



Totally Chlorine Free (TCF) Multistage Peroxide Bleaching of Kenaf Bast Pulp at Different Duration

**Jagedeswary a/p Erison
J19AO139**

**A reported submitted in fulfilment of the requirements for the
degree of Bachelor of Applied Science (Forest Resources
Technology) with Honours**

FACULTY OF BIOENGINEERING AND TECHNOLOGY

UMK

2024

DECLARATION

I declare that this thesis entitled “Totally Chlorine Free (TCF) Multistage Peroxide Bleaching of Kenaf Bast Pulp at Different Duration” is the results of my own research except as cited in the references.



Signature : _____

Student's Name : Jagedeswary A/P Erison

Date : 24/02/2024

Verified by:

Signature : _____

Supervisor's Name : _____

Stamp : _____

Date : _____

ACKNOWLEDGEMENT

I would want to thank University Malaysia Kelantan for giving me the opportunity to learned new things through a project as part of my bachelor education. This final year project guided me a lot in developing my personal values and make me a better person.

I would like to express profound gratitude to my supervisor Dr Boon Jia Geng for his insightful suggestions, guidance, constant support, time and patient instruction he provided throughout the whole process of my research project. Your advice and willingness to give the time has been greatly appreciated and very helpful to me during the project's completion. In this aspect, I am eternally grateful to you.

I also want to extends my gratitude to the faculty and staff of Faculty of Bioengineering and Technology, who have supported and assisted me during my studies. Besides that, I would like to express my gratitude to all laboratory assistants for the assistance with all the issues that I had in the lab.

My earnest appreciation to all the internal examiners and FRIM technicians for all their guidance and assistance in helping me to testing the paper. My gratitude has also been extended to coordinator of Final Year Project, Dr Nurul Akmar Binti Che Zaudin and Dr Nur Sakinah Binti Mohamed Tamat, Lecturer, Faculty of Bioengineering and Technology. I would like to thank all my fellow undergraduate students who are always willing to share the ideas, opinion and the sincere comments.

Finally, I would like to thank my family deeply for their love. They always give me the greatest moral support in my life and prayed for my success. That encouragement to me make me to complete the research project successfully. Thank you.

ABSTRACT

There is an increasing of global demand of paper and needed short rotation pulpwood. Hibiscus cannabinus also known as Kenaf is a species of fast-growing warm-season annual. There are still limited of scholarly information of Kenaf as pulpwood. Kenaf fibre is much suitable to bleached using mild bleaching agent such as hydrogen peroxide. This research aims to provide information of multistage peroxide bleaching effect on the mechanical properties and optical properties of handsheet made from the pulp that derived from kenaf. This including tensile strength and bursting strength. The process of pulping is for remove the lignin without loosing the fibre's strength. Bleaching stages are designed to completely remove the remaining lignin because only 80% to 90% maximum can removed during the pulping. Pulp produced from using Kenaf was bleached with hydrogen peroxide at the 3%wt based on the weight of pulp, respectively. According to standard of TAPPI, the mechanical properties and brightness of handsheet made from bleached pulp were evaluated. Handsheet made from bleached pulp have had their brightness improved by increasing the bleaching time. Moreover, bleaching duration of 60 minutes produces pulp with maximum brightness. On the other hand, mechanical properties of handsheet were increase from 0 minutes to 60 minutes. Multistage peroxide bleaching to a certain extent are capable of improving both the optical properties and mechanical properties of handsheets made from Kenaf pulp. Excessive bleaching times can also have a negative impact on the mechanical properties of kenaf bast handsheets. Based on the overall results, this study can conclude that kenaf bast pulp has the potential to improve the properties of handsheet.

Keywords: Kenaf, TAPPI standard, Hydrogen peroxide, mechanical properties, fast-growing

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ABSTRAK

Terdapat peningkatan permintaan global kertas dan memerlukan kayu pulpa putaran pendek. *Hibiscus cannabinus* juga dikenali sebagai Kenaf ialah spesies tahunan musim panas yang cepat tumbuh. Maklumat ilmiah Kenaf sebagai kayu pulpa masih terhad. Gentian Kenaf sangat sesuai untuk diluntur menggunakan agen peluntur ringan seperti hidrogen peroksida. Penyelidikan ini bertujuan untuk memberikan maklumat kesan pelunturan peroksida berbilang peringkat ke atas sifat mekanikal dan sifat optik kertas yang diperbuat daripada pulpa yang berasal daripada kenaf. Ini termasuk kekuatan tegangan dan juga kekuatan pecah. Proses pulping adalah untuk mengeluarkan lignin tanpa kehilangan kekuatan serat. Peringkat pelunturan direka bentuk untuk mengeluarkan sepenuhnya lignin yang tinggal kerana hanya 80% hingga 90% maksimum boleh dikeluarkan semasa pulpa. Pulpa yang dihasilkan daripada menggunakan Kenaf telah dilunturkan dengan hidrogen peroksida pada berat 3% berat berdasarkan berat pulpa, masing-masing. Mengikut piawaian TAPPI, sifat mekanikal dan kecerahan kertas yang diperbuat daripada pulpa yang diluntur telah dinilai. Kertas yang diperbuat daripada pulpa yang diluntur telah dipertingkatkan kecerahannya dengan meningkatkan masa pelunturan. Selain itu, tempoh pelunturan selama 60 minit menghasilkan pulpa dengan kecerahan maksimum. Sebaliknya, sifat mekanikal kertas meningkat daripada 0 minit kepada 60 minit. Pemutihan peroksida berbilang peringkat pada tahap tertentu mampu meningkatkan kedua-dua sifat optik dan sifat mekanikal kertas yang diperbuat daripada pulpa Kenaf. Masa pelunturan yang berlebihan juga boleh memberi kesan negatif terhadap sifat mekanikal kertas kulit kenaf. Berdasarkan keputusan keseluruhan, kajian ini dapat menyimpulkan bahawa pulpa kulit kenaf berpotensi untuk meningkatkan sifat-sifat kertas.

Kata kunci: Kenaf, standard TAPPI, Hidrogen peroksida, sifat mekanikal, pertumbuhan cepat

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LIST OF ABBREVIATIONS

OECD	Economic Co-operation and Development	1
CEPI	European Paper Industry Confederation	1
ARS	United States Agricultural Research Service	2
EC	Elemental Chlorine	2
TCF	Total Chlorine Free	3
ECF	Elemental Chlorine Free	2
NaOH	Sodium Hydroxide	25
Na ₂ S	Sodium Sulfide	25
Cl	Chlorine	12
ClO ₂	Chlorine dioxide	12
H ₂ O ₂	Hydrogen peroxide	12
O ₂	Oxygen	12
H ⁺	Hydrogen	14
-OOH	Perhydroxyl ions	14
ISO	International Organization for Standardization	15
H ₂ O	Distilled water	24
TAPPI	Technical Association of Pulp and Paper Industries	28

LIST OF SYMBOLS

°C	Temperature (Degree Celcius)	10
°F	Temperature (Fahrenheit)	17
%	Percentage	1
mm	Millimetre	11
G	Gram	27
N	Normality	28
gsm	Grammage	27
wt%	Percentage by Weight	25
KPa m ² /g	Kilopascal-meter square per gram	30
m ²	Meter square	27
Nm/g	Newton meter per gram	32
g/m ²	Grams Per Square Meter	28
cm	Centimeter	5
kg/cm ²	kilograms per square centimeter	20

CHAPTER 1

INTRODUCTION

1.1 Background of Study

Over the world, papers shaped the society and consider it as one of mankind's most great invention. Global papers production continued decline moderately for several years from the year 2018 to year 2020 but will hit a record high of 415 million tons in 2025. If compared to year 2020, paper production in year 2021 increased by 4%, which means that paper production has increased significantly. Global paper demand in year 2018 was 415 million tons (Ismail et al, 2020). Digitization continues the downward trend in production of newsprint, printing paper and writing paper. Based on findings by the organization of Economic Co-operation and Development (OECD), these papers were declined by an average of 2.4 percent per year from 2010 to 2017, then dramatically accelerated to 8.6% per year from 2018 to 2020. The European Paper Industry Confederation (CEPI) has shown that sanitaries and household papers production will increase around 2.2 % in 2022 compared to 2021, accounting for 9.3 % of the total papers and board productions (Wortmann, 2023).

Expecting the world demand for papers and paperboard will grow by about 1% annually through 2030 (Hodgson et al, 2022). Measures to increase material efficiency can help limit production increases. China produces more than 125 million tons of paper and paperboard and making that as the biggest paper producer around the world by 2021. Meanwhile, China has launched its 14th Five-Year Plan (2021-2025), envisioning building a circular economy with 60 million tons of waste papers by 2025. Decarbonization roadmap released by Japan for its pulp and paper industry in early 2022 (Hodgson et al, 2022). New standards have implemented recently in Indonesia to improve energy and material efficiency in paper production for its paper and corrugated paper industry.

Malaysia's first and newest greenfield paper mill is CHH Pasific Papers (CHHPP) Sdn.Bhd. located in Bentong, Malaysia (Zuryati, 2018). Malaysia's three major industries are pulp manufacturing, printing and publishing, and paper and paper products. In addition, paper production is dominated by wrapping papers such as kraft paper, test liner and medium paper. Malaysia's paper product production index stood at 133.8, up more than 17 percentage points in 2021 from the previous year, according to the Bureau of Statistics and Research. Domestic paper product production declined in 2020, but increased again in the following year (International, 2020).

Subsequently, paper-based products can be made from a variety of wood pulps, fibre plants and recycled materials. Wood chips are one of the most common sources today and can be made from logs, but they are also often obtained as a residual product from sawmills, furniture factories and other wood related industries (Biering, 2021). Objects embedded in trees can end up as wood chip contaminants. Pulp and paper mills have been known to use old fence posts, metal bolts and even bullets.

In 1960, the United States Agricultural Research Service (ARS) studied 500 plants as non-wood alternatives to paper and Kenaf was chosen as the best among them (Alexopoulou et al, 2007). Countries like America South Kenaf is a hemp like fast-growing plant that grows well in warm and humid places. At the beginning of the 20th century, the kenaf plant is native to East-Central Africa and was introduced to Eastern Europe. There are two main fibres that are separated from the stem in the outer layer, while the core fibre is in the inner stem in this fast-growing species. The outer core of this species contains 40% fibre similar to softwood fibre and the inner core is similar to hardwood. The lignin content of kenaf is relatively much lower and the cellulose content is comparable to that of wood (Montgomery, 2018). The plant's cell wall contains lignin, a naturally occurring substance that turns paper yellow when left untreated. Typically, most trees used in papermaking contain 25% lignin, but kenaf contains only 12.5% lignin. That lower lignin content means less energy and chemical use in the pulping process, especially when pulp bleaching is involved.

Raw pulp is high in lignin and discolorations; therefore, it needs bleaching process to produce the white papers recommended for many products. Chlorination and oxidation are often used to further remove lignin from fibres by dissolving excess lignin from the pulp (Gao et al, 2022). For example, there are chlorine gas, hydrogen peroxide, chlorine dioxide, sodium hypochlorite and oxygen. The chlorine in the traditional pulp bleaching method called Elemental

Chlorine (EC). The process releases huge amounts toxic chemical compounds known as dioxins and another is furans. To solve the problem, the industry of pulp and paper has adopted TCF which is Totally Chlorine Free bleaching technology and the Elemental Chlorine Free (ECF) bleaching technology. However, TCF bleaching considered relatively more environmentally friendly compared to other bleaching cycles. The most common TCF agents for pulp bleaching are oxygen, ozone, peroxides and peracids, but no single TCF agent can bleach pulp to full brightness without impairing its properties.

1.2 Problem Statement

The paper business has expanded within the past fifty years. Nonetheless, due to the production of chlorinated organic compounds, the pulp and paper industry is acknowledged as the most polluting sector. For instance, chlorinated furans and dioxin. This led to persistent pollutants in the bleaching sequence of conventional by use the elemental chlorine and its compounds as the bleaching agent.

Instead of polluting and jeopardizing the environment and society, a solution is introduced to overcome the problem. The totally chlorine free (TCF) sequence were applied in Malaysia for bleaching the pulp. Therefore, this project was proposed to produce full bleached pulp from kenaf by using TCF bleaching sequences.

1.3 Objectives

The experiment was carried out with objectives:

1. To determine the TCF sequence effect on strength properties of whole kenaf fibres.
2. To evaluate the influence of different duration on the bleaching effect of peroxide on bast pulp.

1.4 Scope of Study

This research includes the determine the TCF sequence effect on strength properties and also to evaluate the influence of different duration levels on the bleaching effect of peroxide on kenaf bast pulp. The performance was determine based on the strength properties of kenaf bast pulp, including tensile strength, tearing resistance, brightness, folding endurance, bursting strength and opacity. The duration influence on kenaf pulp bleaching will affect the strength properties of bast pulp.

1.5 Significant of Study

Bleaching kenaf bast pulp with TCF sequence produce paper that requires less energy while reducing substantially environmental pollution. Basically, the bast fibres of kenaf are more suitable for paper industries due to its lower of lignin content, higher of cellulose content, and lower of hemicellulose content which is compared to core of fibres. Research of this study will indicate whole stem of kenaf as an attractive raw material of forest resources where more suitable to high quality of printing paper production and other paper related products. This is to ensure that the paper produced in a good quality and cost saving plan for paper industry.

CHAPTER 2

LITERATURE REVIEW

2.1 Kenaf

Kenaf known as *Hibiscus cannabinus* is a warm-season annual species belonging to the malvaceae which is as same as plant family like okra and cotton (Ludvíková et al, 2019). Kenaf plants under favourable condition it able to grow until height of 20 feet. The fourth or fifth months of growing season the heights commonly average between 8 to 14 feet. The branches may develop or not and they depend on the cultivar, growing conditions and seed spacing. After the planting periods around five to eight months can harvest 6 tons to 10 tons of dry matter per acre (Ibrahim et al, 2019). The kenaf flower are 8-15 cm diameter in white or yellow with the centre of reddish to maroon coloured or dark purple as shown below Figure 2.1.



Figure 2.1: Kenaf plant

(Source: Angel Duenas-Lopez, 2020)

Kenaf has used as one of the source of fibre for make cordages or coarses fabrics. Kenaf used commonly as a replacement of jute. Fiber of kenaf is found in the bast and core as shown in Figure 2.2. Basically, there are two different kind of fibres the stalk consist and it is outer fibre which is bast and inner fibre called as core. The inner fibre core comparable to hardwood fibres and outer fibre bast comparable to softwood tree fibre. It became an alternative reinforcement for composite products. Northern Africa was first domesticated and used the kenaf. People at Africa used to called kenaf plants as ‘Guinea hemp’. Although it has been used in Africa first, for long it been used throughout world. Kenaf cultivated almost 3000 years before by the Egyptian people. They also used to eat kenaf leaves and used to feed animals. India has been producing and using kenaf for the last 200 years. In India particularly the Manipur people cooked and eat the kenaf leaves, where also called as *sougri* there (Islam, 2019). Russia started in 1902 the producing of kenaf and in 1935 introduced crops to China. The kenaf crop has been introduced into Southern Europe in the early of 1900s. Kenaf mostly grows in countries like Senegal, India, USA, Mexico and also China. The third traditional world crop after the bamboo and wood is kenaf fibres where they originated from Asia and also Africa (Tholibon et al, 2019).

In the West until the late 18th century, kenaf was unknown, then became popular when sacking and cordage made of fibre were introduced to Europe (Kiron, 2021). Kenaf remained less important and little known as a bagging material until the second World War, the shortage of jute and also other bagging fibre is the main reason where there are new interest in people followed after the world war also, due to insufficient supply of materials that established and rising prices (Islam, 2019). Kenaf production has been fairly stable throughout the years, although many producers have go through decline of substantial in 1999. Countries like India, Nepal, China, Bangladesh, Thailand and Myanmar are the main producers of kenaf (Kiron, 2021).

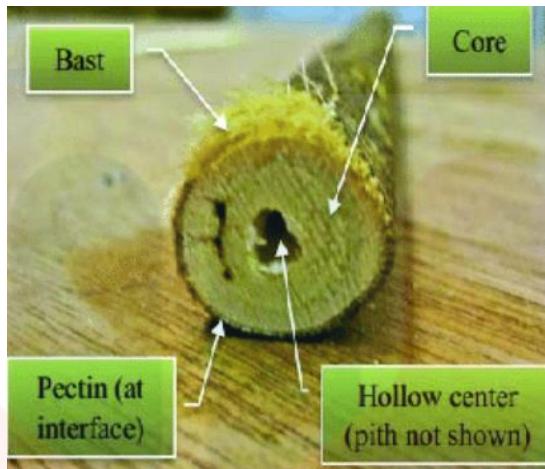


Figure 2.2: Physical appearance of Kenaf plant

(Source: Amin et al, 2017)

The demand for natural fibres is increasing around the world due to their renewable and biodegradable properties. Variety of fibres as raw materials the textile industry using (Gray, 2022). Several fibres are well known by people and especially used it in before civilization year, as well as during modern era and kenaf fibres is one of that. Kenaf fibres are well-known fibres by natural used as a reinforcement especially in the composites of polymer matrix. Kenaf was came from the plant named *Hibiscus cannabinus* and used it as fibre source to make coarse fabrics and cordage. It is mainly used as a substitute for jute. Kenaf fibres are found in shell and kernel. Kenaf fibres are gain an increasing attention as reinforcement for the production such as composite products because of it cost is low, environmental impacts reduce and also their mechanical properties are attractive (Sapuan et al, 2018).

Kenaf known as very sustainable fibre, because of its rate of growth and replenish ability. It did not need a lot of water for cultivation and also for processing. Besides that, almost there no fertilizers or the pesticides are used for cultivation process. The water separating the kenaf fibres, where mechanical retting and water retting combination is based on facilities and proficiency in site. Tensile strength and the chemical composition for fibres of kenaf shows the great variabilities in each location and for every technique in processing used (Abdullah et al, 2020). The visual observation and also colour tests indicate kenaf fibres, when soaked in water for a long time, have higher luminosity and finer fibres. A slightly decrease in absorption of moisture observed with an increase in crystallinity index. Commercialization increasement of kenaf appears to be limited not by agricultural production or the availability of suitable harvesting and

processing system, but for the harvesting understanding and production systems also involved in production of kenaf. Kenaf production and products will develop the management of the culture and continues to compete in the market place.

Fibers of kenaf has been used to make textiles for over thousands years. The kenaf can grow in many parts in the world. For example, the countries like United States making fibres as a prime candidate for use by the local fibre and the textile manufacturers. Kenaf trees can grows very quickly. This shows that only less risk when over-harvesting or drive to extinction to meet the production requirements. This plant grown at places where not freezing, they also been grow a year round. The kenaf have the absorb ability where can absorb a large amount of CO₂, a greenhouse gas, which is three times more than a single tree. They also convert more CO₂ during growth than rainforests. In a single growth cycle, each hectare of kenaf uses as much carbon dioxide as 20 cars emit annually (Thomas, 2019). It also can improve the soil conditions while fixing nutrients of soil.

2.2 Paper

Most paper pulp comes primarily from as well as bamboo, cotton, and a variety of other plant materials. Materials such as China clay are often added to the smooth paper subsequently used for magazines, packaging. Additionally, it can be printed with a more colourful and glossy finish. Many different tree species can be used for make paper. However, hardwoods make up the bulk of the fibre in paper, while softwood fibres are used more for strength. Softwoods are very valuable for paper due to its long fibres in the wood (DeAngelis, 2022).

Aside to that, fibre of plant is a type of natural fibres that is obtained from the various plants as shown in Figure 2.3. It is made of cellulose, complex carbohydrate which are strong, durable, and versatile. These fibre plants usually used in the textiles and paper production. Plant fibres can be classified into two namely primary and secondary where it would be depends on their utility. Primary utilities such as hemp, jute and kenaf are usually stronger and have a greater length to width ratio compared to other plant fibres. Secondary utilities such as coir, pineapple are fibres extracted from plants which have renewable sources and also polymer-based material

supplements. These plant fibres are environmentally friendly, renewable, inexpensive, partially or fully recyclable and biodegradable material.

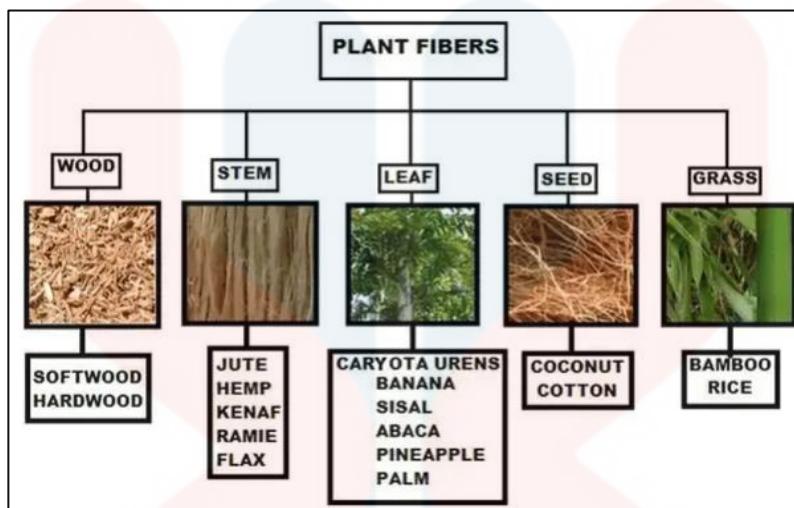


Figure 2.3: Plant fibres classification

(Source: Textile blog, 2023)

Paper can be made from almost any plant subsequently cutting down trees to make paper is ridiculous. It requires a huge amount of space, time, energy and chemical processing. Fortunately, deforestation is a thing of the past, but there are still many fast-growing plants that can be used to make paper. These plants improve soil health and contribute to diverse agricultural systems. The cellulose fibres length deciding the most suitable paper types to made. In addition, fibre varies greatly by geographic location and native species. Coniferous woods such as fir and spruce usually contain long fibre. Short fibre have usually products like newspapers or old magazines and other used paper products. The suitable non- wood fibre selection is difficult because of the quality, fibrous fraction, ease process and final fibre-based product cost (Mannai, et al, 2019).

Plants and the trees are important sources for pulps to papermaking and they contained an important polymer called lignin. This serve to transport water and give the plant structural strength. The second most common biopolymer on earth is lignin after cellulose. Synthesized of natural lignin from monolignol precursors and there are three such as p-hydroxyphenyl (H unit), guaiacylphenylpropanoid (G unit) and syringylphenylpropanoid (S unit). Softwood lignin is mainly composed of G units, whereas hardwood lignin contains both G and S unit (Ruwoldt et

al, 2023). In addition, lignin that get from the annual plants, also like a grass and straw contains all the three monolignolic units.

The lignin is to plants what concrete is to walls. When the wood is pulverized, the resulting pulp contains lignin and fibre. It takes a lot of lignin to make the hard, strong paper you find in supermarket bags. The problem is that lignin degrades over time, releasing acids particularly the carboxylic acids. These kinds of acids can yellow the papers which is fine for brown paper bags, other dark and short-lived products. Compared to cellulose, lignin is more vulnerable to oxidation by oxygen in air (Małachowska et al, 2020). Basically, comic books collectors tend to store comic books in the plastic bags, so exposure to the light accelerates this process when exposed to the ambient air. By-products of the lignin breakdown damage the cellulose and make paper brittle. Because of this, old newspaper tends to turn from yellow to brown and tear at the creases.

One of the methods of removing lignin is the bleaching. Once the pulp been extracted this can treated with the mild base, such as magnesium bicarbonate or calcium. This is for neutralize naturally occur acid. The additional base can be added for avoid acid formation because of sizing. During sizing, an acidic polymer is usually applied to the paper surface. This basically prevents the ink from penetrating too far into the paper fibres. The paper for the color laser printing if large, then that is difficult to write using the fountain pen. This is due to ink is not absorbed and thus takes longer to dry. The extraction and neutralization of lignin turns the papers white, and brown papers bags can contain up to 55% of unbleached pulp.

Kraft pulping process is consisting of the breaking down and dissolving extracts, lignin, and some hemicelluloses. Kraft pulp is important process in paper and pulp industry because it converts the raw wood to wood pulp and convert that to pure paper (Asif Hanif et al, 2022). Hemicellulose contributes to many properties of paper, so it is important to preserve as much hemicellulose as possible in the pulping process. One of the most important kraft pulping processes is treating cut wood with white liquor, sodium hydroxide a hot mixture of water and sodium sulfide. The action of white liquor is to break the bond between lignin and cellulose, thereby separating the cellulose. Furthermore, the digestion (delignification) reaction takes 0.5–3 hours at elevated temperatures (150–175 °C).

During cooking or pulping, cellulose fibre from raw materials is separate, where the raw materials containing lignocellulose by use chemical, mechanical, and semi-chemical methods.

Chemical cooking is the predominant method as a higher quality product than the mechanical pulping process. The main common pulping method known as kraft process, which produces almost 85% of all the pulp in the world (Sharma et al, 2023). The overview process for kraft pulping shown in Figure 2.4:

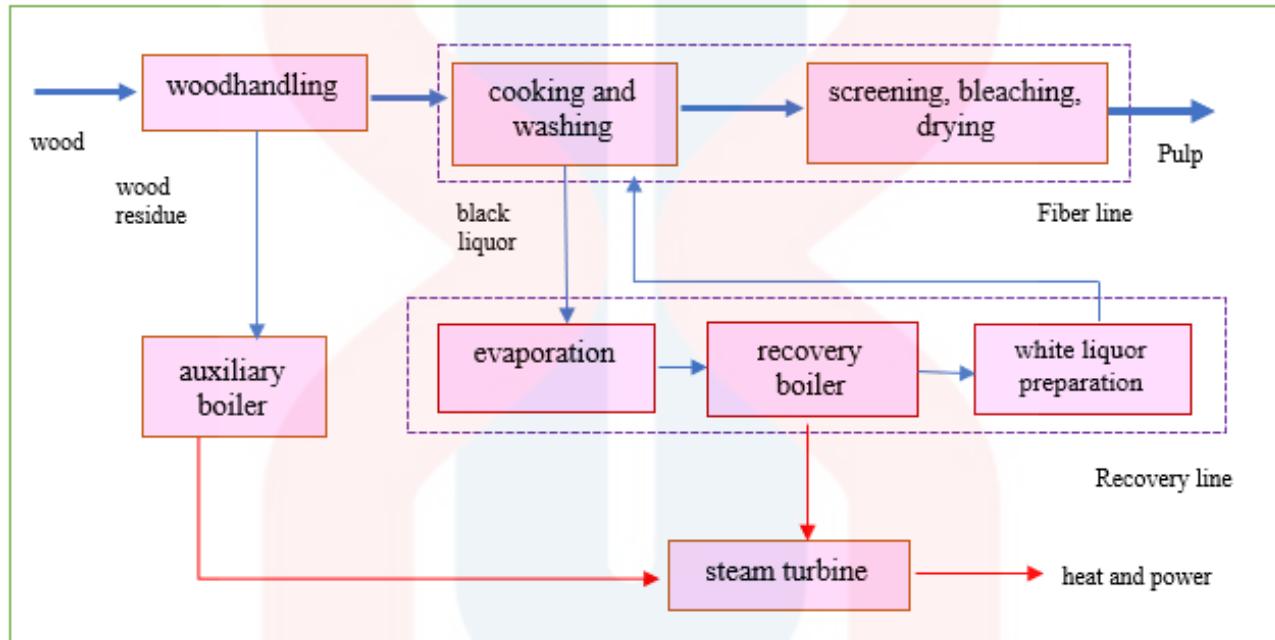


Figure 2.4: Overview process for kraft pulping

In research conducted by India's institute of Central Pulp and Paper Research, bleaching and papermaking processes and reported strength loss from 0 to 35% due to fibre damage during kraft cooking. The average intensity release at the end of cooking process is 75 percent approximately. The mechanism of fibre damages is the damage in walls of fibre during the cooking process. In addition, post-cooking mechanical action when the pulp blown from the digester into the blow tank which reduces fibre strength by breaking the fibre walls. The conventional pulping process has been observed to be effective for chips with a thickness of 2 mm. Chip grains thicker than 5 mm are undercooked in the centre of the chip. This produces unevenly cooked chip particles (Sharma et al, 2023).

This will increase the demand for pulp and paper for packaging and accelerate the rise of the e-commerce industry. Therefore, the rapid expansion of online trading in developing

countries is expected to help expand the global pulp and paper market. Growing environmental concerns are now forcing consumers and manufacturers to rely on sustainable paper packaging. Advanced paper packaging solutions should serve the market, as paper is a recyclable and sustainable packaging material. Therefore, the market expansion is expected to be driven by increasing demand for eco-friendly packaging materials in the coming years. In addition, it is the most recyclable and environmentally friendly packaging material on the market today. The effort to create a sustainable and environmentally friendly method, several countries have enacted various regulations limiting the use of conventional plastics. There is also a growing demand for paper bags as a convenient and cost-effective alternative to plastic bags. All these restrictions and regulations are making stores, supermarkets and storage companies more willing to accept paper-based packaging.

2.3 Bleaching

In the bleaching process, the industry faces a serious problem of reducing emissions of chlorinated organic compounds from bleaching plants. Therefore, pre-bleaching has become common in the delignification process. O₂ delignification emerged as the common process of pre-bleaching. Thus, the unbleached pulps interact with the chemicals that are used for bleaching such as chlorine (Cl), oxygen (O₂), chlorine dioxide (ClO₂), hydrogen peroxide (H₂O₂) and ozone to obtain the pulp that bleached with needed brightness. The modern bleaching sequences involve a multi-step process, with different chemicals and conditions used in each step. Washing is usually done during the bleaching step.

The pulp is bleached in several stages and washed in between. This is to prepare the pulp in the great condition for the next level of bleaching stage (A.M. Sousa et al, 2023). The great results in quality and economy are achieved with multi-stage bleaching that allows you to distinguish between alkaline and acid bleaching stages. Alkaline or acid stages alone do not achieve the desired brightness, so both stages are always used in bleaching.

Raw pulp contains large amounts of lignin and other discolorants. Bleaching is required to produce the light and white papers that are preferred for many products (Samani, 2023). The fibres delignified when removing additional lignin from the cellulose by oxidation and chlorination. A strong alkali which is sodium hydroxide extract lignin that dissolved from the

fibre. In the order of use bleaching based on various factors. For instance, the bleach relative cost, type of pulp and the condition are factors that play a major role.

Mechanical pulp bleaching is not same as chemical pulp bleaching, that both are different. The main goal for mechanical bleaching is to minimum lignin removal in pulp which is reduces fibre yield. The chemicals used to bleach mechanical pulp selectively destroy colour producing impurities while leaving lignin and cellulosic materials intact. This including the sodium bisulfite or the zinc where it not currently applicable in the United States which is calcium or sodium hypochlorite, sodium peroxide or hydrogen. Process of sulfur dioxide boron is contrast of the process of sodium hydrosulfite. The pulp bleaching process removes or to some extent changes the colorants in the pulp (Demchishina, 2011).

Pulp bleaching plays an important role in papermaking. Its main purpose is to improve the whiteness of paper pulp and obtain high-quality pulp with a certain degree of whiteness, great physical properties, chemical properties and purity. Cellulose bleaching treatment opens up a wide range of possible applications. Bleached pulp can be used to make fine paper and refined pulp.

2.3.1 Peroxide bleaching

Peroxides are oxygen-containing anions with the molecular formula O_2^{2-} . Two oxygen atoms are attached to each other by a covalent bond, and each oxygen atom has an oxidation number of -1. Peroxide anions usually combine with H^+ , other Group 1 or Group 2 cations, or other cations such as transition metals to form peroxide compounds. Additionally, they can occur as components of some organic compounds.

The oxygen-oxygen single bond in peroxide is not very stable. Therefore, it readily undergoes hemolytic cleavage to generate two radicals. Peroxides are therefore highly reactive and do not normally occur in nature. This anion is a strong nucleophile and oxidant. It should be stored in a cool, dark place as it is prone to chemical reactions when exposed to light and heat. Hydrogen peroxide is a highly efficient and highly competitive among bleaching chemicals in few aspects like low cost, delignification efficiency and its reduce the impact of ecological (Li et al, 2011).

Performed under alkaline conditions, the peroxide bleaching process effectively bleach the natural fibres while providing a similar effect to alkaline treatment. Under the alkaline conditions, basically the hydrogen peroxide decomposes into hydrogen (H^+) and perhydroxyl ions (-OOH), as shown in Figure 2.5 (Enriquez et al, 2016).

Perhydroxy ions are strong nucleophiles and are therefore it using for the bleaching action of natural fibres (Enriquez et al, 2016). However, hydrogen peroxide can be decompose to other compounds while reducing ability to brightening of the solution. Hydrogen peroxide can decompose under alkaline conditions, thus sodium silicate and magnesium sulfate as additives added to stabilize solution of bleaching.

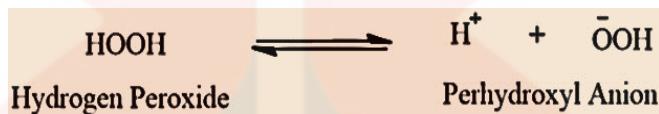


Figure 2.5: Hydrogen peroxide dissociation

(Source: Enriquez et al, 2016)

Natural fibres peroxide bleaching such as kenaf, corn husks, jute, oil palm empty crop tresses and oil palm has fibres like mesocarp. By peroxide bleaching the corn husk fibres achieve a high degree of whiteness and it would maintain the fibre tensile properties. The consensus is peroxide bleaching removes non-cellulosic components, resulting in whiter, lighter fibres.

Hydrogen peroxide known as weak oxidizing agent as well. That also react with the through lignin. A reactions complex series between hydrogen peroxide and lignin involves with the groups of side chain carbonyl reaction and the double bonds also. This is for oxidizing lignin and changing structure of chromophoric group to become colorless. Various free radicals produced during the bleaching process can also react with lignin to some extent. Water solution that non-volatile is a hydrogen peroxide, where the anion of hydrogen peroxide is known as main reactant. Thus, in the bleaching process of hydrogen peroxide, it is necessary to ensure sufficient ion concentration to reduce hydrogen peroxide decomposition and allow to improve the bleaching effect (Liu et al,2018).

2.3.2 Totally Chlorine Free Bleaching Sequences

Multistage bleaching treatment for separating pulp entrained water in the pulp of the present invention, multi-stage bleaching treatment is preferred. Processing stages of the multi-stage bleaching process used commonly in TCF bleaching processes are combined. For instance, Z (ozone treatment stage), A (acid treatment stage), Eo (alkaline treatment stage combined with oxygen), P (hydrogen peroxide treatment stage), Eop (alkali treatment using oxygen and hydrogen peroxide in combination), Pa (peracetic acid treatment stage), Ep (alkali treatment stage combined with hydrogen peroxide) and many more. For examples, sequences comprising this processing stages of multistage bleaching such as Z-Eop-P, A-Eop-Z, A-Ep-Z, Z-Ep-PP and Z-Eo-P.

Besides that, the hydrogen peroxide or oxygen addition, the lignin extraction improves by the already fragmented lignin is further oxidising thus it is facilitating dissolution. Those stages are commonly such as (Eo), (Ep), and (Eop) respectively (Montet, 2022).

Greater benefits were obtained when bleaching chemicals were applied in multiple stages (Ashori, 2005). Achieving the high level brightness requires a multistage bleaching sequence. Interstage washing to remove dissolved of bleaching by-products such as oxidized lignin, partly responsible to improving bleaching extent and the efficiency. Moreover, the multistage sequence takes advantage of different reactivity for each chemical to different bonds within lignin, resulting in synergistic effects on bleaching and lignin removal.

The brightness obtain with the TCF sequence was higher than comparing to that obtained with ECF sequence (Ashori, 2005). Lower effluent treatment costs because of the TCF sequences can be used to bleach to higher brightness. The highest brightness which is 90.4%, International Organization for Standardization (ISO) obtain with pulp treated with the Q₁(PO)Q₂P sequence. It is about L% unit higher than the brightness of bleached DIED2EP pulp. Higher levels of brightness achieved in both processes when peroxide is use in the final stage. The pulp brightness would be increase with increasing chemical charge. Three TCF sequences [(Q₁ (PO)P, OZQ₁P, Q₁ (PO) Q₂P] and two ECF sequences (D1 ED2 EH, D1 ED2 EP) to increase the brightness to acceptable level for printing paper manufacturing.

The pulp is thoroughly washed between different bleaching stages (Saad, 2014). The stages such as D, P, A, Q, and extraction stages like n and e carried out inside sealed plastic bags

in a water bath, while (OO)- and (EOP)- stages carried out inside a Teflon-lined stainless autoclave. Most importantly every bleaching chemical is assigned a capital letter to provide a definition of the various bleaching sequences. The letter designations for the above chemicals are shown in table 2.1.

Table 2.1: Bleaching stages and the chemicals

Bleaching stage	Chemical		OXE/kg
C	Elemental chlorine	Cl ₂	28.20
D	Chlorine dioxide	ClO ₂	74.12
E	Alkaline extraction	NaOH	
H	Hypochlorite	NaClO	26.86
O	Oxygen	O ₂	125.00
P	Hydrogen peroxide	H ₂ O ₂	58.79
Paa	Peracetic acid	CH ₃ CO ₂ OH	26.30
Q	Metal chelator	e.g. EDTA	
Z	Ozone	O ₃	125.00

(Source: Starrsjö, 2021)

2.4 Factor for TCF bleaching

Type of bleaching agent, bleaching technique, and pulp quality are the main variables that have an impact on bleaching performance. Other parameters, such as various raw materials, acidity, pH, temperature, time, agitation, effect of moisture, and oxidation, can also affect the bleaching condition.

2.4.1 Effect of pH

The term pH is stands for "power of hydrogen," is used to indicate whether an aqueous solution is acidic or alkaline. Depending on the context, the exact meaning varies, but in the paper business it refers to how basic or acidic water is. The pH value in neutral is 7, and the pH scale increase from 0 to 14. Something is more acidic and harder for bacteria and other microorganisms to exist in if its pH is lower than 7. Something that has a higher pH is more alkaline and hence more conducive to the survival of bacteria and other microorganisms (ECHEMI, 2022).

The white pulp is placed into a solution with a pH of about 9 to begin the bleaching process. The higher concentration of hydrogen in this solution makes it simple to remove any lingering colours, tannins, and lignin from the pulp, resulting in the production of very white paper. At high and alkaline pH values, the concentration of H⁺ ions is decrease. Hydrolysis rate is based on hydrogen ion concentration. At alkaline pH, acid hydrolysis occurs from β (1→4)-glycosidic bonds, so the hydrolysis rate is based on hydrogen ion concentration (Chryssou et al, 2021). The pH of the water must be between 10 and 11, else bleaching will not occur, and the paper will not be in brightly coloured. Rewashing is the final stage. Bleaching waste is flushed with water before being added once more to the process. The water's pH should range from 6 to 8.

Bleaching with hydrogen peroxide from an initial pH of 11 gives the highest level of whiteness and brightness. An initial pH that lower represents weakly alkaline conditions that cannot provide enough OOH⁻ for the bleaching system (Li et al, 2011) Moreover, when bleaching is insufficient, the whiteness and brightness are lowered. However, the initial pH if too high, the excess alkalinity will increase hydroxyl ions and produce perhydroxyl ions that are too rapidly used. This can lead to reactions such as,



Therefore, hydrogen peroxide is decomposed before it can be used for bleaching. At the same time, the pulp can be darkened because of the alkaline darkening reaction, which can be simply explained as follows,



2.4.2 Effect of Temperature

The strength properties of paper are said to be diminished by higher temperatures, according to Malachowska et al, (2020). Temperature from 15.5°C (60°F) to 48.8°C (120°F), there is a 25% drop in tensile strength (Elvin, 2021). In general, when the temperature rises, the stretch increases but the apparent modulus declines. When compared to the starting temperature, the energy absorption exhibits a slightly different behaviour, increasing first before decreasing again at higher temperatures (Elvin, 2021). The exothermal process may be expected to result in a reduced moisture content at higher temperatures, which supports the conclusions made by Skogman and Scheie in 1969 (Johnsson et al, 2021).

In their experiment, Al-Khier Hamamah et al, (2016) was founded that when the temperature rises, the bleaching reactions rate as well increases. As a result, more hydrogen peroxide is consumed during the bleaching process as opposed to being consumed in unfavourable reactions like decomposition brought on by alkaline conditions or heat, which results in higher brightness levels. A state of equilibrium between bleaching and decomposition reactions may have taken place at temperatures above 60°C, resulting in a very small brightness gain. This could be the result of the thermal decomposition of H_2O_2 , which is shown to accelerate with temperature increase in figure 2.6.



Figure 2.6: Equation of thermal decomposition of H_2O_2

(Source: Al-Khier Hamamah et al, 2016)

According to Ventorim et al, 2016, the cooking temperature had not affect the kappa number results of the bleaching stages [O and (EP)] (Table 2.2). Free phenol group and S:G ratio affected by temperature, but did not influence kappa number of bleached pulp. Consequently, temperature of pulping did not affect the reversion of brightness of bleached pulp. The brightness reversion of bleaching sequence is lower due to H_2O_2 used in the stage of final for the bleaching sequence is a good brightness stabilizer.

Table 2.2: Kappa number of bleaching stages of [O and (EP)] and the bleaching stages viscosity [O, (EP) and P] in the OD(EP)DP sequences effected by the kraft cooking at different temperatures.

Sample	Temperature(°C)	Brownstock	O	(EP)	O	(EP)	P
		Kappa number			Viscosity, cP		
A	155	16.6	9.7	5.4	29.1	25.0	18.1
	160	16.8	9.7	5.3	29.9	25.8	20.7
	165	16.9	10.3	4.6	30.4	26.2	19.9
B	155	14.6	8.3	3.7	21.3	15.0	13.0
	160	13.9	8.3	3.7	21.3	15.0	13.0
	165	14.5	8.5	4.0	19.2	13.8	12.1
C	155	14.6	9.7	5.1	25.7	18.3	14.8
	160	14.2	8.3	4.1	19.3	15.4	12.4
	165	14.6	8.7	4.2	18.5	12.4	11.8

(Source: Ventorim et al, 2016)

2.4.3 Effect of Duration

Chemicals like hypochlorite solution tend to change interfiber connection, the longer duration of bleaching made pulp fibres less flexible (Xian et al, 2020). Weak interfiber bonding zones create less surface area for the bonding, which affects the internal cohesion of hand sheets and decreases sheet strength. As a result, the tester can readily rip the hand sheet with little energy consumption and a low reading for the tearing index. In actuality, one of the factors contributing to the low ripping strength is the short fibre.

The internal and external fibrillation during the chemical pulps beating can cause fibre surfaces development for bonding. In addition, surface area the bonding is directly will be

proportional to the extent of bonding. However, there are other reasons as well weaken the sheet strength like bleaching agent reaction which can cause fibre degradation.

2.5 Strength Properties

Paper strength is determined by some factors such as strength of the individual fibres in stock, the fibre average length, the interfiber bond capacity of the fibres where it enhanced by the beating and refining action, as well as the structure and also formation of the sheet. Strength properties includes many other factors like bursting strength, compressibility, folding endurance, hardness, surface strength, breaking length, resiliency, softness, tearing resistance, tear factor, tear index, tensile energy absorption, stretch, tensile strength and wet strength.

2.5.1 Tensile Strength

The tensile force is required in a strip of paper or paperboard to produce a rupture is known as tensile strength of paper, where expressed in kg/cm^2 (Johnsson et al, 2020). Furthermore, tensile strength is good indicator of fibre strength, fibre bonding and also fibre length. It can use as potential indicator of resistance to the web breaking when print or convert. Mainly it based on the quality and quantity of the fillers used. It is one of the significant factors for many applications such as printing, packaging papers and converter (Adams, 2022).

Fibers strength and the bonding strength between individual fibres are depends by the paper tensile strength (Johnsson et al, 2020). For example, the zero span measurement has decrease the strength of individual fibres at pH 4.5 by treating with sodium chlorite to remove lignin but increases the strength per unit of paper weight. This can be determined that the lignin in the fibres has tensile strength as well. Below shown electronic tensile strength tester in figure 2.7.



Figure 2.7: Electronic Tensile Strength Tester

(Source: Adams, 2022)

Furthermore, fibre length is very important for wet tensile strength (Liu et al, 2018). Wet paper tensile strength increases with increasing growth length of fibre. Wet paper elongation is determined by all fibre components synergistic action. Furthermore, elongation of wet papers can increase by beating because of increase of the crimp index of the fibres. Even for same pulping, the proper beating make fibres to swell and fibrillate while it is increasing the contacts area which is between fibres, promoting the action of van der Waals force, and achieving higher wet paper strength (Teacă, 2023).

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2.5.2 Brightness

Pulp bleaching purpose is to produce white pulp. One of the main parameters for commercial pulp is brightness. Thus, it must be maintained after the transportation and also storage (Liitiä et al, 2007). Especially for high-brightness eucalyptus pulp in market, brightness stability is an important issue, and much research has recently been done to optimize the pulping process in this regard as well. Unbleached pulp is not suitable for manufacturing because it does not produce high quality white paper. This is because all processed pulps, especially kraft pulps, have very low brightness. In the modern world, most pulp is produced using the kraft pulping process.

Pulp is not only composed of cellulose and hemicellulose, but also contains some impurities that were not completely removed during the pulping process. Cellulose and hemicellulose are white in nature and do not contribute to pulp coloration. Impurities such as lignin and colored organics mainly give color to the pulp. Lignin chromophoric group are generally responsible for this.

Brightness testers that use directional geometry to measure brightness are sensitive to the direction of the handsheet fibres. These directional effects were used to determine the machine direction and cross direction of the paper. Measurement of directional brightness are based on common standards. For the TAPPI method, the standard brightness test is calibrated for 100% reflectance on magnesium oxide test pellets. The values of brightness for pulp and paper materials will vary but it is based on the final target product (J. Ragauskas, 2020)

Particularly environmentally minded the young generation people, are to be expect the driving force behind technological innovation and decline high-brightness demand, high-gloss papers. Additionally, a lot of consumers recognize that not all kind of paper applications require high brightnesses, which in few cases can cause glare and reduce readability. Besides that, the brightness of the paper do not have so high as the text recognizability is deteriorating. Besides that, uselessness aspect of high brightness level can be seen by noting where most papers are printed only once and then after being read, that stored or shredded (Jablonský & Šima, 2022).

2.5.3 Bursting Strength

In general, preparation the quantity of fibres presents in the sheet, their formation, to some degree, internal bond, surface treatment and combining operation all affect bursting strength. It can be compared with edge crush strength, a measurement of the compression forces a sample of the board can sustain before collapsing in the vertical or loading direction. Bursting strength is specifying the pressure that paper can be tolerated before getting ruptured. It is an oldest test conduct on paper strength test or resistance to rupture. This property is important papers or paperboard which used for packaging purpose such as corrugated box or the paper bags (Pacorr, 2020. Its need maximum of hydrostatic pressure to burst rupture a paper. The pressure applied

was increase uniformly across its side and through a rubber diaphragm in specific dimension. This test commonly used Mullen Tester for conduct and measured in kPa units.

This bursting strength test is a complex function of stretch and tensile strength. Both fibre length and interfiber bonding are involved in burst strength (Pego et al, 2022). The longer the fibre length, the higher the bursting strength. It also increases impact. Bursting strength increases up to a certain range, but beyond that the bursting strength decreases due to excessive beating. The drying conditions on the paper machine have a great effect on this strength. Adding tension to the wet sheet increases the tensile strength but decreases the burst resistance. The relative burst resistance obtained were expected for the various paper grades, with higher values for cellophane and lower for ordinary paper.

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CHAPTER 3

MATERIALS AND METHODS

3.1 Materials

3.1.1 Pulp

Kenaf (*Hibiscus Cannabinus*)

3.1.2 Chemical Reagents

Distilled water (H_2O), Sodium sulfide (Na_2S), Hydrogen peroxide (H_2O_2), Sodium hydroxide ($NaOH$).

3.1.3 Apparatus and Equipment

Measuring cylinder, thermometer, beaker, stopwatch, laboratory water bath, electronic balance, mortar and pestle, blender, standard sheet machine, automatically-operated micrometre, colorimeter, bursting tester, tensile testing machine.

3.2 Methods

3.2.1 Sample Source Preparation

Kenaf was debarked to prepare the bast pulp. Then was used woodchipper to make the kenaf bast chipped and removed the excessive moisture air dried. The moisture content was control to 10%. The bast chip was cooked with 20% of active alkaline, Sodium hydroxide (NaOH) and 25% of sulfidity, Sodium sulfide (Na₂S) as white liquor with 1:8 ratio to bast. The cooked pulp was washed to remove the excessive chemicals which might affect the result of the pulp (Mohd Ali et al., 2020). The pulp was disintegrated and beat.

3.2.2 Pulp Bleaching

Pulp at 15% consistency with 1.2 wt% Sodium hydroxide (NaOH) on pulp for 2 hours at 80°C. The NaOH was mixed into pulp and the slurry pre-heated in a microwave oven. Mixture was washed with using distilled water. Then, pulp prepared in a zipping bag and pulp was in 15% consistency with 3 wt% hydrogen peroxide (H₂O₂) in a zipping bag. Afterward, the mixture was heated in a 50°C water bath and subsequently every 10 minutes, the mixture was taken out to make sure the pulp does not sediment and the mixture was well mixed for complete bleaching reaction. The 4 set of pulp was bleached with 4 different durations as 0, 20, 40 and 60 minutes.



Figure 3.1: Kenaf pulp after bleached with 3 wt% of Hydrogen Peroxide at 50°C

3.2.3 Paper Sheet Formation

According to standard (T 205 sp-02), hand sheet was prepared. There was different bleaching duration use in paper sheet. There are 4 set of pulp bleaching duration 0, 20, 40 and 60 applied. The pulp was mixed well with distilled water to reach consistency of 0.3%. The standard sheet machine was used to form the hand sheets. The standard couch roll and standard couch plate was used to extract the hand sheet from the standard sheet machine. Their function is to remove excess water contain from the hand sheet. The hand sheet form allowed to air dry completely in the conditioning room.



Figure 3.2: The standard sheet machine used for the formation of hand sheet.

3.2.4 Cutting Process of the Hand Sheet

Cut specimens from sample where the critical dimension is involved only after the sample conditioning as show in Figure 3.3. The sample sheet was precondition by exposed as specified above 5.3 to the preconditioning atmosphere. The sample sheet was stored in temperature where below 23 and relative humidity below 50% (T 402 sp-08, 2013). Hand sheet was cut out into pieces and strips for the testing process including the tensile strength, bursting strength test.

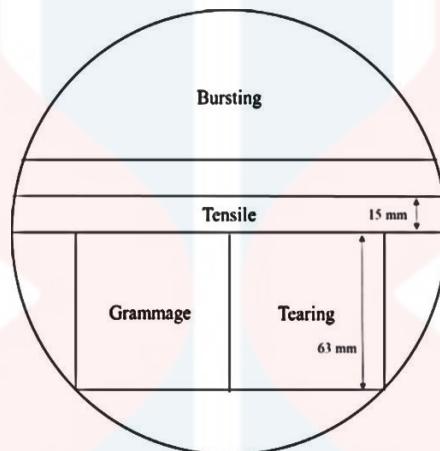


Figure 3.3: The figure shows the standard cutting for paper properties test of hand sheet.

(Source: Syarifah et al, 2021)

3.2.5 Testing of the Paper Properties

Based on TAPPI 410 (T 410 om-08, 2013), the thickness and weight of the hand sheet was determined. The automatically-operated micrometre was used for thickness determination in unit millimetre, mm. The mass of the hand sheet weighted by using electronic balance and measure in unit gram, g. The grammage of the hand sheet was calculate according to TAPPI 411. Below shown the grammage formula according to the TAPPI (T 411 om-97, 1997),

$$\text{Grammage, gsm} = \frac{\text{Weight of hand sheet, g}}{\text{Area of weighted hand sheet, (m}^2)}$$

3.2.5.1 Tensile Strength

The tensile properties of paper were tested using testing machine which provides constant elongation according to standard of TAPPI T 404 cm-92. The hand sheet was cut for testing the tensile strength (Figure 3.4). Tensile testing machine was used to place hand sheet including the specimen from different duration of bleaching as 0, 20, 40 and 60. The average time 5- 15 second was set in the tensile testing machine for the break of the paper to get the accurate reading of data (T 404 cm-92,1992). It was done before the machine start. The machine automatically displays the tensile strength data. The tensile strength was analysed in Nm/g unit.

The tensile strength data was automatically displayed by the device. The tensile index was calculated using the following formula (TAPPI 2001b):

$$\text{Tensile index, } \frac{Nm}{g} = T \times \frac{1000}{G}$$

T = Tensile strength, N

G = Grammage, g/m²

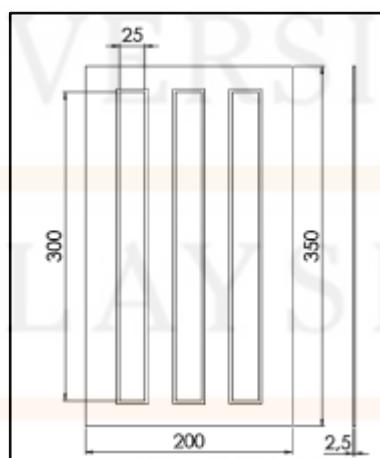


Figure 3.4: Cut scheme for test samples

(Source: Kochov et al, 2022)



Figure 3.5: The tensile testing machine used to measure the tensile strength of the hand sheet.

3.2.5.2 Brightness

Colorimeter was used to measure the brightness of hand sheet according to TAPPI Standard T 524. Data was presented by colorimeter device. Brightness unit was calculated in percentage, % and for analysis result was recorded.



Figure 3.6: The colorimeter was used to measure the brightness

3.2.5.3 Bursting Strength

In this test, the maximum bursting strength of the paper was measured between the 50 kPa and 1200 kPa at a maximum thickness of 0.6 mm. A burst tester was used according to TAPPI Standard T 403 om-97 (TAPPI 1997), to test bursting strength. The smoother side of each slide was clamp toward the diaphragm. This is to avoid inaccurate data before apply the hydraulic pressure. Hydrostatic pressure was applied at the increase of standard rate on hand sheet until the specimen is ruptured. Then, the maximum pressure obtains recorded in the unit KPa m^2/g (T 403 om-97, 1997).



Figure 3.7: The bursting tester machine used to measure bursting strength of hand sheet.

3.3 Statistical Analysis

In this study, the effect of TCF sequence and duration for paper formation on the strength of paper was tested and determined using one way ANOVA test. Result is considered significant for p values ≤ 0.05 alpha. Post Hoc Test which is Tukey's W-test also was used to determine the data that differ from each other.

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1 The Physical Properties of the Kenaf Hand Sheets

The hand sheet physical properties were measured and recorded, this including the thickness and grammage. According to TAPPI, physical properties are used as control variables to fulfil the specification. Purpose of hand sheet was produced to have a comparison between similar strength properties. There are great change in the handsheet's mechanical properties due to the variable changes.

All handsheets grammage was range from 45.65gm^2 to 50.22gm^2 . The handsheets weight can directly influence the grammage and the thickness of the handsheets. The thickness of the hand sheet falls in the range between 0.1248mm to 0.1415mm . For the sake of the experiment, the variation in grammage between the hand sheets was controlled since grammage affects the physical properties of the hand sheet. Table 4.1 showed the reading of thickness and grammage of the hand sheets get from the experiment.

When subjected to certain conditions, these properties affect paper behaviour allowing for structural characterization, surface, arrangement and fibre connections. Properties of paper like physical properties have heavily influenced by fibre blending due to its significant variation in fibre characteristics. As a result, physical properties must be focused on while doing fibre blending research.

In the paper structure which is net formation, organization and mechanical properties particularly tensile strength, interfiber bonding play an important role. They can be described as connections between fibre by the Van der Waals interaction, molecular entanglement and chemical bonding. Improves the cohesion of paper (fibre network) when the fibres are kept together as a consequent to its physical properties and mechanical properties. Thus, interfiber bonding evaluation is an essential property that can influence fibre bonding. Fibre blending

works with distinguished fibres affect in paper structure is expected. Short fibres may function as fines in the paper structure.

Table 4.1: Physical properties of the Kenaf hand sheet

Bleaching Duration, min	Thickness, mm	Grammage, gsm
0	0.1283 ± 0.0005	47.45 ± 1.8043
20	0.1305 ± 0.0050	48.87 ± 1.4325
40	0.1308 ± 0.0050	48.62 ± 2.1280
60	0.1320 ± 0.0085	46.89 ± 1.2019

4.2 The Tensile Strength of the Paper

Mechanical characteristics investigated in this study include the tensile index and the burst index. Paper's tensile strength is primarily determined by the bonding ability, flexibility, strength, and length of individual fibre. Furthermore, bonding of inter-fibre is a key aspect in determining the mechanical strength of hand sheets. As indicated in Figure 4.1, the hand sheet made from a pulp duration at 60 minutes had the greatest tensile index which is 2.81 ± 0.17 (Nm/g) when compared to the others.

In the literature, it has been pointed out that the quality of fines is most important during the initial phase of consolidation of the paper structure and to achieve strong final fibre-fibre bonds in wet-pressing. The strength properties of the fibre network, where that related to level of inter-fibre bonding was identify through tensile index parameter. The increase in tensile strength is majorly due to the increased surface charge of the fibre, where there are more hydrogen bonds in the fibre network. Therefore, the similar increasing trend of tensile index with the apparent density is more comprehensible. The reading of tensile higher when tensile strength

is higher. There are influence of fibre length, fibre strength, bonding between fibres in tensile strength.

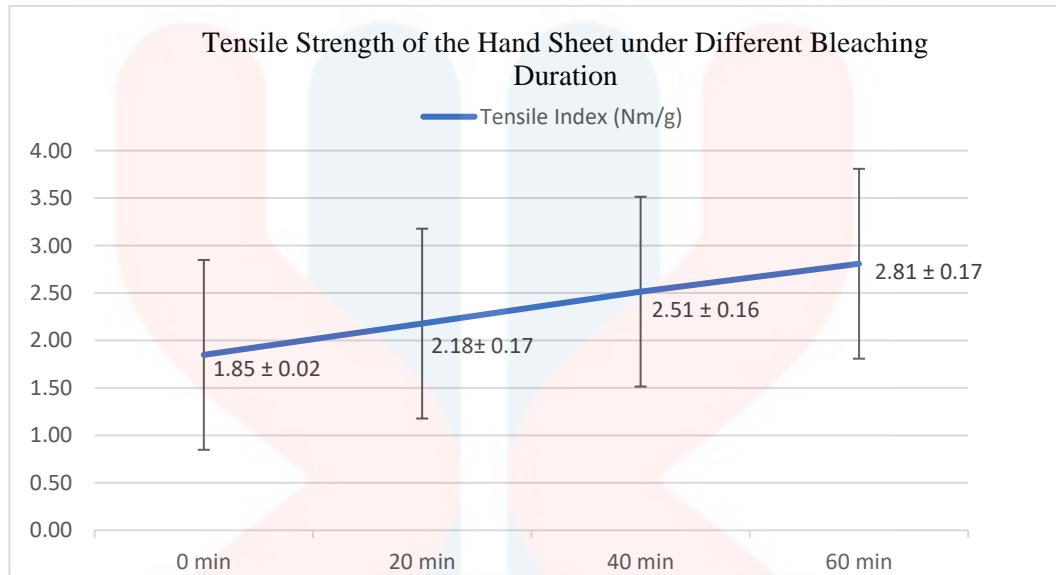


Figure 4.1: Graph representing the tensile strength of the hand sheet under different bleaching duration at 0, 20, 40, 60 minutes.

Figure 4.1 shows that the tensile index of paper handsheets gradually increased from 1.84 ± 0.02 to 2.81 ± 0.17 Nm/g for the bleaching duration of 0 to 60 minutes. The tensile index values are obtained by Yahya and others (2020), who found that increasing the cooking time from 60 to 120 minutes resulted in an increased of tensile index from 54.35 to 77.45 Nm/g. This is probably due to longer cooking time soften the fibres and make it easier to grind and produced a finer fibre structure in the handsheet. This strengthens the packing of the fibres and increase the inter-fiber bonding. Therefore, increasing of duration also has a significant impact on the tensile strength.

One of the indicators for paper quality is tensile strength. The greater tensile strength indicates a quality of paper is better. Trend of the tensile strength is increasing from bleaching from 0 min until 60 minutes of bleaching duration. The tensile strength data for 0 minutes, 20 minutes, 40 minutes and 60 minutes bleaching duration are 1.84 ± 0.02 , 2.18 ± 0.17 , 2.51 ± 0.16 and 2.81 ± 0.17 Nm/g respectively as shown in Figure 4.1.

The improvement of the interfiber bond between fibres was the cause for the growing trend. The fibres must hold firmly to one another in order to withstand the force applied vertically to the paper, which requires the lignin to be removed. Bleaching the lignin out of the fibre, fibre

entanglement can be encouraged by softening and increasing the fiber's flexibility. The number of bonds and contact area between the fibres in the fibre web can be increased with the aid of this phenomena. All of these elements to overcome the force applied to the paper and making the paper improving its quality.

Tensile index and tear index are affected by fibre bond, fibre strength and fibre length, but tear strength commonly depends more on the strength of individual fibres. The tensile index of hand sheet is significantly affected by sodium hydroxide concentration. According to Zhang and others (2013), the tensile index increased when the sodium hydroxide concentration was 3%. This is because the reduction of lignin reduces the elastic modulus of the single fibres, thereby reducing the stiffness of the pulp. The decrease in stiffness indicates that the individual fibres are more flexible, and it is easier to form fibre-fibre bonds. This then increases the tensile index of the paper.

4.3 The Brightness of the Paper

The brightness was significantly improved by increasing the bleaching duration with the constant temperature which is 50°C. Lignin are solubilize when bleached using regular bleaching agent like hydrogen peroxide and sodium hydroxide. As the bleaching time is increased, more lignins are hydrolyzed and solubilized and making the paper brighter. The primary reason of the paper is in brown colour due to lignin (Sadeghifar et al, 2020). The kappa number is negatively correlated with brightness. The lower the kappa number, the brighter the handsheet. Thus, from the result we can understand that the lignin was much decreased when multistage peroxide bleaching duration was increased. The effect of sodium hydroxide and hydrogen peroxide treatment on brightness of paper are optimized at 60 minutes.

As the bleaching time is increased by the hydrolyzed and solubilized more lignin and making the paper brighter. The primary reason of the paper is in brown colour due to lignin. The kappa number is negatively correlated with brightness. The lower the kappa number is the brighter the handsheet. Thus, from result we can understand that the lignin was much decreased when peroxide bleaching duration was increased. The sodium hydroxide and hydrogen peroxide treatment effect on brightness of paper optimized at 60 minutes.

The brightness of kenaf bast pulp handsheets after multistage peroxide bleaching process was shown in Figure 4.2. The pulp with less stiffness results in paper with high density. Lignin contributes to the stiffness of the pulp but when the pulp was beaten, the cell walls was ruptured before the lignin was removed and making it flexible. After that, the effect of lignin removal on stiffness reduction was no longer significant.

The elimination of lignin derivatives throughout the pulping and bleaching processes is most likely what caused the noticeable rise in the brightness of the paper. The pulp's light-absorbing substance, which comes from the lignin of the absorbing constituent, allow the increases amount of light that the paper reflects. To extract these light-absorbing materials from the pulp, they undergo oxidation and reduction processes that render them soluble in aqueous solution (Histed et al, 1996).

As a result, the pulp's multi-stage bleaching treatment significantly provide much greater improvement in brightness. The removal of dissolved impurities by interstage washing is partially responsible for the increase in bleaching efficiency and extent. Bleaching reduces the light absorption which is necessary to achieve high brightness.

Pulp that unbleached has high light absorption at short wavelengths in the blue part of the spectrum. When bleached mechanical pulp, the goal is not to remove lignin, but to convert chromophores into low light-absorbing molecules. This is accomplished by bleaching with hydrogen peroxide. Lignin removal (delignification) bleaching provides high brightness that lasts for a relatively long time. This occurs in a multistage bleaching sequence that uses bleaching chemicals and sodium hydroxide as alkali. The brightness development at the P-stage is determined by the starting brightness and the peroxide charge. Brightness improvements of 1-7 points may be achieved when 0.1-0.6% peroxide on pulp is utilised (Hart, 2019).

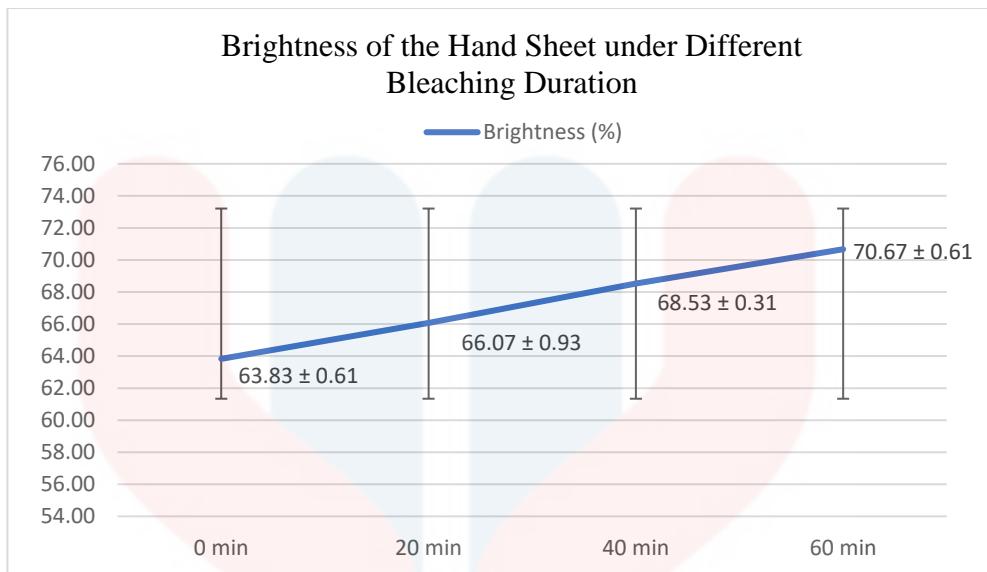


Figure 4.2: Graph representing the brightness of the hand sheet under different hydrogen peroxide bleaching duration including 0, 20, 40, 60 minutes.

4.4 The Bursting Strength of the Paper

A pressure gauge on the device measures the bursting pressure required to break the paper during the bursting test. The bursting index shows highest result 1.24 ± 0.03 at 60 minutes. Tensile breaking strength and bursting strength are closely related. In addition, fibre characteristics and papermaking techniques was improved the tensile breaking strength also tend to improve bursting strength (Khair et al, 2022).

Throughout the bleaching durations, the bleached handsheet's bursting index was increased somewhat in comparison to the unbleached handsheets. After bleaching for 0, 20, 40, and 60 minutes, the bursting strength results are 4.16 ± 0.26 , 4.48 ± 0.24 , 4.68 ± 0.26 , and 4.58 ± 0.28 kPa m^2/g , respectively. The outcome was displayed in Figure 4.3. The main pressure that is provided at the standard rate of rise until the handsheets ruptured is known as hydrostatic pressure. In general, the primary component influencing a paper sheet's strength properties by the individual fibres bonding. Besides that, the degree of fibre bonding was largely determined via the individual fibre's flexibility and compressibility (Sadiku et al, 2019). Consequently, high burst strength, tensile strength, tensile stiffness, compression strength and also the elasticity of

paper will be formed as a result of the fibres collapsing. In addition, collapsed fibres have a greater surface area that can be bonded to and are more flexible. Furthermore, the ability of fibres to conform around other fibres was influenced by their flexibility. They are affect the quantity of bonds, the bonded area in the sheet, and the number of fibre-fibre contacts (Xian et al., 2020). A fibre that flexible always has a wide fiber-to-fibre contact area and conforms to one another with ease. In all, the pulp fibres will collapse due to the extended hydrogen peroxide bleaching time (Wu et al, 2019). Chemically, flexibility increases the fibres surface area for fibre bonding which is fibre-to-fibre bond in the network and giving the handsheets a high bursting index.

Mechanical properties of the kenaf paper positively impacted by fibre elasticity and collapsibility. The number of bonds which is representing the number of bonding areas was affected by fibre flexibility. Furthermore, the flexibility fibre will bond easier because of it has more surface area. Interfibre bonding plays a major role in both paper tensile and bursting strengths (Suhaimi et al, 2022).

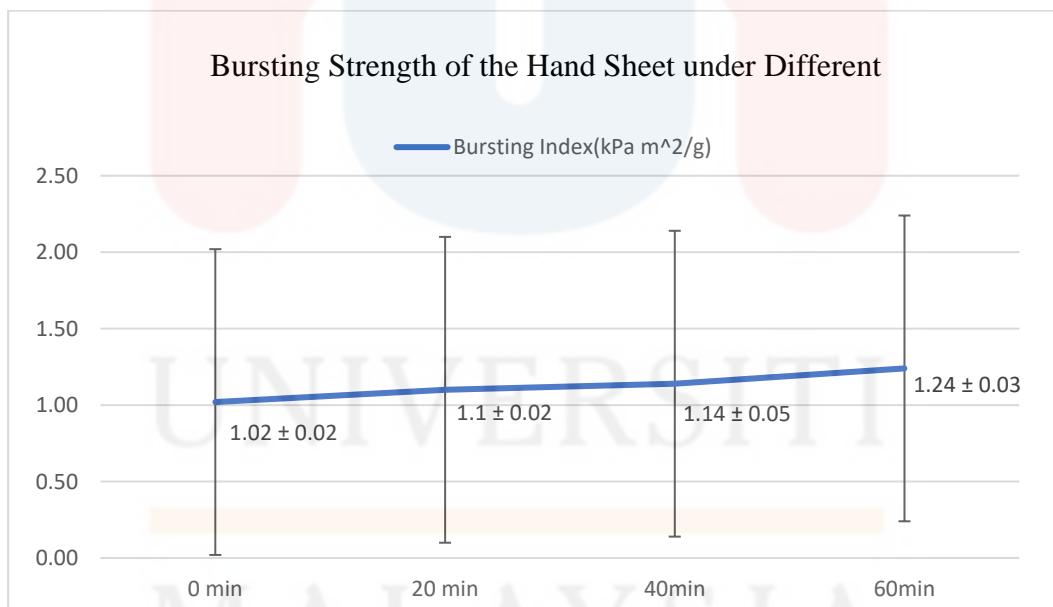


Figure 4.3: Graph representing the bursting strength of the hand sheet under different hydrogen peroxide bleaching duration including 0, 20, 40, 60 minutes.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

TCF multistage peroxide bleaching of Kenaf bast pulp at different duration was successfully studied. Kenaf bast fibres are long, slender and thick-walled while core fibres are much shorter and wider. Therefore, kenaf bast pulp is much more suitable to make into handsheets. Kenaf bast pulp is seems more suitable raw material which can improve the strength properties of handsheets, especially the tensile strength. It is obviously possible and more attractive the kenaf bast pulp to use for the same purpose, if the end properties that are needed commercially can be achieved.

In the process changes especially the environmentally friendly bleaching agents use may prove to be a better option to reduces the industry's environmental impact. Hydrogen peroxide is greatly beneficial in the terms of store and use, easy to transport, highly flexible and scarcely volatile. Besides that, its reaction products are fairly non-toxic. This reagent can be employed in the last step of a bleaching sequence to increase brightness and stability in the final pulp.

The optimum bleaching duration for 3 wt% hydrogen peroxide on Kenaf bast fibre is around 60 minutes. Bleaching duration result in maximum interfiber bonding strength in the network without compromising the fibre strength. It gives the optimum mechanical properties include maximum tensile strength and bursting strength. Among all the parameters, the brightness of hand sheets bleached at 60 minutes also range relatively satisfactory. Bleaching for 60 minutes gives the pulp maximum brightness. Bleaching duration of 60 minutes showing the maximum capacity of lignin elimination by hydrogen peroxide in the pulp.

In a nutshell, the longer the bleaching duration with a multistage peroxide bleaching, the more the lignin can be eliminated. The bleaching time should be determined based on the paper properties to be emphasized.

5.2 Recommendations

The research gives useful information and prospects which can serve as a future reference. Moreover, multistage peroxide bleaching can improve the result of pulp's strength properties of the produced hand sheets. The longer the bleaching duration, the more increase in brightness. This is due to the removal of the lignin from the kenaf bast pulp. Brightness stability is a main issue and much research has recently been done to optimize the pulping process in this regard. The water bath of pulp during bleaching better to be control at the temperature around 50°C to prevent the fibre degrade by over heat. This also affect the fibre strength and result of strength properties. Recovered of all the pulp during the pulp washing process is very important to remove chemicals from the pulp like hydrogen peroxide bleaching agent.

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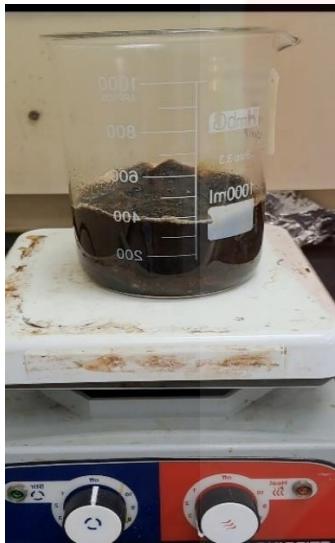
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APPENDIX A

Image taken during the research



APPENDIX B

Image of Handsheet



APPENDIX C

One Way ANOVA Analysis Result of Tensile Strength Using SPSS

Table C-1: Description statistic on tensile strength

Bleaching Duration, min	N	Mean	Std. Deviation	Minimum	Maximum
0	3	1.8483	0.01762	1.83	1.87
20	3	2.1777	0.16765	1.99	2.30
40	3	2.5747	0.07842	2.52	2.67
60	3	2.8080	0.16808	2.67	2.99
Total	12	2.3522	0.39891	1.83	2.99

Table C-2: Test of between-subjects effects on tensile strength.

	Sum of Squares	Df	Mean Square	F	Sig.
Between Groups	1.625	3	0.542	34.486	0.000
Within Groups	0.126	8	0.016		
Total	1.750	11			

Table C-3: Post Hoc Tukey HSD test and analysis result of tensile strength.

Multiple Comparisons						
(I) Duration	(J) Duration	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval	
					Lower Bound	Upper Bound
0	20	-0.32933*	0.10232	0.049	-0.6570	-0.0017
	40	-0.72633*	0.10232	0.000	-1.0540	-0.3987
	60	-0.95967*	0.10232	0.000	-1.2873	-0.6320
20	0	0.32933*	0.10232	0.049	0.0017	0.6570
	40	-0.39700*	0.10232	0.020	-0.7247	-0.0693
	60	-0.63033*	0.10232	0.001	-0.9580	-0.3027
40	0	0.72633*	0.10232	0.000	0.3987	1.0540
	20	0.39700*	0.10232	0.020	0.0693	0.7247
	60	-0.23333*	0.10232	0.182	-0.5610	0.0943
60	0	0.95967*	0.10232	0.000	0.6320	1.2873
	20	0.63033*	0.10232	0.001	0.3027	0.9580
	40	0.23333	0.10232	0.182	-0.0943	0.5610

*. The mean difference is significant at the 0.05 level.

APPENDIX D

One Way ANOVA Analysis Result of Brightness Using SPSS

Table D-1: Descriptive statistic on brightness.

Bleaching Duration, min	N	Mean	Std. Deviation	Minimum	Maximum
0	3	63.833	0.6110	63.3	64.5
20	3	66.067	0.9292	65.0	66.7
40	3	68.533	0.3055	68.2	68.8
60	3	70.667	0.6110	70.0	71.2
Total	12	67.275	2.7400	63.3	71.2

Table D-2: Tests of between-subjects effects on brightness.

	Sum of Squares	Df	Mean Square	F	Sig.
Between Groups	79.176	3	26.392	61.977	0.000
Within Groups	3.407	8	0.426		
Total	82.583	11			

Table D-3: Post Hoc-Tukey HSD test and analysis result of brightness.

Multiple Comparisons						
(I) Duration	(J) Duration	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval	
					Lower Bound	Upper Bound
0	20	-2.2333*	0.5328	0.013	-3.940	-0.527
	40	-4.7000*	0.5328	0.000	-6.406	-2.994
	60	-6.8333*	0.5328	0.000	-8.540	-5.127
20	0	2.2333*	0.5328	0.013	0.527	3.940
	40	-2.4667*	0.5328	0.007	-4.173	-0.760
	60	-4.6000*	0.5328	0.000	-6.306	-2.894
40	0	4.7000*	0.5328	0.000	2.994	6.406
	20	2.4667*	0.5328	0.007	0.760	4.173
	60	-2.1333*	0.5328	0.017	-3.840	-0.427
60	0	6.8333*	0.5328	0.000	5.127	8.540
	20	4.6000*	0.5328	0.000	2.894	6.306
	40	2.1333*	0.5328	0.017	0.427	3.840

*. The mean difference is significant at the 0.05 level.

APPENDIX E

One Way ANOVA Analysis Result of Bursting Index Using SPSS

Table E-1: Descriptive statistic on bursting index.

Bleaching Duration, min	N	Mean	Std. Deviation	Minimum	Maximum
0	3	1.0233	.01528	1.01	1.04
20	3	1.0967	.01528	1.08	1.11
40	3	1.1367	.04726	1.10	1.19
60	3	1.2433	.02517	1.22	1.27
Total	12	1.1250	.08660	1.01	1.27

Table E-2: Tests of between-subjects effects on bursting index.

	Sum of Squares	Df	Mean Square	F	Sig.
Between Groups	0.076	3	0.025	30.333	0.000
Within Groups	0.007	8	0.001		
Total	0.082	11			

Table E-3: Post Hoc Tukey HSD test and analysis result of bursting index.

Multiple Comparisons						
(I) Duration	(J) Duration	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval	
					Lower Bound	Upper Bound
0	20	-0.07333	0.02357	0.057	-0.1488	0.0021
	40	-0.11333*	0.02357	0.006	-0.1888	-0.0379
	60	-0.22000*	0.02357	0.000	-0.2955	-0.1445
20	0	0.07333	0.02357	0.057	-0.0021	0.488
	40	-0.04000	0.02357	0.384	-0.1155	0.355
	60	-0.14667*	0.02357	0.001	-0.2221	-0.712
40	0	0.11333*	0.02357	0.006	0.0379	0.1888
	20	0.04000	0.02357	0.384	-0.0355	0.1155
	60	-0.10667*	0.02357	0.008	-0.1821	-0.0312
60	0	0.22000*	0.02357	0.000	0.1445	0.2955
	20	0.14667*	0.02357	0.001	0.0712	0.2221
	40	0.10667*	0.02357	0.008	0.0312	0.1821