papermaking process consumes about 68 million trees each year in the US and about 15 billion each year in the world; basically,186302 trees per day in the US and 41 million trees per day in the world [31, 32]. Softwood such as pine, fir, spruce, and hardwood such as aspen, birch, eucalyptus, maple, and oaks are some of the woods used. The softwood fiber is long and thick while the hardwood fiber is short and thick; the softwood pulp has a lower density compared to the hardwood pulp; in addition, the softwood has higher flexibility and tensile while the hardwood has higher opaqueness and stiffness. Softwood and hardwood pulps can be used individually or blended at different percentages to make paper with different properties of characteristics.

The papermaking process is intensive and heavily uses other resources such as water, electricity and chemicals. The ten top papermaker countries in the world in 2018 are China (109 962 000 metric tons), the United States of America (72 062 000 metric tons), Japan (26 070 000 metric tons), Germany (22 282 000 metric tons), Indonesia (12 478 000 metric tons), Republic of South Korea (11 532 000 metric tons), India (15 214

000 metric tons), Brazil (10 557 000 metric tons), Finland (10 544 000 metric tons) and Sweden (10 141 000 metric tons) [33]. Multinational such as International Paper (USA), Nine Dragons Paper Holdings (China), WestRock (USA), UPM (Finland), Stora Enso (Finland), Oji Paper Company (Japan), Sappi (South Africa), Smurfit Kappa Group (Ireland), DS Smith (United Kingdom) and Nippon Paper (Japan) hold the largest papermaking and pulp products manufacturing plants around the globe [34].

Most pulp and paper products are useful and necessity materials; the paper-making process also creates employment around the globe; however, many environmental organizations raise their concerns about the papermaking process by citing deforestation, air pollution, water pollution, land pollution, and paper waste [35].

Deforestation is simply removing trees from a wide area. The area or the land may be used for other purposes such as human habitat and mining; in some cases, the trees grow back, or other plants or farms are grown on the cleared land. Deforestation has many impacts on the environment. Trees that are cut down cannot absorb and store carbon dioxide (CO_2); an increase of CO2 in the atmosphere has a direct effect on global warming. In addition, animals' habitats are destroyed or negatively affected by deforestation. Deforestation simply shuffles the ecosystem and displaces the rural or Indigenous communities and the wildlife. Biodiversity is severely affected as the population of certain species is reduced or endangered. Papermaking, especially from virgin pulp, consumes trees and has a high footprint on the ecosystem and biodiversity [36].

Air pollution is another reason why environmentalists decry the papermaking process. Pollutants such as hydrogen sulfide (H_2S), sulfur oxides (SO_x), nitrogen oxides

(NOx), carbon dioxide (CO_2), volatile organic compounds (VOC), and particulates are produced during the process. The air pollutants mainly come from the digester, evaporators, recausticizing plant, and wastewater treatment plant [35]. Studies [37] reveal that papermill workers experience more dermatitis and airway inflammation and the communities around papermills are exposed to strong odor. Furthermore, air pollutants from the mills can increase the risk of certain cancers such as large intestine cancer, esophagus cancer, kidney cancer, and pleural mesothelioma. H_2S and VOC are known to cause irritation, dizziness, and skin problems; SO_x and NO_x are known to contribute to acid rains by reacting with oxygen and water in the air to produce sulfuric acid and nitric acid.

Water pollution is among the reasons why environmentalists see the papermaking process as a harmful process. In general, every papermill has a wastewater treatment plant. The plant processes the water to meet certain criteria before it is reused or it is rejected in the water stream (rivers, lacs…). Processed water may sometimes contain suspended solids (fiber, bark particles, dirt…), dissolved organic compounds (lignin, sugars, turpentine…), dissolved inorganic compounds (NaOH, Na_2SO_4), heavy metals, and other additives such as starch, Alkyl Ketene Dimer (AKD), Polyamide epichlorohydrin (PAE), Glyoxalated Polyacrylamide (GPAM), Per- and polyfluoroalkyl substances (PFAS) and chlorinated compounds. Although some of the pollutants are naturally occurring in the wood, the amount rejected by the mills is so high that it has negative impacts on humans and the environment. The discharge of the waste can change the pH, the turbidity, and the color of the rivers and even affect the aquatic ecosystem. Pratibha et al. show that papermill water is mostly deficient in dissolved oxygen and high in BOD (biological oxygen demand) and COD (chemical oxygen demand) values [35, 38, 39].

Land pollution is another complaint environmentalists associate with the papermaking process. The irrigation with polluted water from the mill causes a nutrient imbalance in the land and, thus, in the crops. Elements in the mill wastewater such as sodium, magnesium, calcium, sulfates, and heavy metals increase the pH of the soil, imbalance macro and micro nutrients, have negative effects on soil microbial activities, deplete oxygen supply in soil and decrease the germination rate. The pollutants can further enter the food supply chain through farming and affect human health [39].

Environmentalists are questioning the biodegradability of pulp and paper products. Although studies [40, 41] report that paper can naturally degrade in the soil within 2 to 6 weeks, certain grades of paper have been seen in nature after years without going through the degradation process. This is due to the fact that paper makers are adding or mixing the pulp with polymers to make their products; in addition, there are paper makers who make products lined with plastic and the final products become un-biodegradable. Certain examples of products are plates that contain SBR and PFAS, cups, and milk boxes that are lined with polyethylene or other non-biodegradable polymers [42, 43].

Furthermore, the fully biodegradable pulp and papers which were thought to be good and safe for the natural life cycle are now scrutinized; the main reason is the decomposition process of the biodegradable papers in the landfills produces methane [44]. Methane is a greenhouse gas that traps heat and ultimately contributes to global warming. The EPA [45] defines the global warming power (GWP) of carbon dioxide as 1 while the GWP of methane is between 28 to 36. This simply means that one ton of methane traps about 28 to 36 times more energy compared to one ton of carbon dioxide. In brief, in equal amounts, methane contributes more to global warming than carbon dioxide. Paper is sadly known to be among the largest contributors to the methane generated in landfills [46].

Many solutions are proposed to decelerate the negative impacts of the papermaking process and paper products degradation. Reforestation, reusability, and recycling are part of the solutions.

One of the solutions to curb the pulp and paper products environmental impacts is to recycle the paper products. Recycling reduces the presence of paper in the landfills and this reduction indirectly reduces the methane gas generated in the landfills. In addition, recycling saves trees, water, energy, and oil. Many sources, including the EPA, agree that recycling one ton of office paper can save on average 17 trees, 7,000 gallons of water, 463 gallons of oil, 3 cubic yards of landfill space, and enough energy to heat an average home for six months trees. The paper recycling process saves on average 64% energy, 58% water, and 60 pounds less air pollution. The advantages of recycling obviously make the fiber a gateway to sustainability business [47, 48].

Although the Japanese started recycling paper in the 9th century, the first paper recycling patent was granted to the English papermaker Mathias Koops on April 28, 1800 [49, 50]. Paper recycling started in the US around 1690 with William Rittenhouse who planted his mill in Philadelphia. Although the recycled paper made by Rittenhouse was mainly sold to print the Bible and newspapers, the amount of recovered and recycled fiber was insignificant. During World War II and after the war, campaigns were intensified in the US to recycle paper. By 1985, Americans' recycling rate reaches only 10%. Five years later the recycling rate exceeds 30 %. Figure 2-3 shows that the paper recovery for recycling reached 50% of the paper produced for the first time in the US in 2003 [51].

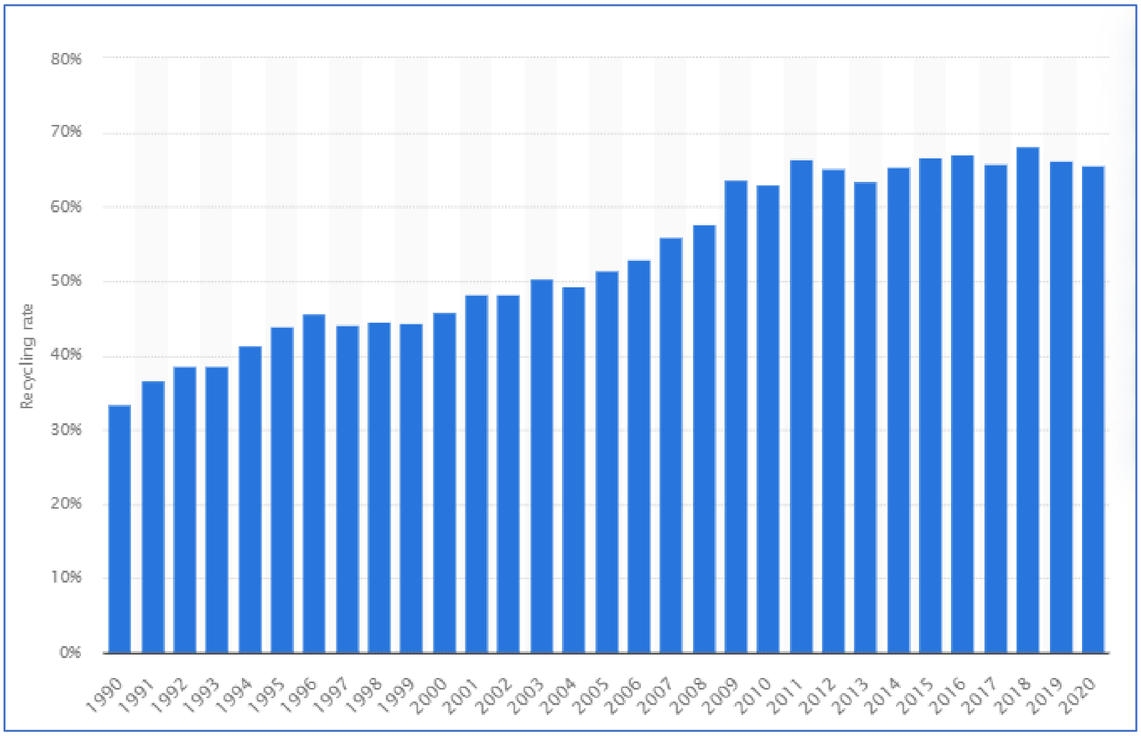


Figure 2-3. Paper recycling rate in the United States from 1990 to 2020 (Statista) [52]*

On January 1st, 2018, China enacted a ban [53] that would stop the import of certain waste materials including paper waste. The impacts of the Chinese ban on the US waste papers affect the rate of recycling more paper in the US. The paper recycling rate reached 68.1% in 2018 for the first time but the rate is currently decreasing [Figure 2-3]. The rate will decrease by about 13.6% by 2020 mainly due to the market restriction; part of the paper recovered in the US is not recycled here but is sold to China who in return recycles it. The current dilemma is the US will need to develop technology to recycle all its paper waste or find new markets where the wastepaper can be sold. Reaching a 100% recycling rate is the ideal goal but it will take the willingness to recover the paper, the capability to process it, and the acceptance of the customer to reach that ultimate goal.

The willingness to recover paper is increasing almost every year if the overall trend of Figure 2-3 is considered. Different types of trash bins to separate recyclables paper and plastics wastes can be seen in many cities across the globe. Environmentalists are making their voices heard about the importance of recycling at schools, on TV, on social media, and the internet. As a result, people are more educated about the importance of recycling, climate change, and global warming. More customers are willing to purchase recycled paper products and they carefully read details on the packaging or search for logos that certify the product as recycled or recyclable before buying the item [54]. Although the paper recycling rate reached 65% in 2018 [Figure 2-3], the current willingness to recycle paper could bring the rate upward in the next decades.

Even if the willingness to recover waste papers is high, the capability to process the recovered papers and isolate the fibers becomes the new challenge. Copy paper can be easily deinked and the fiber can be used to make products such as toilet paper, facial tissue, paper towel, and more. Although the technology is advanced to recycle copy paper, not all paper products can be now recycled. Milk cartons made of fibers and laminated with polymers can be recycled but diapers, feminine pads, and certain types of paper cores are challenging to recycle.

The willingness and the capability to recycle will fail if product acceptance is not considered. Product acceptance is the voice of the customer. When the customer denies the product, the willingness and the capability that drive the paper recycling rate will fade. The concept here is very simple: will a customer buy milk in a half-gallon milk carton that was made from 50% recycled fiber from diapers, feminine pads or fiber from municipal waste? If the technology used to recover such fibers costs more than traditional recycling, is the customer willing to pay more? These questions are complex and difficult to answer as opinions will differ from one person to another. Although reaching a 100% recovery rate is the ideal goal of recycling, it will be difficult to reach the ultimate goal if the customer acceptance equation remains unsolved.

In recycling, the papers are collected, hydropulped, screened, floated, screened, washed, bleached, refined, formed, dried, reeled, and converted. Although the refining stage is the main objective of this study, it is important to mention that each stage is critical and dependent on the manufacturing process. A 100% recycling process is perfectly circular as it does not use any virgin fiber or cut any new trees. Figure 2-4 shows on the right the general steps of the paper manufacturing process from recycled pulp.

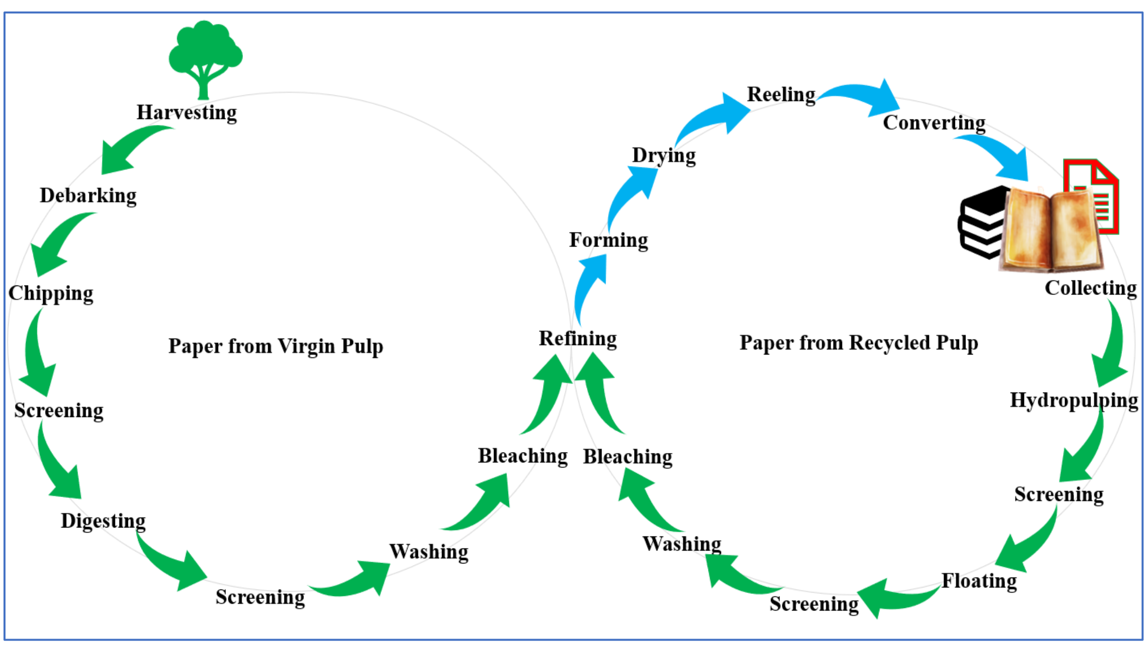


Figure 2-4. General steps of the paper manufacturing process from virgin and recycled pulp. Virgin pulp: from the circle at left to the blue area in the right circle. Recycled Pulp: the entire circle at right.

The lifecycle of a paper made from virgin pulp, if not recycled or used for any other purpose, is similar to the cradle-to-grave principle. The cradle-to-grave cycle has a negative environmental impact as trees will always need to be cut to produce paper and generate polluting wastes. The lifecycle of paper made from recycled pulp is similar to the cradle-to-cradle principle; at the end of the life of the manufactured paper, the fiber can be used or reused to make new paper which is a new life for the fiber. Recycling itself, if done properly contributes to the circular economy and has less footprint on the environment compared to the virgin pulping process [55, 56].

Although recycling is more appealing, the process has many challenges such as dealing with contaminants (metals, glasses, Styrofoam, oils, hot melt, asphalt…) found in the recovered papers and the runnability of the paper machine due to stickies, fines, and weak sheet tensile. The weak sheet tensile challenge reduction on the paper machine is one of the main goals of this study.

- **Paper Machine Sections**

A typical paper machine has a headbox, a forming section, a press section, a dry section, and a reeling section. Figure 2-5 and the Figure 2-6 show the profile of a paper machine. The green line in Figure 2-6 represents the path of the paper web from the headbox to the reel.

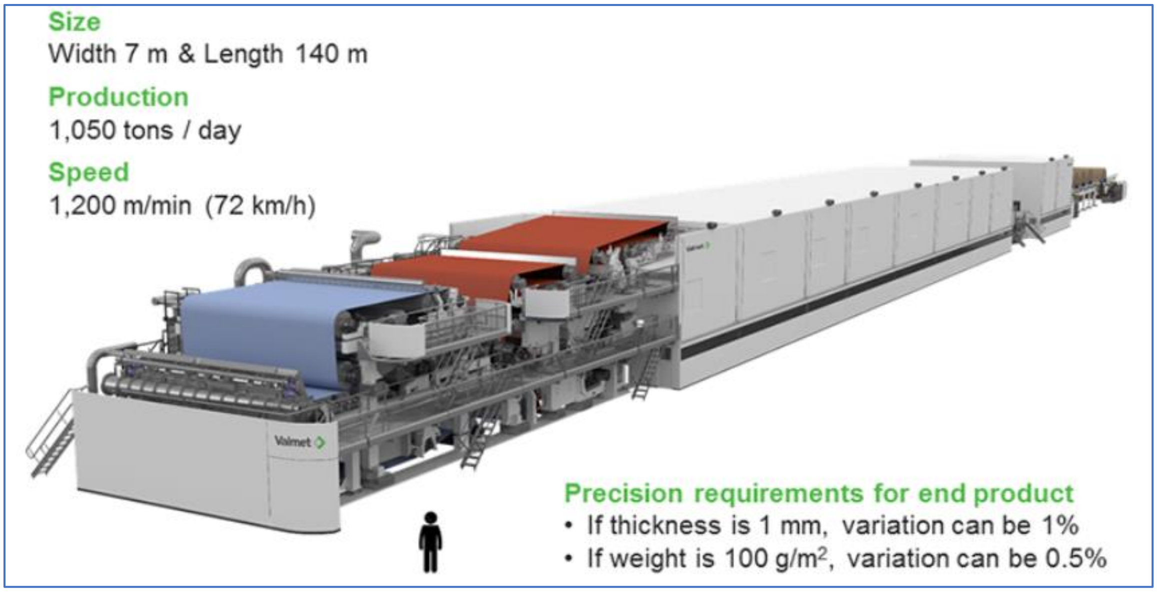


Figure 2-5. Typical Dimensions of a Paper Machine (Valmet) [57]

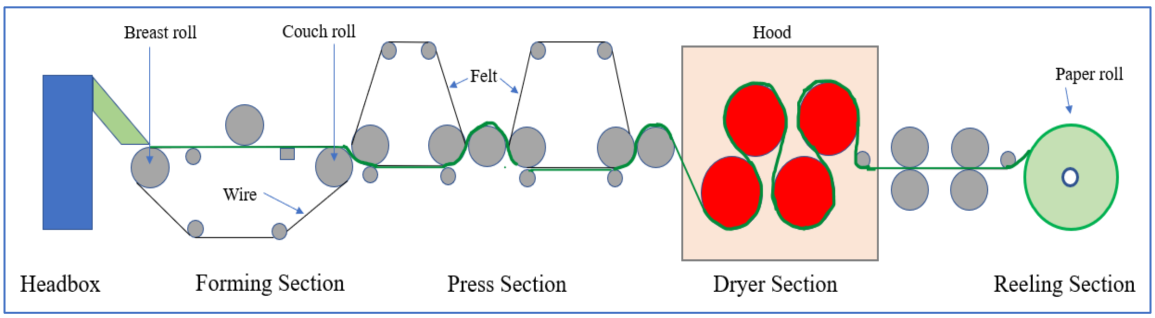


Figure 2-6. General Profile of a Paper Machine

The headbox supplies low consistency pulp or diluted pulp to the forming section. The fiber slurry is distributed uniformly across the wire. The headbox controls the fiber dispersion, turbulence, and velocity with respect to the wire. Early design headbox are open wooden boxes in which a sufficient stock level was maintained to give desired efflux velocity through a slice; the flow is laminar and gravity-fed. Modern headboxes are advanced and allow better formation of paper. Air padded headbox, hydraulic headbox, and gap former are the main types used in the pulping industries. The pressure, the dispersion, the turbulence, the velocity, the jet impingement point, and the fiber misalignment are better controlled with advanced headboxes. The average solid content of the pulp at the headbox can range from 0.2 to 0.5% [26, 58].

The forming section extends from the breast roll to the couch roll and has a continuous rotating wire mesh. A vacuum system under the wire dewaters the pulp and a wet sheet is formed. Surface tension and Van der Waal forces are the main forces holding the fibers to each other at this stage. The hydrogen bond between the fibers is weak and the average solid content of the wet sheet is about 10%. [26, 58]

The press section extends right after the couch roll to the drying section gate. The inter-fiber bonding is increased in this section as the wet web is pressed between hard rolls and more water is removed. The sheet goes through the nip of the rolls which squeeze the fibers; this action not only dewaters the sheet but also densifies the web and increases the sheet strength. The average solid content in the press section is about 45%. [26, 58]

The dry section is usually covered or hooded to slow the loss of energy of the heated rolls. A system of thermocompressors using high-pressure steam is used to uniformly heat and maintain the rolls at a desired temperature. The felt presses the web against the hot rolls to accelerate the water loss. As a result, the sheet is dried and hydrogen bond becomes the main force holding the fibers together. At this stage the web is fully made with about 95% solid [26, 58].

The reeling section comes after the dry section. In general, there is a section between these two sections called calendering. The calendering section is a succession of rolls used to modify the surface characteristics of the sheet. The nip pressure of these rolls adjusts the overall thickness and the uniformity of the sheet. The sheet is wound in a roll after the calendaring section with an average of 95% solid [26, 58].

From the couch roll to the reeling section, the web is no longer on the forming table and can break at any point. The quality of the fiber is critical for the web to hold together. Unrefined fiber and fiber that is recycled several times can lack the proper strength properties to make better paper.

- **Mechanical refining**

Refining of the pulp is a mechanical treatment to modify the fiber structure for better papermaking. The device used to achieve this goal is called a refiner [Figure 2-7]. The refiner is made of two metallic plates (a stator and a rotor). The plates have radial bars. The pulp fed from the inlet flows in the groove and is finally trapped between the edges of the opposing bars. Two main types of refiners are used in the mills: the conical refiners and the disc refiners. The conical refiners can be subdivided into two types; the low angle types called Jordans, and the high angle types called Claflins. The disc refiners are subdivided into three types based on the characteristics of the rotating disc and the stationary disc; the three categories are the single rotating disc opposing stationary disc, two opposing rotating discs, and two rotating double-sided discs between two stationary discs [G]. Figures 2-7 and figure 2-8 show respectively the schematic of a single rotating disc mechanical refiner and the mechanism of fiber refining.

Whether the mills use disc refiners or conical refiners, the amount of electricity used is exorbitant. Refiners are among the process units in the mill that consume more energy. Edyta Małachowska et al [59] show from their work that refiners' consumption can go up by 40% of the overall electricity consumption in the mill. This energy is required for the fiber transformation to achieve the desired pulp and paper properties.

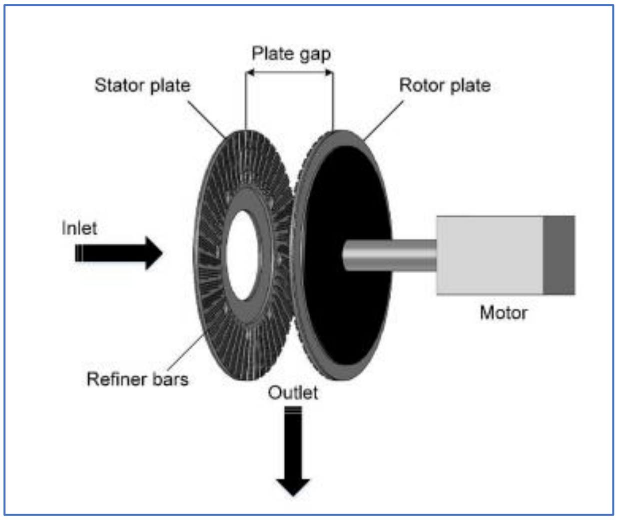


Figure 2-7. Schematic diagram of a single-disc mechanical refiner [60]

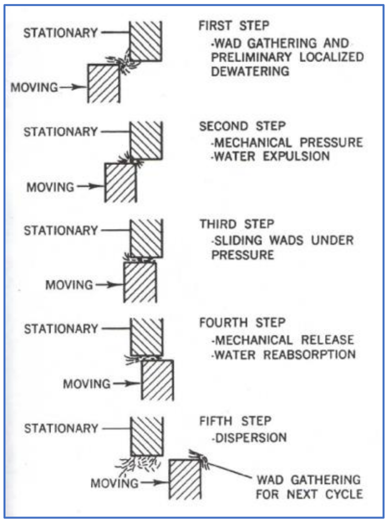


Figure 2-8. Illustration of refining between two bars [26]

The trapped fiber between the bars [Figure 2-8], collapses, ruptures, delaminates, and fibrillates due to the shear force applied by the refiner bars. The surface area of the individual fiber increases and the fiber-fiber contact in the pulp increases. The fiber swells, becomes hairy and is more flexible for better hydrogen bonding. Figure 2-9 illustrates the change in the fiber structure before and after going through the refining process.

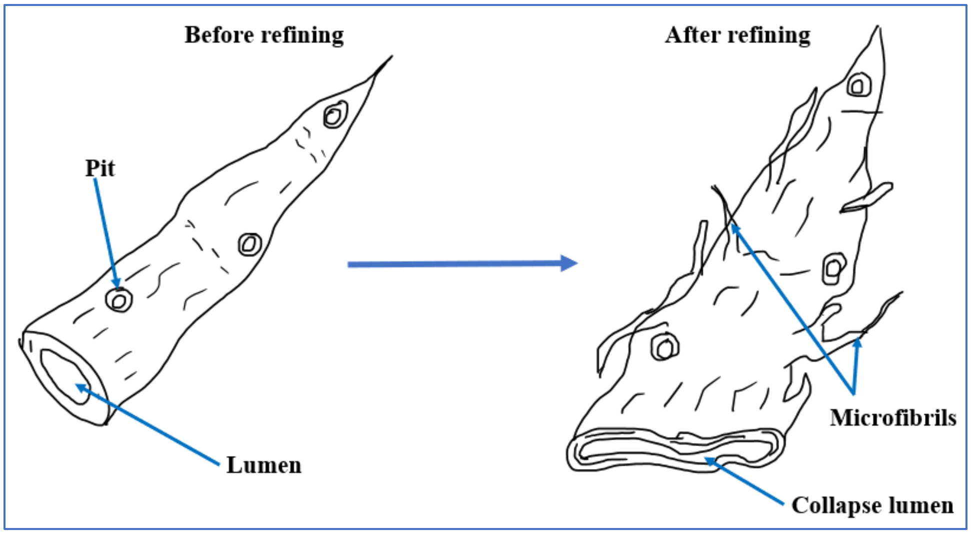


Figure 2-9. Fibrillation -Delamination of the fiber cell wall during refining

The fibrillation of the fiber occurs inside (internal fibrillation) and outside (external fibrillation). Nodes, kinks, slip planes, and micro-compressions in the cell wall are created due to the force applied by the refiner bars [60]. The image at right in Figure 2-10 depicts a paper made of refined pulp with a better network of fibers compared to the image at left of paper made with non-refined pulp.

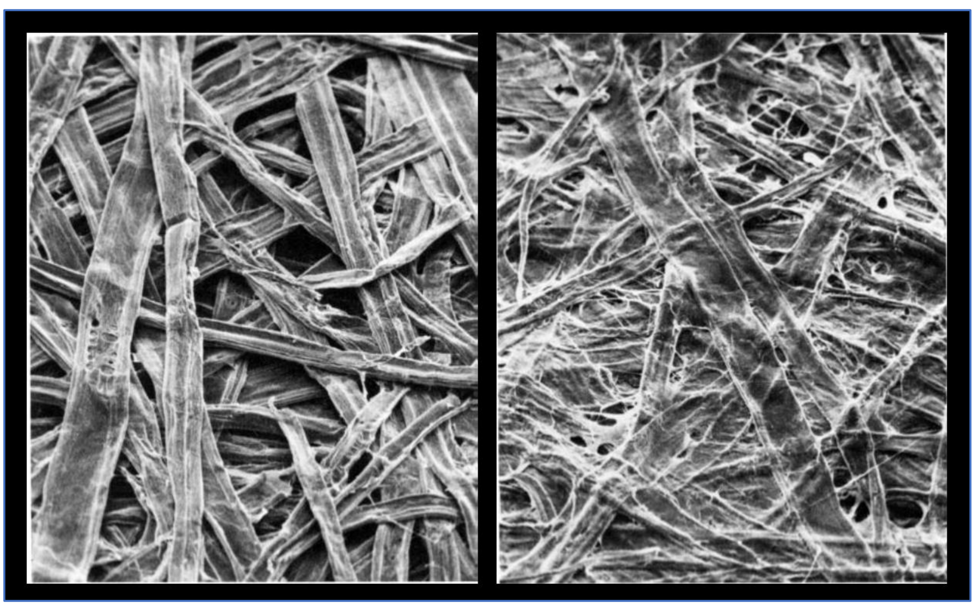


Figure 2-10. Images of fibers before and after refining [26]
(Black background used to enhance the difference between the images)

Overall refining improves the properties of the fiber to make a stronger sheet but some of the drawbacks are fines, low freeness, and weak individual fiber strength due to the mechanical force applied to the fibers.

Fines are fragments of fiber that can pass through a mesh screen 76 micrometers in diameter. There are two types of fines: primary fines and secondary fines. The primary fines naturally exist in the wood and comprise thin-walled parenchyma cells and very small cells in the wood. They remain intact after the digestion of the wood chips and become part of the pulp. The secondary fines are produced during the pulping process due to the mechanical actions applied to the fibers. Secondary fines are produced especially during the refining process due to the actions of the refiner bars on the fibers. Primary and secondary fines can play the role of a bridge between the fibers and increase the chance of the inter-fiber bonds; however, primary and secondary fines can prevent water from draining from the furnish. Excessive fines in the pulp will seriously reduce the drainage or the freeness of the pulp [61, 62].

Freeness can be simply defined as how fast water drains through the pulp. Freeness is measured by collecting the total volume of water discharged from a side orifice on the freeness tester. There are the Schopper Riegler (SR) freeness tester used mainly in Europe freeness and the Canadian Standard Freeness (CSF) tester used mainly in North America. A higher number of SR freeness means slower drainage while a higher number of CSF freeness means faster drainage [62, 63].

In this study, CSF was used. The water drains under gravity freely from the pulp when using the CSF. The consistency of the pulp and the presence of fines can affect the freeness of the pulp. Higher consistency and higher fines for example will prevent the water from draining and lead to low freeness. Low freeness has a direct impact on the paper machine speed. The speed of the machine has to be reduced to give time for the pulp to be drained on the forming section. The wet web on the paper machine that carries too much water is susceptible to break and more energy will be consumed to dry the web at the drying section. Refining generates fines which in turn reduce the freeness [12,26]. The illustration in Figure 2-11 shows the schematic of the freeness tester and two pulps before and after refining; the after-refining pulp has the highest number of fines and, thus, the lowest amount of CSF value.

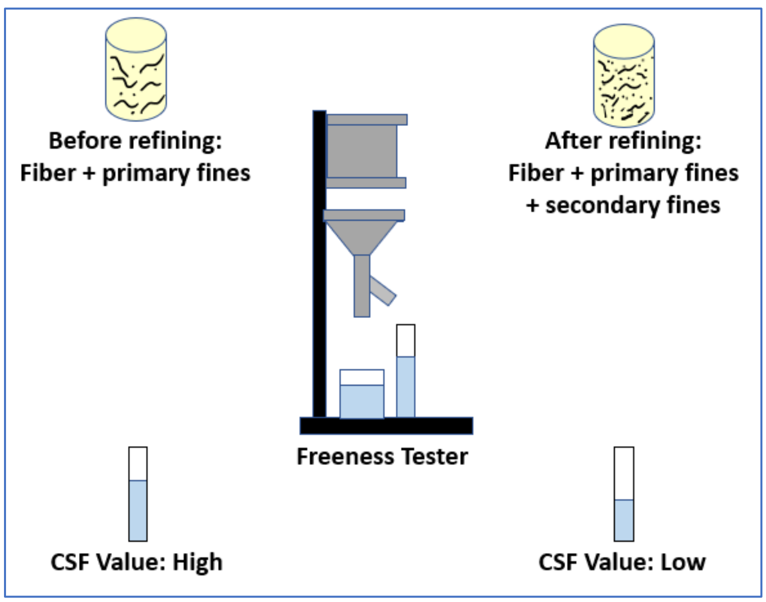


Figure 2-11. Illustration of freeness before and after refining

Loss of strength of individual fiber strength is also considered as a drawback of refining. The native fiber structure collapses, cracks, and fissures during the refining process. The fiber also swells and curls. Although the new fiber structure is good for the fibers' inter-bonding properties and the sheet tensile improvement, the individual fiber becomes weak. Kouko et al. [64] show that the individual refined fiber loses on average about 24% of their tensile strength compared to the unrefined fiber; 640 MPa vs 840 MP respectively for the refined fiber and the unrefined fiber. The paradox here is the refined and weak fibers make strong paper. A recovered fiber from this sheet will not have the same properties as the original fiber.

- **Secondary fibers and degree of recycling**

A secondary fiber is simply a fiber that has been used at least once in the paper or pulp products manufacturing process and is recycled to manufacture another product. The degree of recycling defines how many recycling cycles a fiber has been through. Refining has a significant effect on the fiber each time it is processed. Continuous refining through an infinite degree of recycling will make the fiber weaker and eventually ruin the fiber completely. Paper can be generally recycled five to seven times before the fibers become too short and weak to make poor-quality sheets [26, 65].

Papermills, apart from mechanical refiners, use different approaches to enhance inter-fiber bonding. Blending, fractionation, and chemical treatments are some of the techniques [22]. The recycled pulp is blended with the virgin pulp at a defined ratio to achieve certain properties of the sheet. Fractionation is used when the fibers are screened based on their length and stored separately; each category of the fiber will be used according to the needs of the paper maker. Starch, PAE, and GPAM can be also used to enhance the strength of the sheet.

Starch is used in the recycled mill for many purposes such as flocculant, retention aid, binder, sizing agent, and bonding agent. The versatility of the starch makes it a good candidate to improve the degree of recycling of secondary fiber. However, excessive use of starch in the mill makes the mill stinks and the products malodorous. The starch is used in the wet-end of the recycled mill to enhance the sheet strength ends in the white water. Microorganisms feed on the starch and produce VFA which are mainly acetic acid, propionic acid, and butyric acid [66]. The odor due to the VFA can become serious if not controlled. The wastewater treatment plant in the mill has to invest resources to reduce the starch in the white water and control the BOD. The mill operation has to define a strategy to control the odor not only on the machine but also in the final products.

PAE and GPAM are wet-strength additives in the mill. The wet strength additives are used to improve the paper's resistance to a force of rupture when the paper is wet. The goal here is not necessarily to increase the tensile of the paper, but rather to maintain it or preserve it at a certain level when the paper is wet. The wet-strength chemicals crosslink the cellulose of the fiber with covalent bonds that resist breaking upon wetting. PAE produces higher wet strength than GPAM; PAE is classified as a permanent wet strength while GPAM is classified as a temporary wet strength due to the fact that the PAE-treated sample wet strength decay rate is about 10 to 15% after the paper is subjected to 30 minutes soak test [67]. Wet strengths are mainly used for paper products that are intended to be used under humid or wet conditions such as paper towels and beverage cartons. As their names indicate, the importance of the wet strength is valorized when the sheet is wet. Although wet strengths can improve the sheet's tensile, especially when it is wet, paper makers find the sheet difficult to recycle. The pulps from wet-strength papers have flakes of paper that are difficult to break; the degree of recycling of such pulp is limited.

A quick way to reduce sheet breaks on the paper machine by increasing the sheet strength is to increase the basis weight. The basis weight is simply the weight of the sheet per area; it is expressed in Lbs./ft^2; it is called grammage when expressed in g/m^2[68] By increasing the basis weight, operators increase the amount of fibers per the same area in the sheet. The increase in basis weight densifies the sheet and increases the chance of hydrogen bonding between the fibers; the sheet usually becomes heavier, thicker, and opaquer. This technique can be used to solve the sheet breaks problem temporarily, but it is not generally approved for two main reasons: fiber loss and defective product.

Increasing the basis weight to prevent web breaking is a waste for the mill. The mill is literally putting more fibers than required in the sheet and this fiber loss makes the process inefficient. Fiber is the primary raw material of the paper maker. The cost of recycled fiber is increasing almost every year; The sorted residential paper price increased by about 7% and the sorted office paper price increased by about 6 % in 2021 [69]. Using the basis weight as a solution for sheet breaks creates only a financial loss in the mill.

Defective products are sometimes made when the basis weight is increased to impede sheet breaks. Some products have specific criteria about their caliper, opacity, bulkiness, stiffness, and roughness. Modifying the basis weight can affect one or more of these criteria. A Kimwipe or Kimtech, a paper cleaning wipe used generally in laboratories, has 280 sheets in the standard box [70]. An increase in the basis weight, for example, could jam the 280 sheets in the box and the customer will have difficulty pulling the sheet out; the Kimwipe sheet will often break when the customer is pulling. The pack will be classified as a defective product and a customer complaint can be filed. Furthermore, an increase in basis weight can also make a book thicker and heavier. In brief, a variation in the basis weight for recycled or virgin fiber can affect the properties of the sheet.

Enzymes are another alternative to tensile improvement in the mill. The enzymatic approach to improve the paper tensile can give similar results as mechanical refining with less damage to the fiber.

Enzymes

Enzymes are simply selective biological catalysts made of high molecular weight proteins. In the pulping industry, different types of enzymes are used for deinking, bleaching, and refining; enzymes are also used for pitch control, sticky control, removal of fines, water cleaning, and starch modification. Enzymes are mainly produced by various microorganisms and a combination of enzymes from different strains can be also used to improve the pulp and the sheet properties [8].

Although the conformation of the enzymes can be complex in their 2D or 3D spatial representation, the enzymes have generally 3 parts or regions: the binding module, the linker, and the catalytic domain.

The binding module or carbohydrate-binding module (CBM) functions to assist in the substrate turnover. The CBM targets the substrate, concentrates the enzyme on the surface of the substrate, and disrupts the non-hydrolytic crystalline substrate [71,72]. The binding module can recognize the crystalline and the amorphous regions of the fiber. The function of the CBM is extremely important as it helps the enzyme to adsorb to the fiber surface and penetrate interfibrillar space so the enzyme can start the cleavage of hydrogen bonds. There are known 180 different CBM domains classified into 13 families based on the amino acid sequence similarity [73].

The linker is the flexible region connecting the two adjacent parts (the catalytic domain and the binding module). The linker stiffness and length are critical for the enzyme activity; it is also known that shortening or deleting the linker reduces the enzymatic activity on crystalline cellulose and the linker length affects the thermal adaptation of certain cellulases. [74].

The catalytic domain interacts with the substrate and causes the enzymatic reaction. The catalytic domain interaction comes after the binding module penetrates the cellulose structure. At this stage, hydrogen bonds are cleaved, the cellulose structure is disrupted, and free polysaccharide chain ends are formed [72, 75]. Figure 2-12 is the schematic showing the structure of the enzyme and how the enzyme progressively disrupts the cellulose structure.

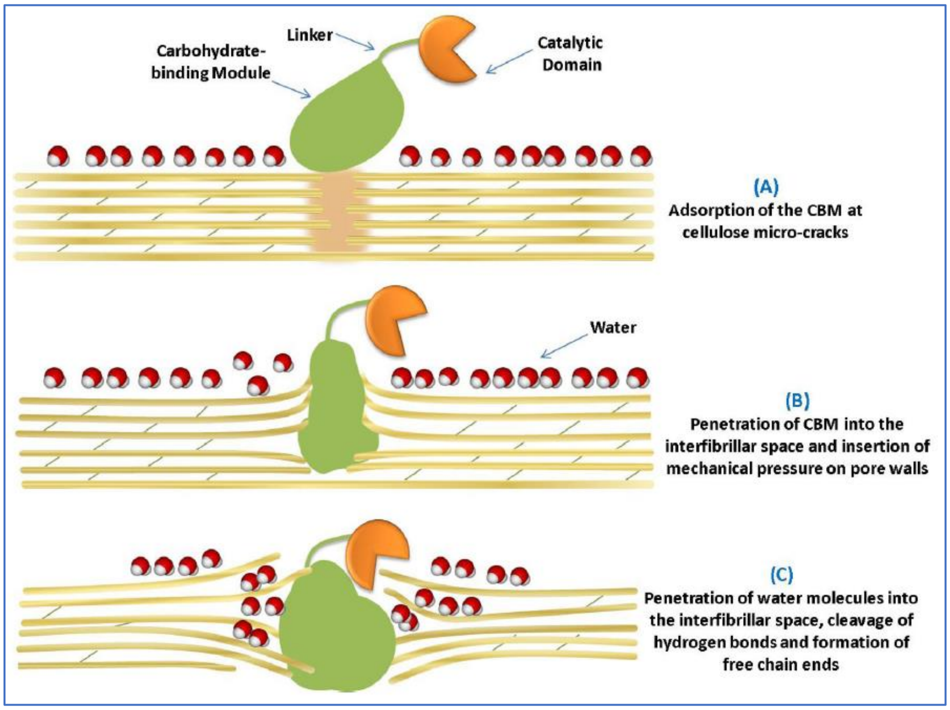


Figure 2-12. Schematic representation of enzyme penetration the cellulose structure. For clarity, the carbohydrate-binding module is oversized compared with the catalytic domain. [72]

After disrupting and penetrating the cellulose structure, the enzyme continues with cellulose hydrolysis which produces polysaccharide chains. Figure 2-13 shows the progression of the enzyme with the green strand of the cellulose off the main bulk of the cellulose. These green strands are the fibrillation that promotes hydrogen bonding between the fibers during the papermaking process; the more strands produced by the enzyme, the more fibrillated the fiber becomes.

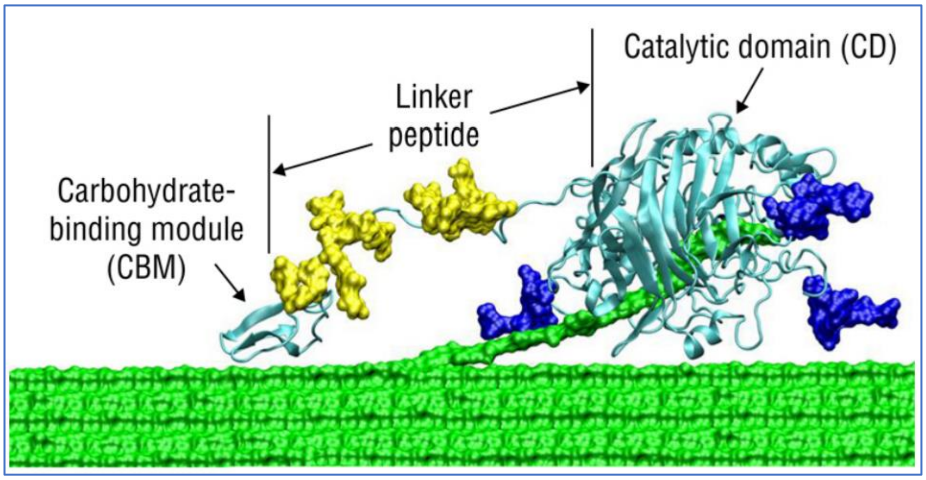


Figure 2-13. Enzyme with cellulose polysaccharide chain [76]

The complex enzyme-substrate conformation, the structure of each part of the enzyme (the binding module, the linker, and the catalytic domain), and the sequence of the amino acids make every enzyme a selective catalyst. Common examples are amylase for starch, cellulase for cellulose fibers, protease for protein, xylanase for hemicellulose, and pectinase for pectin. They catalyze specific reactions by lowering the activation energy.

Figure 2-14 shows an uncatalyzed reaction and a catalyzed reaction. The uncatalyzed reaction required high activation energy (ΔG_{A1}) compared to the enzymatic catalyzed reaction (*ΔG_{A2}*). The activation energy is the difference between the energy level of the substrate and the energy level of the transition state.

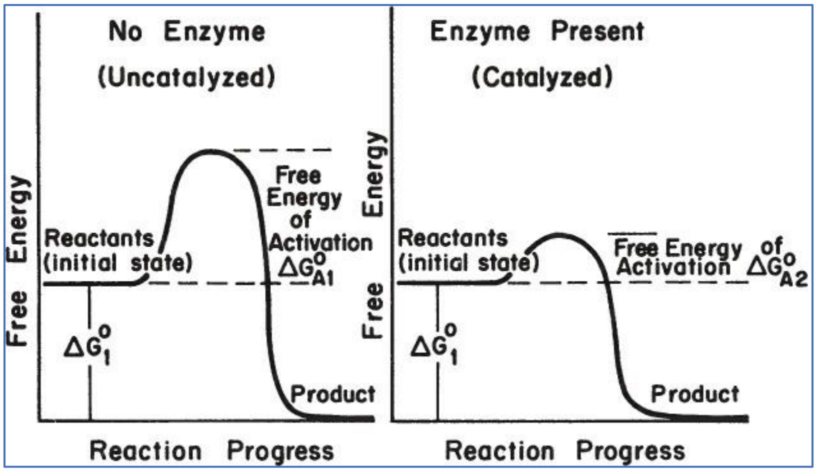


Figure 2-14 *Activation energies of enzymatically catalyzed and uncatalyzed reactions. Note that* $|\Delta G_{A2}| < |\Delta G_{A1}|$. *[77]*

The enzymes reduce the activation energy by either distorting the substrate bonds, or creating a charge distribution, or reducing the reaction entropy, or completely changing the chemical pathway so the reactants do not have to overcome intermolecular forces that oppose the reaction to occur. The complex enzyme-substrate predisposes the substrate to the reaction with less energy. [78]

- **Dosage**

Enzyme dosage is the amount of enzyme charged to the substrate. The dosage and the dosing strategy are important for the effectiveness of the enzyme. The dosage is critical as the overdose will produce an excessive response while the underdose will produce a low-yield response; the right dosage, if known, yields the targeted result. Enzyme dosing strategy is also crucial for its performance; a poor dosing strategy will yield a non-homogeneous result; the enzyme application strategy should be designed in a way that the enzyme is evenly applied to the substrate so the response can be consistent and representative [79, 80]. In this study, the pulp is at low consistency and is continuously mixed at different dosages.

- **Temperature**

Temperature is another factor for enzymatic performance. In general, every enzyme has its active temperature range. At a very low temperature, the enzyme is simply inactive; at a very high temperature, the enzyme denatures. The optimum temperature is needed to determine the optimum yield. This is possible by raising the temperature progressively, so the enzyme and the substrate gain kinetic energy; the increase in energy also increases the frequency of collisions and the formation of enzyme-substrate complexes [81, 82, 83]. Knowing the temperature at which the enzyme has the greatest activity on the fiber is crucial for this study.

- **Time**

Time in this study is how long the enzyme is exposed to the substrate. Time is an important factor as insufficient duration may not lead to the optimal result; not enough product will be formed and the desired sheet tensile will not be reached. In the beginning, the reaction proceeds mainly in one direction since there are only the enzyme and the substrate. However, as the reaction continues and more products are formed over time, there are chances of back reaction which decelerates the overall rate. If the exposure time to the substrate is too long, the product formation rate becomes very low or plateaued [81, 82, 84].

In addition, excessive exposure of the enzyme to the cellulose can produce shorter polysaccharides than needed. The objective is not to convert the cellulose entirely to polysaccharides but to create a few hairy chains to improve the bonding capability of the fiber; the optimum duration is needed to achieve this goal.

- **pH**

Enzyme activity is pH dependent. Extreme pH can change the shape or denature the enzymes [84]; as a result, the enzyme performs poorly even if the dosage, time, and temperature are optimal. Although pH is an essential parameter of enzyme performance, it is not considered as a parameter in this study. The main reason is the recycling mill water average pH does not fluctuate a lot. In general, the pH of water in Kraft paper mills and most recycled mills is above 7. The alkaline pH is mainly due to the white liquor residues carried in the lumen, cracks or fissures, and layers of fiber. The recycled mill water in this study has an average pH of 7.9 and each sample pH during the experiment has been adjusted to 7.9.

- **Enzymatic refining**

Like mechanical refining, the enzymatic refining of the pulp is a treatment to modify the fiber structure for better papermaking. The goal is to fibrillate, swell, and make the fiber more flexible for hydrogen bonding. Unlike the bars of the mechanical refiner that chop, crack, split, tear, and curl the fiber [60], the enzyme penetrates the cellulose structure, cleaves hydrogen bonds, and frees short polysaccharide chains. Figure 2-15 is a schematic of the enzyme fibrillating and generating polysaccharide chains from cellulose. The chains can be entirely free or hairy on the cellulose structure.

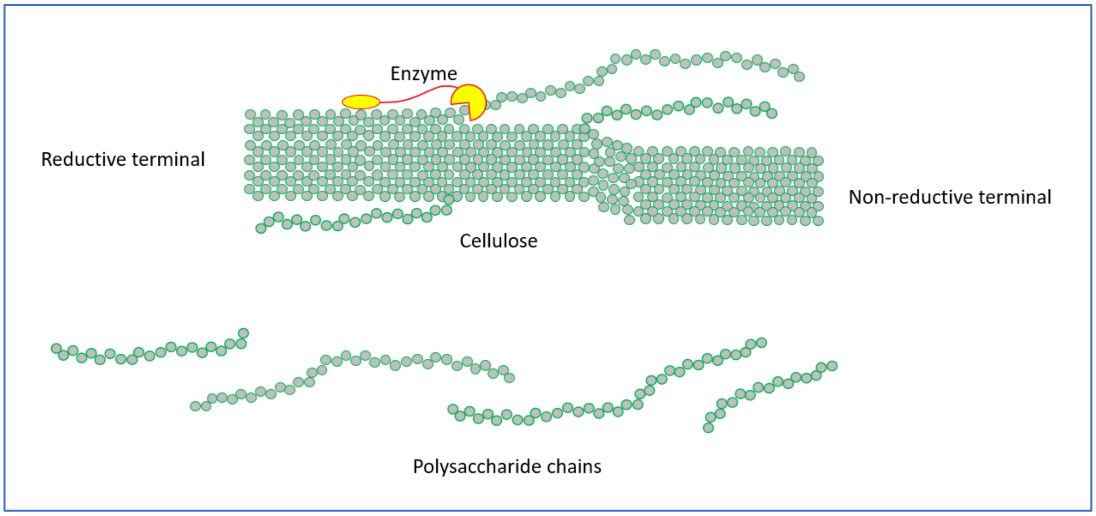


Figure 2-15. Enzyme fibrillating and generating polysaccharide chains from cellulose

The enzymatic approach applies less stress on the fiber compared to the mechanical approach. The process is purely chemical and requires very low energy consumption. Sandeep Tripathi and al. showed in their work that energy saving with enzymatic refining can go up to 30% compared to mechanical refining [85]. The work of Skals using cellulase (Novozym 476) reduced the energy consumption by 160 kWh/t pulp while the work of Yang decreased the energy consumption from 10%-25% [86]. In addition, Lecourt et al also determined that up to 60% of refining energy could be saved by enzymatic refining [87].

Figure 2-16 shows the fibers before (left) and after (right) the enzymatic refining. The fibrillated fibers appear hairy; their structure has been modified for better fiber inter-bonding and higher sheet strength.

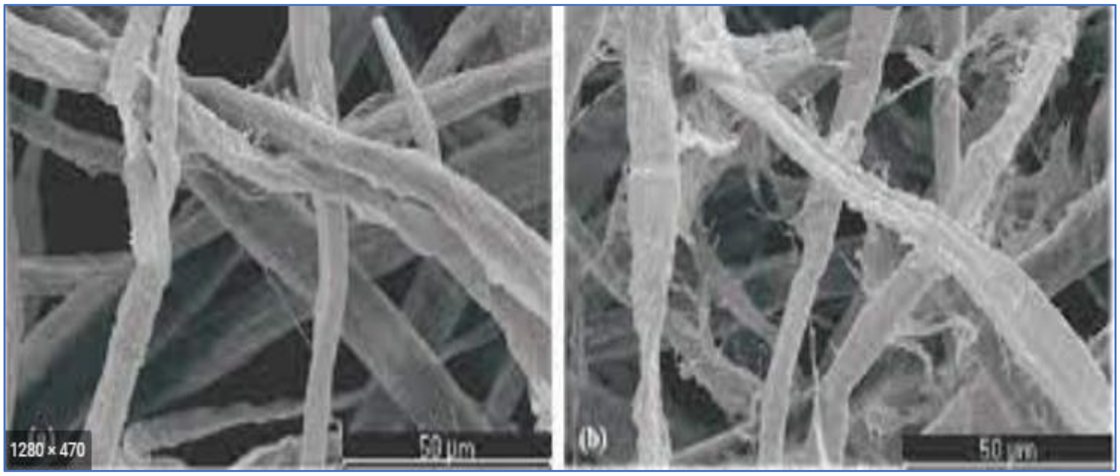


Figure 2-16. Enzyme assisted pulp refining: Before (left)vs After refining (right) [19]

- **Limitations of Enzymes**

Enzymatic refining can outperform mechanical refining if the enzyme is stored and used properly within a defined period. Enzyme denatures over a long period while refining bars last longer. Enzymes need to be stored in the appropriate area; the storage conditions for enzymes are more restrictive than the storage conditions of the metallic refiner bars. The temperature in the mills can become extreme, very hot, or cold, depending on the location of the mill and the season of the year. The fluctuations in the environmental conditions, if not controlled, can negatively affect the performance of the enzymes. Some enzymes lose their activity when frozen while others simply denature at very high temperatures [83].

Enzymatic refining is also reported to reduce the pulp viscosity. The pulp viscosity gives an indication of the average degree of polymerization of cellulose. Although the enzymes have the ability to improve fiber properties such as fiber bonding, Kirk et al [84] reported that the pulp viscosity decreases when cellulases cleave cellulose chains. As a result, the degree of cellulose polymerization decreases. The authors also acknowledge that researchers attempted to get around this issue by using enzymes from mutant microorganisms.

The lack of full understanding of the fibrillation mechanism and trade secrets among the enzyme suppliers also contributes to the enzyme limitations. The exact mechanism of enzymatic pulp fibrillation is not totally understood [88] and more research need to be done in this area. The trade secrets between the enzyme suppliers also make it difficult to associate enzyme sources with their performance. Critical trade secrets information about the enzyme is legally withheld from the Safety Data Sheets. Various microorganisms are used in enzyme production and a combination of enzymes from different strains gives different levels of performance [8].

The use of enzymes should be appropriate for each mill. There is no one-size-fits-all solution as the mills' conditions differ from one to another. The type of enzyme, the optimal dosage, the temperature, and the time should be studied for each mill if satisfying results are intended to be obtained. This approach not only will reduce the negative impacts of the enzyme limitations but also define the right amount of enzyme needed to reach a specific goal.

Fiber: Sustainability and Circular Economy

A recycled fiber has gone through at least one time the mechanical refining process. The fiber is already swollen, fibrillated and the lumen collapsed. Sending the same fiber into the mechanical process again will obviously reduce its length and strength. Enzymes can give the fiber a better performance by reducing the mechanical chopping, cracking, splitting, and tearing of the fiber [60]. Enzymes' effect on the fiber is mild compared to the mechanical bars.

Sustainability promotes the avoidance of natural resource depletion while the circular economy promotes the reusing of raw materials as long as possible [89]. Both concepts find their place in the papermaking process as long as the same fiber can be reused as long as possible. A recycled fiber lifecycle through refining bars is harsher than going through the enzymatic process. Enzymes, if needed, can also be used as a complementary fiber refiner to the mechanical refiner to reduce fiber degradation.

An enzymatic pulp properties improvement on the paper machine will reduce web break downtimes for the papermaker and also reduce the energy consumption in the mill. Improving the pulp and the paper properties with the enzymatic approach will not only improve the paper products but also improve the process of making the products more efficient and sustainable.

CHAPTER III

EXPERIMENTAL PROCEDURES

- **Central Composite Design**

Minitab was used to generate a central composite design experiment with 3 factors (dosage, time, and temperature) at 3 replicates. 60 runs were needed in total and hand-sheets were made from 4% consistency recycled bleached kraft pulp by following the Minitab randomized order (Appendix 1). Table 3-1 shows the factors and ranges used in the study.

Factors	**Low**	**High**
Dosage (mg/Kg)	200	500
Time (min)	30	60
Temperature (^oC)	30	50

Table 3-1. Factors and ranges

- **Pulp Preparation and Enzyme Treatment**

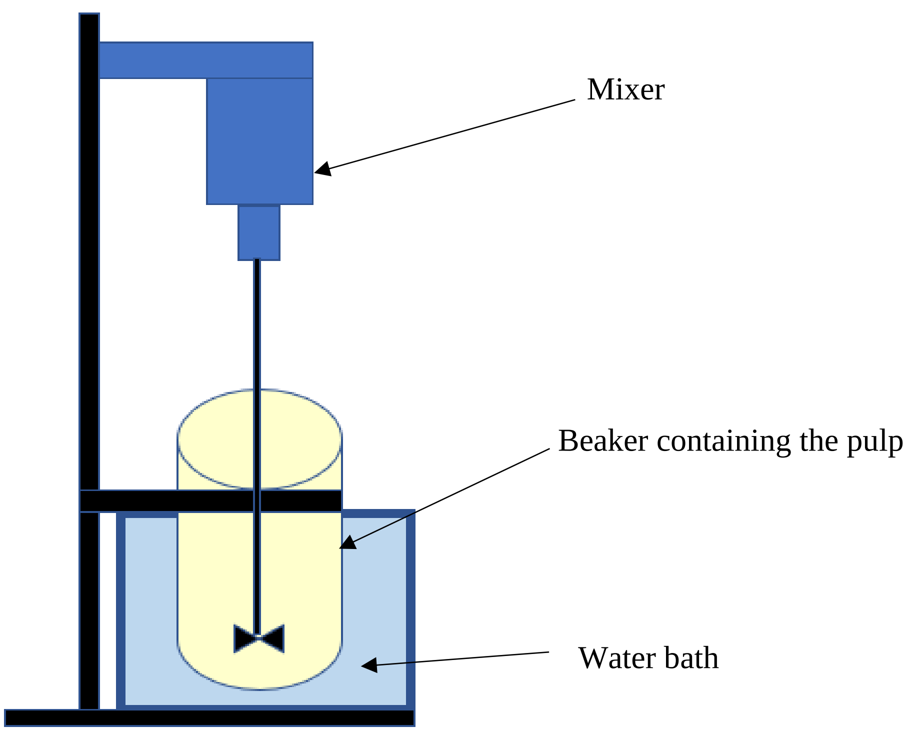


Figure 3-1. Pulp mixing apparatus

Figure 3-1 shows the schematic of the mixing apparatus during the experiment. The pulp was mixed continuously, and the temperature of the pulp was controlled and maintained with a water bath. The precaution was taken to prevent the container from touching the bottom of the bath and the pH was adjusted to 7.9 (average pulp pH in the mill). This solution is stock S_0. The corresponding dosage of enzymes was charged, and the pulp was mixed for the duration associated (Appendix 1). The enzyme activity was 4509.8 CNU (R)/g.

A sample calculation of the enzyme dosage is as follows for the test "Dosage 350 mg/Kg, Time 45 min and Temperature 40 C in Appendix1:

- In a clean 100 ml volumetric flask, 1 g of the concentrated enzyme was diluted to mark with deionized water. This is solution S_e with a density of 10 mg/ml.
- The volume of enzyme v_e is calculated using the formulae below:

$$m_{OD} = C * m_P \qquad Equation\ 1$$

$$m_e = D * m_{OD} \qquad Equation\ 2$$

$$v_e = \frac{m_e}{\rho_e} \qquad Equation\ 3$$

Where m_{OD} = mass of oven dry pulp in Kg, C = the consistency of the pulp in %, m_P= the mass of the pulp in Kg, m_e = the mass of enzyme needed in mg,
D = the corresponding dosage in the Minitab table (Appendix 1) in mg/Kg, v_e = the volume of the enzyme solution S_e needed in ml and ρ_e = the density of the solution S_e in mg/ml.

Using the equations 1, 2 and 3, v_e becomes:

$$v_e = \frac{D*C*m_P}{\rho_e} \qquad \text{Equation 4}$$

- Using the formula of equation 4, 2.8 ml of the solution S_e was added to 2000 g of 4% consistency pulp at 40 °C and timed for 45 minutes.

The temperature of the pulp was raised to boiling point at the end of the treatment to prevent residual effects of the enzymes during testing.

Aliquot of the stock S_0 was diluted to 0.3% consistency and the freeness was measured according to the TAPPI method T 227. The amount of pulp needed to make the 1000 ml solution for the test was calculated using:

$$v_i = \frac{C_f*V_f}{C_i} \qquad \text{Equation 5}$$

Where v_i = the amount of pulp needed for the dilution to 1000 ml, C_f = the final consistency (0.3%), v_f = the final volume (1000 ml) and C_i = the initial consistency of the pulp which is 4%.

Figure 3-2 Image of the Canadian Standard Freeness Tester

A Canadian Standard Freeness tester, manufactured by Robert Mitchell Inc., was used to measure the freeness [Figure 3-2]. The bottom lid of the tester was closed, and the freeness chamber was filled with 1000 ml of the 0.3 % consistency pulp. The top lid and the air valve were closed after the chamber was filled. A graduated cylinder was put under the side orifice of the tester. The bottom lid and the air valve were respectively open, and the drained water was collected in the cylinder. The temperature of the water was measured, and the volume was recorded. The freeness chart was used to make temperature corrections when needed. The freeness is reported in milliliters.

In addition, an aliquot of the stock S_0 was used to make hand-sheets according to the TAPPI method T205. The amount of pulp needed to make the hand-sheet was calculated using the following formula:

$$v_p = \frac{BW * A}{C} \qquad \textit{Equation 6}$$

Where v_p = the volume of the 4% consistency pulp needed in ml, *BW*= the basis weight of the sheet, *A*= the area of the mold screen, and C = the consistency of the pulp in %.

For a target hand-sheet of basis weight of 40 g/m^2, and a screen size of 201.6 cm^2, 20.2 ml of pulp was used.

Figure 3-3 Image of the Hand-sheet Mold

A hand-sheet mold [Figure 3-2] British Sheet Machine, manufactured by Robert Mitchell Inc, was used to make the hand-sheets. The pulp was loaded on the screen and the cylinder was filled with water. The water was drained after a perforated stirrer was used to disperse the fibers in the cylinder. Two blotting papers were put on the wet sheet and the sheet was manually pressed with a roller. The blotting papers and the sheet were gently removed from the screen and another blotting paper was used to sandwich the sheet. The sheet and the blotting papers were hydraulic pressed at 345 kPa (50 psig), and the sheet was carefully removed and dried in the drying ring. The weight of the dry sheet was divided by its area to calculate the basis weight.

Figure 3-4 Image of the Brightness Tester

The brightness of the hand-sheets was measured according to the TAPPI method T452. The brightness tester [Figure 3-3] Color Touch X, manufactured by Technidyne Corporation, was used during the measurement. The instrument was set on 45° illumination and 0° viewing geometry and measured the directional reflectance factor at 457 nm of the sheet. The sheet was loaded on the pad and pressed by the 1-kg backing weight. The start button was pressed to measure the brightness.

Figure 3-5 Image of the Tensile Tester

The tensile index of the hand-sheets was measured according to the TAPPI method T494. The Instron tensile tester 5965 [Figure 3-4], manufactured by Instron Corporation, was used to measure the tensile. The hand-sheets were cut into 2.54 cm (1 inch) strips and the strips were clamped between the jaws of the tester. The start button was pressed, and the tester stretched the strip until it broke. The tensile result displayed by the tester was recorded and divided by the basis- weight of the sheet to determine the tensile index. The tensile index is reported in Nm/g.

CHAPTER IV

RESULTS AND DISCUSSIONS

The freeness, the brightness, and the tensile index data are normal [Appendix 2]. The following *P-values table*, the *regressions equations, the main effects plots, the interaction plots*, and the *contour plots*, were respectively used to determine the significance of the factors [Table 1]and the best conditions to improve the freeness, the brightness, and the tensile index responses.

- ***P-Values***

	Freeness	**Brightness**	**Tensile Index**
Factors	***P-Values***	***P-Values***	***P-Values***
Dosage	**< 0.001**	**0.719**	**< 0.001**
Time	**< 0.001**	**0.726**	**< 0.001**
Temperature	**< 0.001**	**0.097**	**< 0.001**
Dosage*Time	**< 0.001**	**0.694**	**< 0.001**
Dosage*Temperature	**0.001**	**0.644**	**0.002**
Time*Temperature	**0.002**	**0.554**	**-**

Table 4-1. P-Values of Freeness vs Brightness vs Tensile Index

Table 4-1 shows the p-values for each factor vs each response; the p-values of the interactions between the factors are also shown. All the factors and their interactions are significant for freeness as the p-values are less than 0.05. On the contrary, all the factors and their interactions are not significant for the brightness as the p-values are greater than 0.05. Lastly, for the tensile index, all the factors and their interactions are significant as the p-values are less than 0.05 except for the interaction Time*Temperature.

- ***Regressions***

Three regression equations are generated from the experiment data. The equations are used to determine the predicted freeness, brightness, and tensile index based on the mill conditions.

The freeness regression equation:

Freeness = 218.2 + 0.0886Dosage + 0.761Time + 10.741Temperature - 0.000063Dosage*Dosage - 0.00424Time*Time -0.10647Temperature*Temperature + 0.003000Dosage*Time - 0.002417Dosage*Temperature - 0.02111Time*Temperature

The brightness regression equation:

Brightness = 82.615 + 0.00111Dosage + 0.0041Time - 0.0167Temperature - 0.000001Dosage*Dosage - 0.000081Time*Time + 0.000107Temperature*Temperature - 0.000007Dosage*Time - 0.000013Dosage*Temperature + 0.000162Time*Temperature

The tensile index regression equation:

Tensile Index = - 2.09 + 0.02090Dosage - 0.0512Time + 1.779Temperature - 0.01886Temperature*Temperature + 0.000486Dosage*Time - 0.000559Dosage*Temperature

The main objective is to keep the tensile index greater or equal to 42.2 Nm/g. The average pulp temperature is 40.8 ℃ and there is an estimation of 45 minutes for the pulp to be at the headbox from the enzyme injection point. The calculated dosage, using the tensile index regression model generated by Minitab, is 273.2 mg/kg oven-dry pulp. The expected freeness and brightness for the 273.2 mg/kg at 41.8 ℃ for 45 minutes are respectively 496 ml and 82.4 using the freeness and the brightness equations.

- ***Main effects and interaction plots***

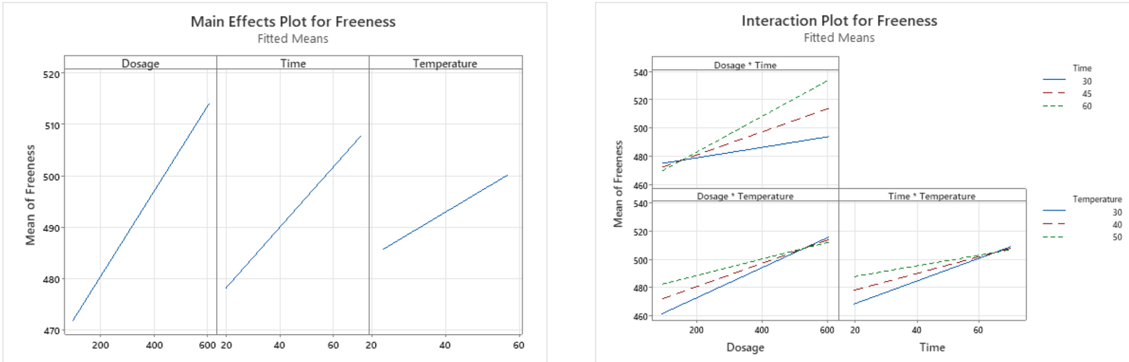


Figure 4-1. Main Effects and Interaction Plots of the Freeness

The main effects plot shows that the dosage has the most significant effect on the freeness followed by time. When observing the interaction plot, one can deduce that the overall mean of the freeness is high when the dosage, time, and temperature are high.

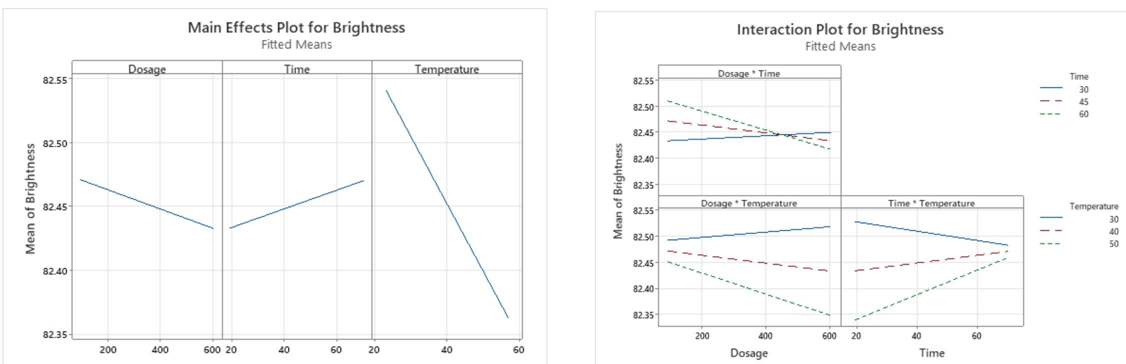
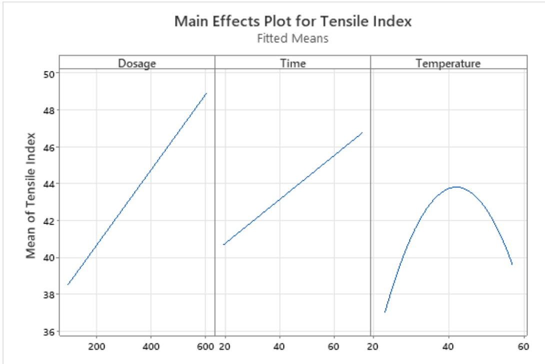


Figure 4-2. Main Effects and Interaction Plots of the Brightness

The main effects plot of the brightness shows that the temperature has the most significant effect. The interaction plot does not show significant improvement as all the changes occur between 82.30 and 82.55.



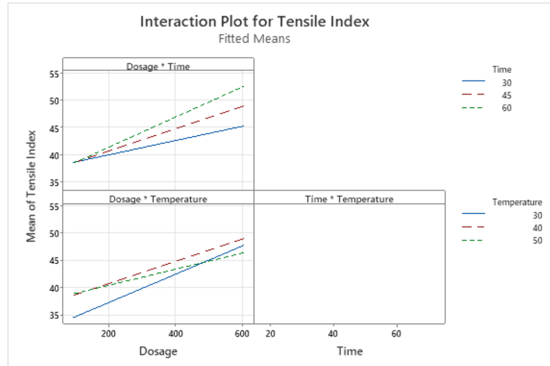


Figure 4-3. Main Effects and Interaction Plots of the Tensile Index

Referring to the main effects plot of the tensile index, the dosage has the most significant effect on the freeness followed by the time; the temperature can improve the tensile index, but an excessive temperature could reverse the improvement. The interaction plot shows that the overall mean of the tensile index is high when the dosage and time are at the highest.

- ***Contour Plots***

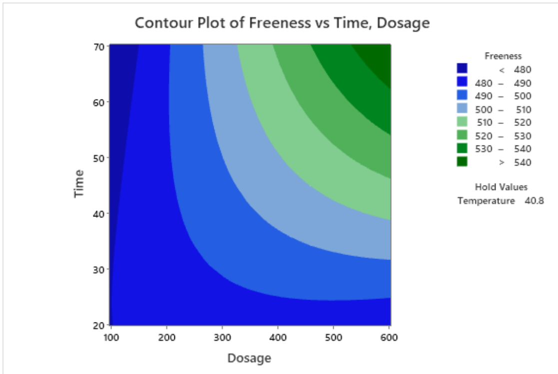


Figure 4-4. Contour Plot of Freeness vs Time, Dosage

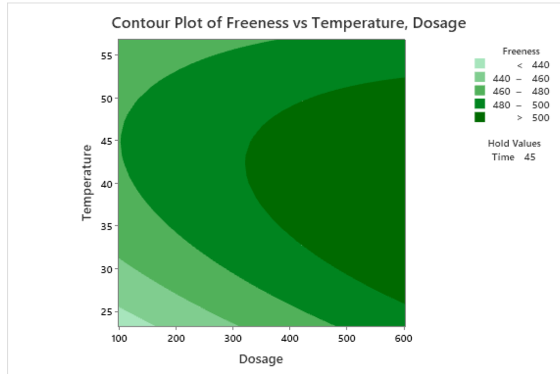


Figure 4-5. Contour Plot of Freeness vs Temperature, Dosage

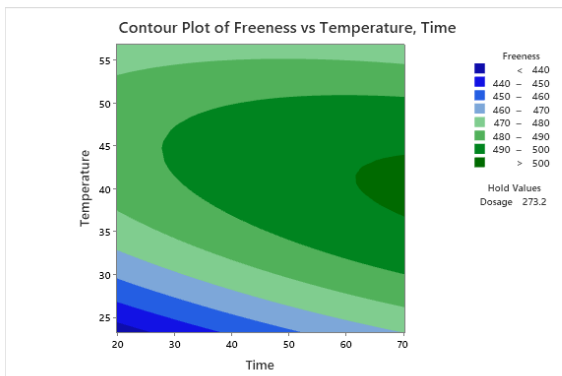


Figure 4-6. Contour Plot of Freeness vs Temperature, Time

The freeness increases when the temperature is held at 40.8 °C and both dosage and time increase [Figure 4-4]. The freeness increases, reaches a peak, and decreases when the time is held at 45 minutes and both dosage and temperature increase [Figure 4-5]; similar profile is seen when the dosage is held at 273.2 mg/Kg and the time and the temperature increase [Figure 4-6]. Overall, the enzymes increase the freeness in a limited range, but excessive use of the enzymes could reverse the freeness improvement.

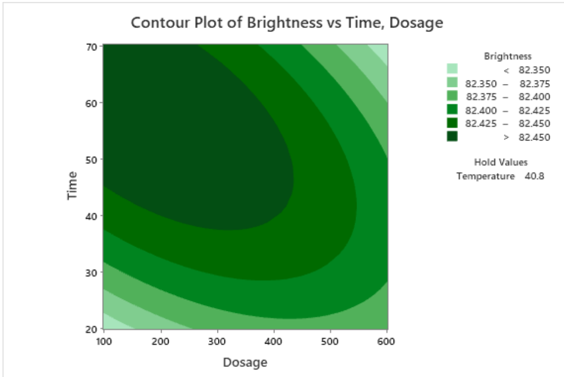


Figure 4-7. Contour Plot of Brightness vs Time, Dosage

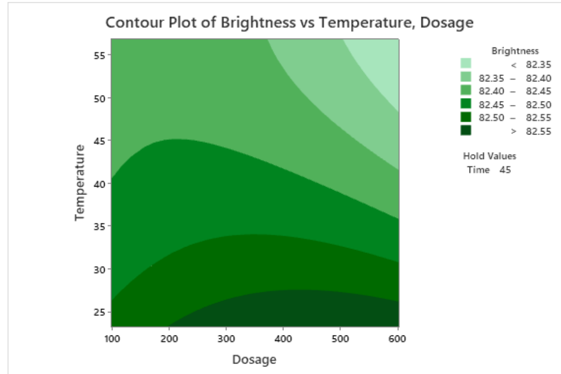


Figure 4-8. Contour Plot of Brightness vs Temperature, Dosage

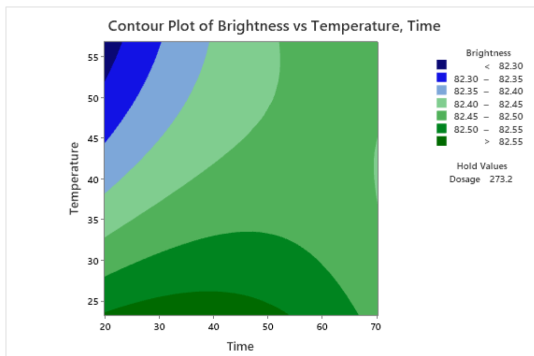


Figure 4-9. Contour Plot of Brightness vs Temperature, Time

Figure 4-7 shows the change in the brightness when the temperature is held at 40.8 °C and the time and the dosage increase; figure 4-8 shows the change in the brightness when the time is held at 45 minutes and the temperature and the dosage increase. Figure 4-9 shows the change in brightness when the dosage is held at 273.2 mg/Kg and the temperature and the time increase. One can deduce from figures 4-7, 4-8, and 4-9 that the brightness contour plots do not show significant change; the overall change lies between 82.30 to 82.55. The effect of the enzymes on the brightness appears not to be significant.

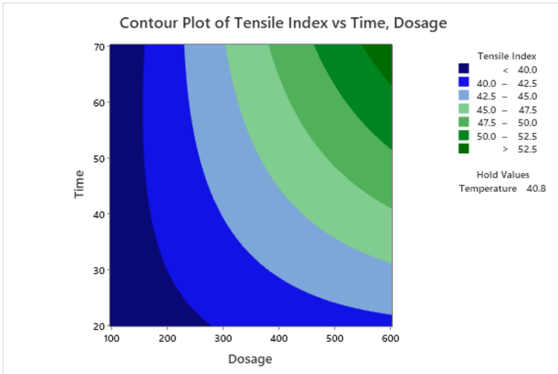


Figure 4-10. Contour Plot of Tensile Index vs Time, Dosage

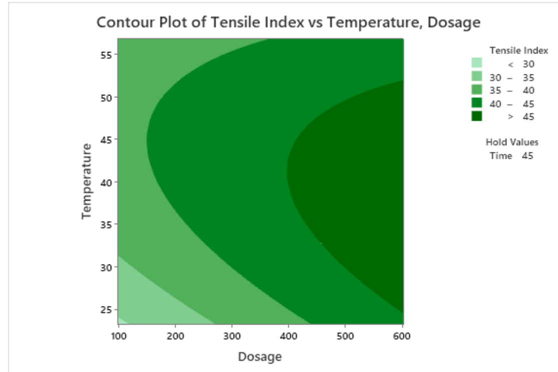


Figure 4-11. Contour Plot of Tensile Index vs Temperature, Dosage

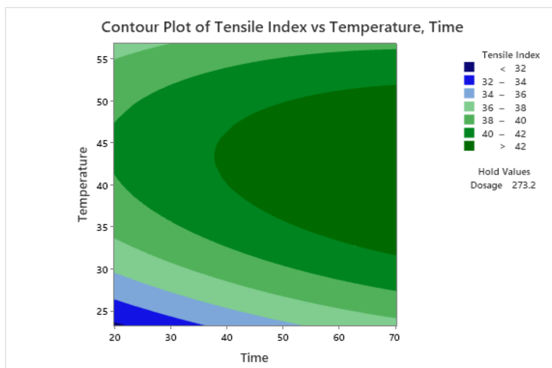


Figure 4-12. Contour Plot of Tensile Index vs Temperature, Time

Referring to the contour plots of the tensile index [Figure 4-10], the tensile increases as the time and dosage increase when the temperature is held at 40.8 °C. When the time is held at 45 minutes and both the dosage and the temperature increase, the tensile also increases [Figure 4-11]; however, the tensile reaches a peak and starts decreasing. A similar profile is found when the dosage is held at 273.2 mg/Kg and both the time and the temperature increase [Figure 4-12]. Like the freeness, the enzymes increase the tensile in a limited range, but excessive use could reverse the improvement. Comparing the freeness and the tensile contour plots, it appears that the change or the improvement occurs faster for the tensile than the freeness.

- ***Model Verification by Real Industrial Process***

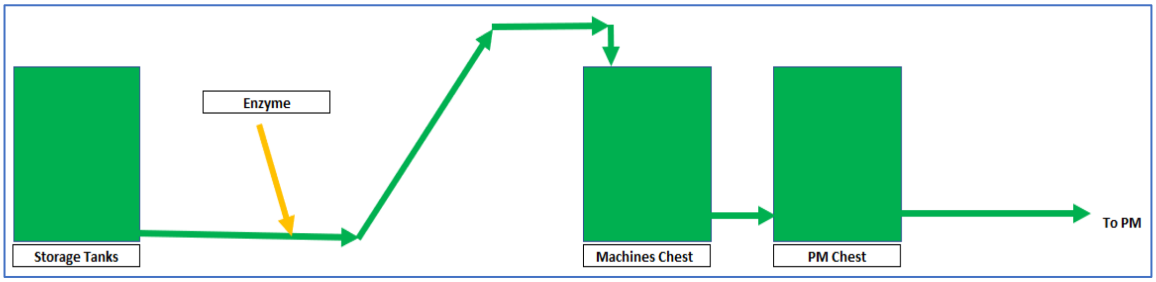


Figure 4-13. Illustration showing the injection point of the enzyme.

Figure 4-13 shows the injection point of the enzyme into the papermaking process. The consistency of the pulp in the storage tanks is 4%; the flow from the storage tanks to the machines' chest is 300 gpm. The system is automated, so the enzyme applied is 273.2 mg/kg oven-dry pulp.

Referring to the central composite design model, a dosage of 273.2 mg/kg at an average temperature of 40.8 °C for 45 minutes should give a tensile index of 42.2 Nm/g and a freeness of 496 ml. The actual results were 44.7 Nm/g (5.2 % error) and 481ml (3.1% error) respectively for the tensile and the freeness. The average brightness is 82.2 and the expected value is 82.4. The historical values are 38.5 Nm/g, 463 ml, and 82.4. The overall tensile increase is 16.1% and the freeness increase is 3.9%. The Table 4-2 summarizes the results:

	Historical Results	Lab Results	Mill Results	Standard Deviation	Percent Improvement
Tensile index (Nm/g)	38.5	42.2	44.7	1.76	+16.1%
Freeness (ml)	463	496	481	9.16	+3.90%
Brightness	82.4	82.4	82.2	0.61	-0.24%

Table 4-2. Historical vs Actual Results

The increase in the tensile above the predicted value is mainly due to traces of materials in the mill water. In the laboratory experiment, deionized water was used but the dilution was done in the mill with water that contains traces of fines, starch, filler, monosaccharides, disaccharides, and fibers [90,91]. It will not be cost-effective to purify the mill water as deionized water and use it on the paper machine. The fibers' orientation and the residual chemicals on the paper machine could also be another source of difference between the predicted and the actual tensile results. Another reason for the tensile increase could be the press section of the paper machine; the press section assists water removal from the wet web and improves inter-fiber bonding by increasing the fiber-to-fiber contact [26,58]. The pressure of the web at the press section on the machine is obviously higher than the manual pressure using the TAPPI T 205.

Although the residual materials in the mill water contribute to the increase of the tensile, the drainage on the contrary is reduced. Damages to the fibers as short fibers or fines during the pulping operation reduce the pulp freeness [92]. The mill water obviously contains fines, filler, and residual chemicals [90,91]. These are some of the reasons why the freeness of 481 ml was below the expected value of 496 ml but above the historical value of 463 ml. Overall, there is a slight improvement in the freeness (3.9%) and the use of the enzymes will not cause a negative impact on the paper machine's runnability.

There was no significant difference between the predicted brightness and the actual brightness (82.2 vs 82.4). The enzymes used in this study are probably not designed to remove residual lignin or remove residual contaminants from the pulp [92,93]. This outcome was expected referring to the p-values in Table 4-1.

The results from this study were also compared to other findings from different authors; the data are summarized in Table 4-3:

Enzyme	**Tensile Index Improvement (%)**	**Freeness Improvement (%)**	**Authors**
Cellulase (complex)	+15.0	-	Jain and Jain (2021) [94]
Cellulase and Xylanase	+14.54	+18.3	Kumar and Dutt (2021) [95]
Cellulase (complex)	+14.7-17.4**	+11.1	Tripathi et Al (2018) [96]
Endoglucanase	+25.2	-	Huang et Al (2010) [76]
Cellulast 1.5L	+34.4	+80	Gil (2009) [76]
Viscozyme L	+43.4	-36	Gil (2009) [76]

Table 4-3. Tensile and Freeness Data Comparison

*** Tensile index not reported; breaking length reported instead (the breaking length is the length of paper strip that, if suspended vertically from one end, would break by its own weight.)*

Overall, enzymes can be used to improve the properties of the pulp and paper. The tensile improvement ranges from 15% to 43% while the freeness varies between -36% to 18%. The results from this study, 16.1% for the tensile index and 3.9% for the freeness, are within these ranges and are acceptable based on the need of the paper mill; the tensile improvement reduced the sheet breaks by more than 50% which is acceptable for the mill. Other improvements such as the paper machine rolls and doctor blades maintenance, the overall web tension adjustment, and personal training could further reduce the sheet breaks.

CHAPTER V

CONCLUSION

Papermakers face many sheet break challenges on the paper machine when using recycled fiber. The time used to rethread the machine after the web breaks makes the process inefficient. As paper makers are under pressure from environmentalists to reduce virgin fiber production, efforts are needed to improve the reusability of recycled fiber.

Recycled fiber is already weak due to previous refining; the refining process not only collapses, delaminates, and fibrillates but also shortens, curls, and cracks the fiber. A better way to re-refine the recovered fiber is to use a smooth approach that encourages sustainability and circular economy. Enzymes are proven to be a good candidate to improve the quality of recycled pulp and paper. Determining the right dosage of enzymes and the right conditions in which enzymes need to be charged are critical for the quality of the web.

A central composite design model, using dosage, time, and temperature as factors is used to determine the amount and the conditions in which cellulases can improve the sheet strength on the paper machine. The enzymes fibrillate the surface of the fibers and also produce short polysaccharide chains; as a result of these modifications, the hydrogen bonding sites increase, and the sheet tensile increases. The freeness of the pulp and the brightness of the sheet are also studied. The tensile of the sheet and the freeness of the pulp improved respectively by 16.1% and 3.9% compared to the historical values. The effect of the enzymes on the brightness is not significant as predicted by the model.

The surface modification of the fibers by the enzymes not only improves the fibers' properties but also makes the fibers more sustainable. The enzymatic approach can ultimately increase the sheet tensile with less damage to the fibers; this approach promotes better recyclability and reusability and is beneficial for the circular economy.

CHAPTER VI

RECOMMENDATIONS

Mechanical refining is traditionally used to improve the fiber structures for better stronger “kraft” paper. It is traditionally known that the degree of recycling of the fiber is five to seven times [26, 66]. This study proves that enzymes can be used to improve fiber properties as well, but the degree of recycling of the enzymatic refined fiber is not known. If the goal of the circular economy is to reuse the raw material as many times as possible, more investigations are needed to determine which refining mechanism conserves the fiber longer.

The work of Kouko et al. [65] shows that the virgin fiber loses about 24% of its strength after the first refining. More study needs to be done to determine if the fiber strength loss is linear as the degree of recycling increases or if it will reach a plateau after a certain number of cycles.

Finally, the enzymatic approach to improve the tensile, freeness, and brightness can be seen as a cheaper approach compared to the mechanical approach. More investigations need to be done on how the enzymes are made and used. The enzymes' production and consumption may seem cheap or efficient but their effects on health, safety, environmental, and global warming standpoints are needed.

APPENDIX

- ***Appendix-1***

Central Composite Design

Design Summary

Factors:	3	Replicates:	3
Base runs:	20	Total runs:	60
Base blocks:	1	Total blocks:	1

α = 1.68179

Point Types

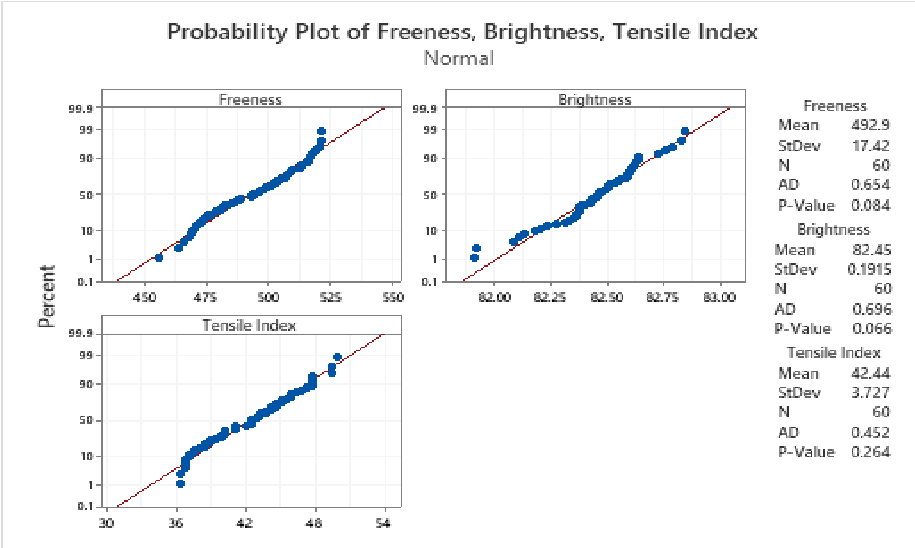
Cube points:	24
Center points in cube:	18
Axial points:	18
Center points in axial:	0

Two-level factorial: Full factorial

↓	C2	C3	C4	C5	C6	C7
	RunOrder	PtType	Blocks	Dosage	Time	Temperature
1	1	0	1	350.000	45.0000	40.0000
2	2	0	1	350.000	45.0000	40.0000
3	3	1	1	200.000	30.0000	50.0000
4	4	-1	1	350.000	45.0000	23.1821
5	5	-1	1	97.731	45.0000	40.0000
6	6	0	1	350.000	45.0000	40.0000
7	7	-1	1	97.731	45.0000	40.0000
8	8	1	1	500.000	60.0000	30.0000
9	9	1	1	200.000	60.0000	50.0000
10	10	0	1	350.000	45.0000	40.0000
11	11	-1	1	350.000	19.7731	40.0000
12	12	-1	1	350.000	45.0000	56.8179
13	13	-1	1	602.269	45.0000	40.0000
14	14	1	1	200.000	30.0000	30.0000
15	15	1	1	500.000	60.0000	30.0000
16	16	1	1	500.000	30.0000	50.0000
17	17	-1	1	350.000	70.2269	40.0000
18	18	0	1	350.000	45.0000	40.0000
19	19	0	1	350.000	45.0000	40.0000
20	20	-1	1	350.000	45.0000	23.1821
21	21	-1	1	350.000	19.7731	40.0000
22	22	1	1	500.000	30.0000	30.0000
23	23	0	1	350.000	45.0000	40.0000
24	24	1	1	200.000	30.0000	50.0000
25	25	0	1	350.000	45.0000	40.0000
26	26	-1	1	350.000	45.0000	56.8179
27	27	1	1	200.000	60.0000	50.0000
28	28	0	1	350.000	45.0000	40.0000
29	29	0	1	350.000	45.0000	40.0000
30	30	1	1	500.000	60.0000	50.0000

↓	C2	C3	C4	C5	C6	C7
	RunOrder	PtType	Blocks	Dosage	Time	Temperature
31	31	-1	1	350.000	70.2269	40.0000
32	32	-1	1	97.731	45.0000	40.0000
33	33	1	1	200.000	60.0000	30.0000
34	34	1	1	200.000	60.0000	50.0000
35	35	1	1	200.000	60.0000	30.0000
36	36	0	1	350.000	45.0000	40.0000
37	37	-1	1	350.000	70.2269	40.0000
38	38	-1	1	350.000	45.0000	23.1821
39	39	1	1	500.000	30.0000	50.0000
40	40	0	1	350.000	45.0000	40.0000
41	41	1	1	200.000	30.0000	30.0000
42	42	1	1	500.000	30.0000	30.0000
43	43	1	1	200.000	30.0000	50.0000
44	44	1	1	200.000	30.0000	30.0000
45	45	1	1	500.000	30.0000	50.0000
46	46	-1	1	350.000	45.0000	56.8179
47	47	0	1	350.000	45.0000	40.0000
48	48	1	1	500.000	60.0000	50.0000
49	49	0	1	350.000	45.0000	40.0000
50	50	0	1	350.000	45.0000	40.0000
51	51	0	1	350.000	45.0000	40.0000
52	52	0	1	350.000	45.0000	40.0000
53	53	-1	1	602.269	45.0000	40.0000
54	54	1	1	500.000	60.0000	30.0000
55	55	0	1	350.000	45.0000	40.0000
56	56	1	1	500.000	30.0000	30.0000
57	57	1	1	500.000	60.0000	50.0000
58	58	1	1	200.000	60.0000	30.0000
59	59	-1	1	602.269	45.0000	40.0000
60	60	-1	1	350.000	19.7731	40.0000

Appendix-2



Probability Plot of Freeness, Brightness and Tensile

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