ADDIS ABABA UNIVERSITY
ADDIS ABABA INSTITUTE OF TECHNOLOGY
SCHOOL OF CHEMICAL AND BIOENGINEERING

# PRODUCTION AND CHARACTERIZATION OF PULP FROM FLAX STRAW

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This is to certify that the thesis prepared by *Tsiye Tekleyohanis*, entitled '*production and characterization of pulp from flax straw*' and submitted in partial fulfillment of the requirement for the degree of Master of Science (Chemical and Bio Engineering) complies with the regulations of the University and meets the accepted standards with respect to originality and quality.

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## DECLARATION

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## ABSTRACT

Flax (Linum usitatissimum) is a bast fiber plant, it has a long length of fiber and good sources of pulp used as input for the production of paper. Pulping of flax straw with Kraft process was studied. Proximate analysis, Chemical compositions, and morphological properties of flax straw fibres were also investigated in this paper. Proximate analysis including ash content (4.13%) and moisture content (11%). Chemical properties including cellulose (51.34%), hemicellulose (25.20%), lignin (14.12%), ash (4.13%) and extractives (5.21%) were determined by assuming flax straw content have only the above compositions. Morphological properties of flax straw including fiber length, diameter, lumen width, and cell wall thickness was 1.41mm, 16.78μm, 9.45, and 3.77μm, respectively. Flax straw has an acceptable Runkel ratio (0.8) and flexibility coefficient (56.32) in the range of non-woods. Morphological analysis of pulp from flax straw by using a scanning electron microscope(SEM) to determine the morphology of fiber. Basic understanding from this results in qualitative determination the structure of fiber even if see the fiber have a crack or not. The quality and length of pulp directly related to the strength and properties of the paper. Pulp production from flax straw including Various pulping conditions including the composition of cooking liquor (10, 15 and 20%) and cooking temperature (130, 140 and 150$^{o}$C) at reaction times (60, 90 and 120 min) were studied in full-factorial design and determine the good pulping conditions. The influence of pulping conditions on the pulp obtained (Yield and Kappa number) are analyzed by three-factor and full factorial experimental design, and optimum pulping conditions are obtained. The best properties of the pulp kappa number and yield were obtained with 10% sodium hydroxide, in the cooking solvent, 131.74$^{o}$C cooking temperature and 120 min as cooking time. The optimum value of yield and kappa number were obtained from experiment 40.56%, 10.45 respectively. Tensile strength, tearing strength and burst strength are fit on the standard. In general, results based on chemical and morphological analysis indicated that flax straw fibres are promising fibrous raw material for paper production.



**Keywords**: Flax Straw, Pulp, Paper, Kraft Pulping, and Full Factorial Design

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## LIST OF SYMBOLS AND ACRONYM

### Symbols

| | |
|---|---|
| K | Kappa Number |
| Kg | Kilo Gram |
| Lig | Lignin |
| m | Meter |
| min | Minute |
| mm | Mill Meter |
| µm | Micro Meter |

### Acronym

| | |
|---|---|
| Alk | Alkali Concentration |
| ANOVA | Analysis of variance |
| C | Carbohydrate |
| Cel | Cellulose |
| CSA | Central Statistical Agency |
| $^{o}$C | Degree Celsius |
| DP | Degree of polymerization |
| eth | Ethanol |
| FAO | Food and Agricultural Organization |
| FTIR | Fourier transform infrared |
| GSM | Grams per Square Meter |
| H - | Factor Factors that depends on both time and temperature AND the temperature dependence is very strong. |
| ISO | International Organization for Standardization |

# 1. INTRODUCTION

## 1.1. Background of the study

Paper is produced from wood pulp that is typically formulated using a mechanical pulping process that grinds wood logs mixed with water or using a chemical pulping process to isolate lignin(Hamza, 2017). Once the raw pulping is done, the fiber is cleaned and removed to improve the quality of the paper(Chandra, 1998). The starting of pulp and paper manufacturing in the 15$^{th}$ century understood a rapid increase in demand for paper for a different purpose (Jahan, Gunter, & Rahman, 2011).

Papermaking was started from non-wood materials in China almost 2000 years ago. During the production process of papermaking from the agricultural waste/ biomass such as textile rags, cereal straw, reeds, grasses, and sugar cane bagasse have been used in pulping and papermaking ever since, especially in Asia(Drahansky et al., 2016), but Now years, the three major issues that would continue to puzzle the development of the paper factory is the lack of resources, environmental pollutions, and the aim of specialized processes production of pulp and paper. The most thing in the world to reduce the deficiency of raw material resources, which is mostly due to the fiber content and environmental free of the raw material and the structure of the fibre resources with a great amount of cellulose. Thereby, non-wood fibres used a colorful variety of superior materials in physical, optical aspects and environmental free, which could be used to upgrade their final output. However, throughout the experience, non-wood material accounts for exclusive a small amount of the raw material for the production of paper and paperboard. To reduce this problem can cultivate by using modern way and save environmental pollution. Different developing countries, almost 60% of the cellulose material comes from non-wood materials, agricultural waste and all biomass including flax straw. So used this biomass for the production of paper and paperboard save environmental quality(Liu & Wang, 2018).

Especially, in China and India, 70% of the raw materials used in the paper factory come from non-wood plants including cereal straw and bagasse. Different researchers study the amount of non-wood material to check enough or not. The annual production of paper from pulp has grown since to a multi-billion-dollar industry, concentrated mostly during a few industrialized country. Today, about 90% of all pulps are being produced from wood this shows there are great deforestation and environmental warming. Now a day numerous researches applied on a worldwide scale are focused on checking alternative non-wood raw materials as a source of

pulp production. Some types of non-wood fibres are being already used in some paper grade productions, although the paper quality varies due to the quality of fibres. Additional, the great issue for the availability of biomass, there are other driving forces behind the growing interest in non-wood pulping. Agriculture waste like flax straw, wheat straw and rice straws constitute the main source of non-wood fibres. The current consumption of pulp and paper in Ethiopia increase. To satisfy the demand there are two options once to import pulp from the aboard and other pulping from the eucalyptus(Drahansky et al., 2016).

Flax (Linum usitatissimum L.) is an annual plant cultivated in temperate climates. It is characteristic of central Europe. That said, the low quality of fibres being produced on farms in Poland led to a rapid decrease in the area of land given over to flax straw over the past few years. Recently, however, there is renewed interest in natural fibres in Europe and the time seems right to reestablish the flax fiber industry. In most Ethiopian area flax straw is cultivated, this indicated that there is enough resource of flax straw from agricultural waste for the production of the pulp as an input of paper production(Taddese & Tenaye, 2018).

Therefore, utilizing these materials as raw material for pulp and paper production is recommended in many ways. In this research, the pulp will be produced from one of the agricultural residues, flax stalks, and tested for its quality. Flax grows in the low fertilities of soil, currently, the soil fertilities become reduced gradually due to the weather condition of the world. Based on the above basic information farmer able to grow flax for the different purposes the first thing for the production of the pulp as an input of paper production and the second thing for production of edible oil. The main aim of this study is to produce pulp as input for the production of paper from Ethiopia origin of flax straw.

## 1.2. Statement of the problem

Paper is becoming an important commodity of today's society. The pulp and paper industries have been rising due to the increased demand of paper-based products and it is a must to find raw material sources for these industries. As the data obtained from central statistical agency the amounts of pulp and papers imported from the year 2014-2017, was 895,835 tonnes for 989 million USD (Lemma, 2018). The consumption of paper has been also steadily increased over the world. Though wood is renewable, the rate at which wood has been used is not commensurate with the rate it is being replaced. The rate at which forests are declining has been estimated to be 13.0 million hectares per year in developing countries. At the national level, the Ethiopian government has developed a policy that promotes agro based industrialization, known as agricultural demand led industrialization. To satisfy the enormous amount of fiber requirement, it becomes stringently necessary to look for alternative fibers sources other than wood. In this regard, non-wood fibers, such as agricultural residues and perennial plants, can be considered as an effective alternative source of cellulose fiber for producing pulp and paper sheets with acceptable properties. In Ethiopia, flax straw is highly cultivated. According to the central statistical agency report from 181,353.74 hectors 879,116.55 quintals of linseed obtained (Ethiopia, 2018), this indicated that a large area used for the production of linseed(Sileshi, Hailemariam, Atero, & Tesfaye, 2019). (Delesa, 2018) reported flax straw is widely cultivated in the high elevations area of Arsi, Bale, Shewa, Gojam, Gonder, Wollo, and Wellega. There for, the availability of these large quantities of fibrous residues has triggered the interest used as input for production of pulp and paper. It needs to grow any agro-ecological zones. Flax straw used for pulp and paper production. It's have high cellulose content and good morphological properties(Marques, Rencoret, Gutiérrez, & del Río, 2014). The cellulose content of flax straw is 51.56% acceptable for paper production(Wietecha, 2017).

## 1.3. Objective

### 1.3.1. General objective

The general objective of this study was Production and Characterization pulp from flax straw and find optimize pulping conditions.

### 1.3.2. Specific objectives

This study has also the following specific objectives: -

1. To characterize the proximate properties of flax straw
2. To investigate the effect of time, temperature and active alkaline on the yield of pulp and kappa number
3. To find the optimized condition and characterize physicochemical properties pulp
4. To characterize properties of the paper produced from flax straw

## 1.4. Significance of the study

- This study show that flax straw can serve as an alternative raw material source for pulp and paper production.
- Generate knowledge in pulp and paper process technology.
- Promote biomass used as input for production of pulp and paper.
- This work will show the possibility of minimizing environmental load emissions.
- Flaxseed production would get more recognition and flaxseed growers will be beneficial from selling of flax straw.
- Land coverage for cultivation of trees of raw material for paper manufacturing can be used for other purpose.
- Collection of flax straw from the fields and reaching them to factories for the production of pulp will generate rural employment.

## 1.5. Scope of the study

The thesis work generally covers the proximate analysis, morphological analysis, chemical composition of flax straw and its characteristics of pulp and paper from flax straw. Conduct the numerous techniques of pulping condition which are cooking time, temperature and active alkaline. Chemical pulping which uses delignification chemicals and produces quality pulp methods are used. From different chemical pulping methods kraft pulping process was selected for the study uses sodium hydroxide and sodium sulfide chemicals used as cooking flax straw and changed to a pulp. The study overall production process steps, raw material characterization, flax straw delignification, pulp characterization, paper sheet making and characterization of paper properties including tensile strength, tearing strength and burst strength.

# 2. LITERATURE REVIEW

## 2.1. Background of the study

Non-wood materials were used for papermaking in China nearly 2000 years ago until formulated countries adopted the operation of manufacturing pulp and paper from wood sources. This activity was invented in Germany by Friedrich Gottlob Keller in 1840. Nowadays, almost 90–91% of pulp and paper production is produced from wood. It involves the isolation of cellulose from hardwood and softwood fibers. The cellulose obtained is processed into pulp, utilized in papermaking. The domain demand of paper consumption has increased to almost 400% within the last 40 years ago and continues to develop around 2.1% yearly since 2009 with North America, Europe, and Asia accounting for quite 90% of total paper and paperboard product needed. All the above researcher finds the input of fabric for pulp production out of wood. The steady growth within the use of paper has resulted within the utilization of just about 35% of worldwide harvested trees within the production of pulp and paper(O. em A. Access & Azeez, 2018).

The standards of papermaking from pulp were set down in A.D. 105 when Ts‟ai Lun of China macerated the bark of mulberry trees, dunked a silkscreen form into the decreased macerate and on ended molded the early piece of paper more than 600 years sooner, squeezed sheets from papyrus were generally utilized in Egypt. Nevertheless, these sheets couldn't be considered to be paper, since they were collected of strips cemented together randomly. Paper was vital to the traditional Egyptians because it transformed Egyptian society in numerous ways. Once the knowledge of papermaking was developed, it had been kept a secret, allowing the Egyptians to accumulate a monopoly thereon because this technology is new at that point (M, K, & Baptist, 2013).

After the economic revolution, non-woody fibres were fundamentally raw materials for pulp and paper production. The input of fibre then included textile rags, cotton, cereal straw, reeds, grasses, and sugar cane bagasse. In 1970, the quantity of worldwide ability for the assembly of non-wood fibres papermaking pulp was only 7 million metric tons compared with the entire papermaking pulp ability of 113 million metric tons. This quantity indicated that only 6.7% of the entire. However, since that point, there has been a dramatic increase in non-wood fibres pulping capacity. By 1993, the entire amount of papermaking pulp ability supported on utilizing non-wood fibres amounted to just about 21 million metric tons out of a complete

papermaking pulping ability of 197 million tonnes, adequate to 10.6%. From 1970 to 1996, non-wood fiber pulping ability on a world groundwork enhanced 2-3 faster than the power for production papermaking pulp. For instance, during the amount from 1988–1993, non-wood papermaking pulp ability enhanced on calculate 6% yearly or 3 times faster than papermaking pulp ability. There's scope for 10–15% of pulp being replaced by non-wood pulp without significantly affecting strength, optical, and surface properties of most paper grades(Daud, Awang, Mohd Kassim, Mohd Hatta, & Mohd Aripin, 2014).

The manufacture of pulp, paper and paper products ranks among the world's largest industries. Mills are found in more than 100 countries in every region of the world and directly employ more than 3.5 million people. The major pulp and paper producing nations include the United States, Canada, Japan, China, and France(Drahansky et al., 2016) and (Ivana., 2016).

Globally the production of pulp is led by North America, which accounts for over one-third of the pulp production and generates an excess supply of 5%. Europe and Asia follow, each with close to one-fourth of global pulp production. The overall production of pulp in 2014 is 178.5 million tones, with a total consumption of 179.6 million tonnes. Whereas the global production of paper and paper board in 2014 was 406 million tonnes, with 407.6 million tonnes consumed. Asia is the leader in both production and consumption with about 45% in both categories(Roth et al., 2016).

In 2015, the regional distribution of pulp and paper production was as follows: Asia-Pacific, 195 million tonnes (48%); Europe, 104 million tonnes (26%); Northern America 83 million tonnes (21%); Latin America and the Caribbean, 21 million tonnes (5%); and Africa, 4 million tonnes (1%)(Hunsigi, 1989; Paper & Process, n.d.) and (Jahan & Gunter, 2009).

## 2.2. Pulping process of biomass in past researcher

The hemp straw and flax straw are the raw material after separation from bast fibres of hemp and flax plants. sodium hydroxide/hydrogen peroxide digestion method (TP) was performed in a revolving digester with a capacity of 15 $dm^3$. The pulp sample after pre-steaming was placed in a container and a cooking liquor was added at about 60 °C containing: 5% NaOH, 5.5% $H_2O_2$, 0.3% EDTA, 0.5% $MgSO_4$ and 5% liquid glass, per sample bone dry weight. The pulp was stirred for about 10 minutes. The liquor ratio was 4:1 (amount of liquor ratio to biomass material). Next the pulp was placed in the digester and cooked at 110 °C for 60 minutes. sodium hydroxide digestion method (TA) was performed in a revolving digester with a capacity of 15 $dm^3$. The pulp sample after pre-steaming (from 0.5 to 0.7 kg as bone dry weight) was placed in a container and a cooking liquor was added at about 60 °C containing 7% NaOH, per sample bone dry weight. The pulp was stirred for about 10 minutes. The liquor ratio was 4:1 (amount of liquor ratio to biomass material). Next the pulp was placed in the digester and cooked at 110 °C for 60 minutes(Wietecha, 2017).

The active alkali charges for hemp stalks (including flax straw), hemp woody-core and other biomass were 15, 18, 18 and 22% for dried straw raw material expressed as NaOH cooking chemical, respectively. For the Kraft pulping production process, the Sulphidity of the liquor was kept at 25%, with a liquor-to-wood ratio of kept with 5:1 for hemp and bast including (flax straw) raw materials and 4:1 for birch and pine wood chips. In all the cooking experiments, the temperature was raised to 165℃ in the first 90 min and was held there for another 90 min. After produced pulp from those materials, the fibrous material was washed and cleaned with distilled water, first on dense wire mesh and then by diffusion for 24 h in a vacuum filter, after which it was separated the fiber in the pulp. The cooked pulp added to the unbleached pulp slurry and then mixed with a bleaching agent and bleaching chemical. After that, pulp slurries were dewatered and stored in a refrigerator for further research to keep without any effect. The total yield of unbleached pulps was 57.7, 48.4, 52.9 and 46.2%, while the kappa numbers were 24.5, 27.1, 24.2 and 31.7, respectively obtained from the experiment(Danielewicz & Surma-ślusarska, 2010).

Separation of lignin from flax straw with 1.25 M NaOH, at 80 °C for 5 h yielded of pulp after cooking was 92 g $kg^{-1}$ lignin on a flax straw basis separating almost 34% of the lignin present in the flax shives and flax straw. Isolation of lignin from cellulose (main component) temperature the same correlation affected the amount of lignin obtained from alkali treatment

PLPW processing as the highest lignin yield (241 g kg−1 lignin on a flax shives basis) was obtained with alkali treatment pressurized low polarity water (PLPW) extraction with 0.47 M NaOH at 180 °C. This isolation process was nearly 88% of the lignin present in the flax straw. More lignin was obtained in the 0.47 M NaOH-180 °C isolate, 241 g kg−1 , compared to the water-180 °C extract, 27 g kg−1. The separation conditions of water 180 °C yielded less lignin than the 1.25 M NaOH, at 80 °C for 5 h separation condition. The yield obtained expressed the effectiveness of alkali assisted pressurized low polarity water a method for separation lignin from lignin-carbohydrate complexes. Separation of lignin from flax straw is achieved through cleavage and degradation of phenolic α-O-4-linkages, β-O-4-linkages, non-phenolic β-O-4-linkages, and carbon-carbon linkages in lignin and therefore improve in an alkaline isolation medium. Both the separate lignin from the water 180 °C and 0.47 M NaOH 180 °C pressurized low polarity water separation conditions obtained the highest carbohydrate contents of 311 and 302 g kg−1 and free phenolic acid contents of 3.9 and 4.7 g kg−1, respectively. Both pH and temperature have been shown to affect isolation and separation of carbohydrates from lignin-carbohydrate removed from the main component. Increased removal of carbohydrates from flaxseed and flax straw was obtained through the use of neutral and acidic isolation chemical solvents compared to alkaline isolation solvents, which is contradictory to our results with lignin-rich flax straw. Therefore, isolation temperature has a positive effect on carbohydrate separation from the main straw which is flax straw(Ross & Mazza, 2015).

The extraction of the fibres from the non-woody plant was carried out based on the below production process. The raw material or flax straw and other biomass were cut to a length of 2–3 cm and the straw was pulped in an autoclave with white liquor solution preparation of NaOH (16–17 wt%) at the maximum cooking temperature of 165 ℃ and cooking pressure almost 6 bar. The product of pulp from the experiments was washed three times with distilled water and the product from the experiment to a bleaching treatment using sodium chlorite (1.5% $NaClO_2$) at pH 4 to remove the residual lignin and increase the whiteness. Then the pulp was dried before use until the moisture content of the bleached pulp approximately 10%(Alila, Besbes, Rei, Mutjé, & Boufi, 2013).

In flax straw retting, the flax is laid out in a large field at easily access and dew is allowed to collect on it for more production of pulp in the retting process. This production process normally takes a month or more but is almost considered to improve the highest quality flax fibres use as input for a different purpose and it produces the least pollution. Retting and

separation of fiber can also be done in a plastic trash can or any type of watertight container of wood, concrete, earthenware or plastic. Metal containers will not work, as the acid is produced when retting, and it would corrode the metal. If the water temperature was kept at 80°F (27°C), the retting process under these conditions takes 4 or 5 days until the fiber isolate in the solution. If the water is any colder, it takes longer. Scum was collected at the top, and an odor is given of the same as in pond retting and fiber separation. 'Enzymatic' retting of flax has been found as a retting technique to engineer fibers with specific properties. The retting and mechanical processing steps work together to produce fibers, which are more precisely fiber bundles, of a particular fineness distribution. Different isolation in enzyme formulations used in retting can modify fiber properties and pulp properties. For example, color, strength, and fineness and information is needed on the specific fiber properties resulting from enzyme modifications, particularly related to subsequent cleaning(Dhirhi, Shukla, Patel, Sahu, Mehta, et al., 2015).

Pineapple leaves, flax straw and corn straw was cut around 3cm to 7cm for improve the pulping rate and quality of pulp. Biomass was achieved using chemical pulping method (soda pulping). 200g of the biomass (oven-dry weight) was weighted into a flask which was placed in distilled water for white liquor preparation and active alkaline and 42 g of soda pulping was dissolved in 600 ml of water (7% sodium hydroxide) and the solution was transferred into the conical flask. The ratio of white liquor to raw material was kept at 3:1. Cooking time was kept at 180 mins (3hrs)(Rafiu, 2015).

Pulping process were carried out in a 4 L autoclave fitted with different pulping conditions including time and temperature. The white liquor to raw material or biomass was kept at 6:1 ratio to improve the output. The cooking time and cooking maximum cooking temperature were kept at 90 min and 120℃. The different chemical amount used in the white liquor chemical composition. After pulp production, the pulps were mechanically fiber isolated in a three mixer for 1 min at 2% consistency of pulp sample to white liquor in the solution and screened on a flat-plate screen with 0.15 mm slits (a six-cut slot screen). The residual yield was determined on oven-dry weight basis finally calculated the output. The screened pulps were characterized without being further refined and without bleaching the removal of lignin the pulp after cooking. Kappa number of the screened pulps was determined using Tappi method T 236 to determine the lignin content of pulp after bleaching. Hand sheets were made and performed at 23℃ and 50% RH for at least 24 h before testing in accordance with the appropriate Tappi standard methods.

Raw material which is switch grass stock was used in the pulping condition at different parameter. Pulp making process was obtained using a laboratory digester of about 6L capacity. Raw material was prepared with appropriated size to improve the pulp quality and the final out put paper strength which is tearing strength, burst strength and tensile strength of paper. The pulping conditions used were at different pulping conditions which is temperature 170°C: time 35 min; 170°C: 45 min temperature to time pulping conditions; White liquor-to-switch grass was kept at ratio 6:1; liquor composition ($NaOH=Na_2SO_3$ ratio): 10/0, 15/0, 20/0, 15/5, 10/10, 5/15, 0/20. The pulping process was controlled utilizing a computer to improve the quality of pulp. For pulp yield determination, a sample of about 25 g (oven-dry weight basis) was placed in a stainless steel basket which was placed at the middle of the cooking basket containing the bulk of the material (500 g oven-dry weight). After cooking, the material was mixed with blender and washed on a filter paper to isolate the lignin from the main product. The washed material was dried at 105°C overnight until remove excess moisture. The yield was calculated the dried pulp over the initial oven-dry weight and finally expressed in percentage(Law, Kokta, & Mao, 2001).

Agricultural pulp board was firstly cut into small pieces to improve the pulping condition, swollen for 4 h in the water and disintegrated in a standard disintegrator. The obtained pulp was adjusted to a consistency of about 20 wt% after centrifugation and stored under 4°C. The pulp was isolated by 150 mm (100 mesh) opening wire cloth, and followed by passing through a 38 mm (400 mesh) opening filter cloth. The fines were then collected. The obtained fines were mixed with fibres (>150 mm) at ratios of 0%, 25%, 50%, 75%, 100%, and disintegrated before use to improve the quality of the whole fiber. The beating was accomplished by a PFI mill for 300 revolutions to isolate the fiber in the solution and finally formed the uniform sheet with good quality of paper(Luan, Li, He, Kuang, & Mo, 2019).

Biomass samples were cut into 2-5 cm and cleaned and washed to eliminate, isolate and other particle contaminants was removed. Then, the dried straw was ground to 0.40 mm and kept in a tight bottle for fur chemical and morphological analysis. Chemical compositions of cocoa pod husk and corn stalks were conducted according to the Technical Association of the Pulp and Paper Industry (TAPPI) Test Method. The prepared samples were first fed to Soxhlet extraction for 6 hours according to method T 264 om-88 to remove low molecular weight component in the sample and wax. The lignocellulosic content which is lignin and ash content was conducted out in different liquids according to TAPPI standards lignin such as (T 222 om-

06) and ash content (T 211 om-07). All the experiments were done in triplicate of the sample for all determination of the chemical composition of straw. The surface morphology of the cocoa pod husk and corn stalks were visualized in a JEOL JSM-6380LA analytical Scanning Electron Microscopy (SEM). The sample (one-quartered spatula) was sprinkled on the release paper and patted the release paper with a finger into the double-sided tape of the specimen stub. The samples on the specimen stub were lightly pressed by release paper and coated with a thin layer of the gold-palladium film before submitting to SEM for observing the surface morphology characteristic of the sample(Daud, Awang, Sari, et al., 2014).

The raw materials were prepared with appropriate size for improving the pulping conditions. The prepared raw materials were pulped by the pre-hydrolyzed, Kraft pulping process in laboratory scale to check for the yield of pulp and kappa number of pulp after cooking. The pulping conditions were carried out in a rotary digester with indirect electrical heating and controlled the cooking temperature. Pulping conditions to make bamboo dissolving pulp are pre-cooking acid with) cooking with active alkali 20%-22%; sulfidity 30%-32%; H-factor 1500-1600; temperature165 °C; white liquor to straw ratio was kept at 5:1. The cooked pulps were washed and cleaned with distilled water and defibered at 2.5% consistency (sample to water ratio) with a propeller mixer. After washing, the pulp was dried and read to the paper making process. Total pulp yield was measured. Kappa number of yield pulp was determined. Dissolving pulp properties tested by the specifications of regular pulp, parameters were tested alpha-cellulose content, alkali solubility (10% and 18% NaOH), extractive (wax, pectin and other low molecular weight components), ash, acid insoluble ash, viscosity, intrinsic viscosity and brightness of pulp. The content of alpha-cellulose pulp was tested, alkali Solubility is tested based on SNI ISO 692, extractive tested accordance with SNI 7197, ash content tested according to SNI 7460(Marques, Rencoret, Gutiérrez, & Río, 2010).

The pulp samples (30 g oven-dry weight) were homogeneously mixed with distilled water. The slurries were decanted into a 500 ml dried flask equipped with a mechanical stirrer under an inert nitrogen atmosphere. The temperature of the pre-treatment process was controlled by oil bath to maintain cooking temperature. Pre-treatment completed was accomplished by pouring water (100 ml) into the slurry. The pulp was then washed thoroughly to remove the residuals. The pretreated pulps were observed in an optical microscope to ensure that the macro appearance of the fiber to determine the morphological analysis of the sample. The sample to

water ratio was kept with 10% consistency for 30 min at room temperature(Pang, Chen, Dong, Yang, & Liu, 2013).

The biomass including flax straw was cooked in a 15 L batch reactor that was heated by an outer jacket containing electrical wires to controlled cooking temperature. The reactor contents were stirred by rotating the reaction vessel via a motor to improve the pulping conditions. Rice straw was placed in the autoclave together with the chemical pulping including soda pulping sulfite pulping and kraft pulping process and pulped by using active alkaline, cooking temperature, cooking time and white liquor were determined. The operating conditions with a white liquor to sample kept at 6:1 ratio. The cooked material was washed and cleaned to remove residual cooking liquor and fiberized in a disintegrator at 1200 rpm for 30 min, after which the pulp was beaten to isolate the fiber in the solution and the paper was made with a uniform sheet. Finally, the pulp was drained in a centrifuge and allowed to dry to a moisture content at 10% moisture at room temperature.

Lignin was isolated from the samples using two different methods. The first step for both isolated methods involved drying the flax in an oven at 60 °C for 16 h. Frist methods were conducted by following the alkaline cooking procedure with some modifications. Briefly, as a first step, ground flax shives were dewaxed for 5 h using toluene and ethanol (2:1, v/v) using a Soxhlet apparatus. To determine alkali-soluble lignin, the dewaxed flax shives were subjected to hydrolysis with 1.25 M NaOH at 80°C for 5h and used Spectrophotometer by measuring the absorbance. The cooked pulp was filtered with a glass filter and washed with water to remove the black liquor in the solutions this process was followed by ethanol (2 × 10 mL, and acetone. This created two fractions, a filtrate and an alkaline treated residue. The pH of the filtrate was reduced to 5.5 by addition of 6 N HCl. The hemicelluloses were separated from the filtrate by precipitation of the neutralized filtrate in 3 volumes of ethanol. After filtration with a glass filter, the precipitated material was washed with 70% ethanol and allowed to air dry. Ethanol was evaporated from the filtrate, and the alkali-soluble lignin's were obtained from the filtrate by precipitation at pH 1.5 by addition of 6 N HCl. The alkali-soluble lignin was washed with acidified water (pH 2), centrifuged and freeze-dried(Ross & Mazza, 2015).

## 2.3. Fiber dimensions and derived(indices)

Five straw were determined from different non-wood raw materials and cotton, whereas five branches were collected from olive and almond trees respectively. To get good results from each raw materials, three samples from each straw were taken at 10% (base), 50% (middle) and 90% (top) of its height/length respectively, for fiber length determination, small fibers were obtained and macerated with 10 ml of 67% $HNO_3$ and boiled in a water bath for more isolation of fiber in the solution (100 ± 2℃) for 10 min. The straw in the solutions were then washed, placed in small flasks with 50 ml distilled water and the fiber bundles were separated into individual fibers using a small mixer with a plastic end to avoid fiber breaking. The macerated fiber suspension was finally placed on a slide (standard,7.5cm to ×2.5cm) utilizing a medicine dropper. For fiber diameter, lumen diameter and cell wall thickness determination, cross-sections were obtained from the same height/length as above and were stained with 1:1 aniline sulfate–glycerin mixture to enhance cell wall visibility (cell walls retain a characteristic yellowish color) and easily viewed the value using the apparatus. All fiber samples were viewed under a calibrated microscope; a total of 25 randomly chosen fibers in the solutions were measured from each sample for a total of 75 fiber measurements from each straw from the total sample and 375 measurements for each of the four fiber dimensions of each species. For kenaf, measurements were made for bark/core fibers and for reed for nodes and internodes fibers(Ververis, Georghiou, Christodoulakis, Santas, & Santas, 2004).

Fiber lengths were determined from the actual pulp get using a Fiber Quality Analyzer (FQA, OpTest Equipment, Canada), whilst the fiber length arrangement curve was determined by plotting the fiber frequency data generated finally related the two plot and the fiber length was determined. The fiber quality analyzer was used optical imaging of fiber to yield length, coarseness and shape. In the measure, a very dilute fibers suspension was used about 800 mL with continuous stirring for more diluting fiber in the solutions. The solutions were not normally determined but it was usually fixed at almost 20 fibers passing through a small tube per second and the fiber image was obtained. The total fiber count could range from 5000 and up and viewed the image. Fiber diameter, cell lumen width and cell wall thickness were measured directly from the magnified image with 100 measurements made on each types of straw fiber. Proximate chemical analyses of the raw material were determined such as ash, extractives and lignin, were carried out following the appropriate Tappi standards. Polysaccharide composition including cellulose, hemicellulose and lignin of the non-wood material was analysed by using gas chromatography (GC) according to Tappi standard T249

with slight modification. Acetic anhydride–pyridine mixture was employed for acetylation of polysaccharide instead of the usual standard of acetic anhydride sulphuric acid. The GC system used in this study is the Hewlett Packard HP6890 Plus, equipped with a flame ionization detector (FID) and the column used is of the capillary type Supelco SP-2380 (30 m × 0.25 mm× 0.20 m). Finally, properties of each straw were determined and clearly understand how much importance used this straw for production of pulp and paper.

**Derived values**

Three derived values were also calculated using fiber dimensions which are fiber length fiber diameter and lumen diameter: slenderness ratio as fiber length/fiber diameter, flexibility coefficient as (fiber lumen diameter/fiber diameter) × 100 and Runkel ratio as (2 × fiber cell wall thickness)/lumen diameter. The values were then compared to those of softwoods and hardwoods to assess the suitability or checked whether in range of the non-wood or straw used for pulp and paper production(Ververis et al., 2004).

The morphological properties of the fiber, seems like fiber length and width, are good parameters in predicted pulp and paper qualities. Fiber length is that the most vital property for pulping because it generally influences the properties of paper of paper example tearing strength. High quality the fiber length, higher are going to be the tearing resistance of paper and high appearance of paper. On the opposite hand, longer fibers tend to offer a more open and less uniform sheet structure. a crucial feature of non-wood fibers is that the wide variability/properties among the lengths of the fibers of different species. a number of these fibers have short lengths almost like the short fibers of hardwoods, while others, and especially flax and hemp bast fibers, present remarkably high lengths (up to 28000 μm fiber length) (Marques et al., 2014).

The fiber dimensions (fiber length, fiber diameter, lumen width, and wall thickness) are essential parameters of lignocellulosic materials because they're similarities to various structural, physical and chemical properties of the plant. they're also high-quality indicators to make a decision the fabric suitability and uniformity for various end products. They affect much wood-product manufacturing, the same as drying process, resistance to cutting and machining and pulpwood quality(Marques et al., 2014) and (Law et al., 2001).

Its fiber length additional low diameter improves it very suitable for finishing paper purposes. Sisal and abaca pulps have a strangely good tearing resistance and high porosity and

are compatible with the assembly of papers where very good strength and high porosity are required. Fiber dimensions any biomass/ agricultural waste also are identified with different pulp quality indices like Runkel ratio, slenderness ratio, rigidity coefficient, and adaptability coefficient. Based on the studied fibers, flax and hemp pulps have traditionally been used because of the early furnish for the rolling paper (burning tube), where strength, opacity, and control of air permeability are important(Lemma, 2018).

## 2.4. Non-wood fibre resource

Nowadays, within the papermaking industry, the environmental problems have brought forward the necessity for cleaner technology where the new non-wood resources are introduced to exchange traditional raw materials like wood resources with non-wood resources. The cleaner technology or green technology is applied to realize increased production with minimum effect especially on the environment and lessen the disposal cost, steadiness risks and resource cost leading to a declined burden on the natural environment and also increase the profits in pulp and paper-based industries(Sridach, 2010), and (Liu & Wang, n.d.).

In China, the consumption of non-wood resources in pulp and paper-based industries is above wood sources from the year 1995 to 2005. The event of those industries will need continuous and sustainable forestry around the world. this is often also because non-wood plant sources have displayed different sorts of advantages in pulp and paper-based production compared to wood resources(Liu & Wang, 2018).

Flax features a very long fiber length and thus good reinforcement properties. But 10% of flax pulp within the mixture would give sufficient reinforcement for brief fiber pulp as shown in earlier studies. Therefore, through careful selection of the staple, the specified paper properties are often achieved from a really wide selection of fiber lengths(Leponiemi, 2011).

In western countries, large areas are left uncultivated thanks to the overproduction of food. These fields might be utilized for non-food production. The cultivation of various non-wood plants for energy, chemicals, or fiber production. These plants include short-fibre plants, like elephant grass, giant and reed birdseed grass, and long-fibre plants, like hemp, sisal, kenaf, jute, and flax (Rousu Pasi, 2002).

## 2.5. Lignocellulose composition of flax straw and other biomass

Current lignocellulosic materials for papermaking are often classified into five categories: hardwoods (aspen, poplar, eucalyptus), softwood (pine, spruce), agricultural byproducts (sugarcane bagasse, wheat straw), herbaceous biomass (switch grass, miscanthus) and woody grasses (giant bamboo, kenaf). The main macromolecular components of all lignocellulosic biomass are cellulose, hemicellulose and lignin. Other components found in lesser proportion are pectin, extractives and inorganic matter. The proportions and chemical composition of those components differ counting on the sort of feedstock. Cellulose, Hemicellulose, and lignin are the three main constituents of any lingo cellulosic source.

i. Cellulose

Cellulose is the main structural component that gives strength and stability to the plant cell walls and its strength. The amount of cellulose is great influences on the properties of paper, the economics of fiber production, and hence the utility of the fiber for different applications. Simply speaking it is the structural element and the major constituents of the cell wall of trees and plants. The empirical formula for cellulose is $(C_6H_{10}O_5)$ n where n is the degree of polymerization (DP) (Biermann, 1996). In pulping, the foremost important lignocellulosic material component to retain and protect is cellulose, which may be a strength bearing, linear, high molecular mass polysaccharide. Cellulose or β-(1→4) glucan may be a linear polymer of glucose or cellobiose units with about 10 800 or 10 300 glucose residues i.e. the degree of polymerization (DP) for grasses and hardwoods respectively.

The chains are packed during a parallel alignment through hydrogen and Van der Waals bonds in so-called elementary fibrils, originally considered to be 3 to 4 nm wide and containing about 36 chains – although larger crystalline fibrils up to 16 nm have also been discovered. These elementary fibrils are then packed in micro fibrils, where the elementary fibrils are connected by hemicelluloses, an amorphous polymer of various sugars, also as other polymers like pectin substances and held together by lignin(Biermann, 1996).

ii. Hemicellulose

Hemicellulose in plants is slightly cross-linked and consists of multiple polysaccharide polymers with a degree of polymerization and orientation but that of cellulose. Mechanically, hemicelluloses contribute little to the stiffness and strength of fibers or individual cells. Unlike cellulose, hemicelluloses are heterogeneous polymers of five-carbon sugars or pentose (β-D-xylose, α-L-arabinopyranose, α-L-arabinofuranose) and six-carbon sugars or

hexoses (β-D-glucose, β-D-mannose, α-D-galactose), also as of some hexuronic acids (β-D-glucuronic, β-D-galacturonic, α-D-4-O-Methylglucuronic) and deoxy-hexoses (α Lrhamnose and α-L-fucose).

In the plant cell wall, hemicelluloses act as filler between cellulose and lignin to increase the stability of the cellulose-hemicelluloses-lignin matrix. Hemicelluloses play a major role in papermaking pulps as they assist to increase the bonding strength of the fibres and improvement of the pulp tensile and burst strength.

iii. Lignin

Lignin may be a highly cross-linked molecular complex with an amorphous structure and acts because of the glue between individual cells and between the fibrils forming the cell membrane. The lignin content of the fibers influences the structure, properties, morphology, flexibility, and rate of hydrolysis. Fibers with higher lignin content appear finer and can be more flexible and adaptable. Mineral substances present in lingo cellulose, especially straw, contain silica that has many undesirable effects. Such a staple is a smaller amount vulnerable to loosening and swelling of the fiber structure. Chemical composition of various sorts of plant biomass (wheat straw, rape straw, rice straw, sunflower straw, and flax straw) (Drahansky et al., 2016) is shown in Table 2-1.

**Table 2-1: Chemical Composition of Different Biomass**

| Plant biomass | Lignin% | Holocellulose% | Alpha-cellulose% | The soluble substance in ethanol% | Mineral substances % |
|---|---|---|---|---|---|
| Wheat straw | 21.65 | 73.75 | 39.17 | 4.57 | 5.53 |
| Rape straw | 19.43 | 72.28 | 45.39 | 3.32 | 4.27 |
| Rice straw | 15.65 | 59.13 | 38.42 | 8.56 | 13.25 |
| Sunflower | 18.24 | 69.33 | 40.16 | 7.51 | 6.89 |
| Flax straw-fiber variety | 17.81 | 75.89 | 58.74 | 3.72 | 2.84 |

**Source:** (Rousu, 2002) and (Drahansky et al.)

Among all studied materials, flax straw, and rape straw were defined by an advantageous composition for the separation of cellulose fibers deliberate for changeover into cellulose nanofibers. The alpha-cellulose content was 58.74% for retted flax straw-fibre type of straw and 45.39% for rape straw. The lignin content in these two materials was 17.81 and 19.43%, respectively (Table 2-1). The organic substances contained within the retted flax straw-fiber variety were 3.72% and in rape straw, it had been 3.32%, which was inferior to within the other

raw materials (Table 2-1). High cellulose content and low content of lignin also as organic and inorganic substances informed the suitability of biomass for the assembly of cellulose fibers. The presence of a serious amount of organic substances soluble in ethanol (>7%) inhibits the delignification activities. The below table shows the chemical composition of flax shives or flax straw per one kilogram of the given sample(Ross & Mazza, 2010).

**Table 2-2: Chemical Composition of Flax Shives or Flax Straw**

| Component | Content(g/kg flax shives) |
|---|---|
| Cellulose | 333±5.0 |
| Hemicellulose | 219±5.0 |
| Acid insoluble lignin | 260±1.8 |
| Acid soluble lignin | 13±0.1 |
| Ash | 15±0.4 |
| Wax | 35±2.4 |

**Source**:- (Ross & Mazza, 2010)

Based on the above chemical composition of flax straw and other biomass flax straw high cellulose content related to other agricultural waste. Flax straws have long fiber and give good quality of the paper. The amount of cellulose content flax straw around 58% based on the above statement.

### 2.5.1. Determination of extractive of flax straw and other agricultural waste

5g of dried raw flax straw was loaded into the cellulose thimble and put within the Soxhlet extractor set up, 400 mL of acetone was used as a solvent for extraction. Residence times for the boiling and rising stages were carefully adjusted to 80 $^{o}$C and 25 min respectively on the heating mantle for a 4 h run period. After extraction, the sample was air-dried at room temperature overnight. The constant weight of the extracted material was achieved in a convection oven at 105$^{o}$C. The %(w/w) of the extractives content was evaluated as the difference in weight between the raw extractive-laden straw and extractive-free flax(Ayeni, Adeeyo, Oresegun, & Oladimeji, 2015).

### 2.5.2. Determination the lignin content of flax straw

Lignin content of flax straw and other agricultural waste were separated, analyzed and identified in a different method based on the properties and nature of the plant. Therefore, the results were analyzed and compared to those for the control plants. The procedure to determine lignin content of most non-wood materials, 10 ml water was added to the dried green

parts of the plants (10–15 mg), and hence the samples were heated for 1 h at 65℃ and stirred every 10 min. Then, the samples were filtered through a GF/A optical fiber filter and rinsed sequentially with water, ethanol, acetone, and yet ether. The filters were put in glass vials and heated overnight at 70℃. then, 25% acetyl bromide (2.5mL) was added to every vial and incubated at 50℃ for 2h. The cooled samples were mixed with 10 ml of two normal caustic soda and 12 ml of ethanoic acid. They were left overnight, and therefore the next day, the lignin content was determined at 280 nm Coniferyl alcohol was used for the calibration curve, and therefore the results are recorded because of the same properties of coniferyl alcohol (Musialak & Wro, 2008).

The low lignin content of most of the fibers seems to be important for his or her use in paper pulp production, as they might be needed/use fewer chemicals and fewer drastic conditions during pulping and bleaching. However, not only the content but the lignin composition also strongly affects delignification rates, chemical consumption, and pulp yields. Generally, the efficiency of pulping is the same/ similarly proportional to the quantity of syringyl (S) units in lignin. The G units have a free C- 5 position found for carbon-carbon inter-unit bonds, which make them fairly immune to lignin de-polymerization in pulping, while the S lignin is comparatively unbranched and features a lower condensation degree and thus is simpler to delignify. the upper reactivity of the S lignin concerning the G lignin in alkaline systems is understood and, therefore, the lignin S/G ratio directly affects the delignification behaviour. Higher S/G ratios would imply higher delignification rates, less alkali consumption, and, therefore, higher pulp yield(Marques et al., 2014).

### 2.5.3. Analysis of the cellulose content of flax straw

The amount of cellulose in the biomass was determined using a colorimetric method with anthrone reagent and other method performed to determine the cellulose content. To give a sequential release of lignin, hemicelluloses, and xylosans, stem samples were incubated with both nitric and acetic acids (1:8, v/v, for 1h at 100℃) and then centrifuged(Reddy & Yang, 2005). The pellet was washed twice with water (0.5 ml) and re-suspended in 1 ml of 67% $H_2SO_4$ (v/v). Then the cellulose level was determined by spectrophotometer at 620 nm against cold anthrone reagent. Cellulose diluted in 67% $H_2SO_4$ (v/v) was used as a standard. The cellulose content was measured in control and transgenic plants from the field trial (ISO, 2006; A. Lignin, n.d.; Musialak & Wro, 2008; TAPPI 2017, 2007).

For hemicellulose and Klason lignin content estimation, milled samples were extracted with acetone during Soxhlet equipment for 8h in 80℃ for proper time set and including heating and subsequently extracted with predicament (3h at 100 ºC). The result from the acetone extract was evaporated to dryness and resuspended in chloroform for chromatographic analysis of the lipophilic fraction. Acid soluble lignin was estimated using a spectrophotometer at 205 nm and calculated the ash from the oven to determine the insoluble lignin content and Ash content was estimated because of the residue after 6h at 575°C(Marques et al., 2010).

The cellulose content of flax straw was determined simply by using calculation by assuming the content of flax straw are cellulose, hemicellulose, ash, extractive and moisture. Cellulose was calculated by subtracting all other content from the initial weight of flax straw and other agricultural waste(Ayeni et al., 2015).

## 2.6. Chemical pulping method of non-wood material

Pulp containing wood or additional lignocelluloses materials that are weakened physically and or chemically such (more or less) discrete fibers are liberated and may be dispersed in water and reformed into the internet so good pulping condition be needed for a good quality of fiber. Recently, the delignification technology in alkaline pulping process of wood materials has been applied in non-wood fiber cooking process. Generally, alkaline cooking requires adding some cooking chemicals, like NaOH, $Na_2CO_3$, and so on. This section provides a summary of alkaline pulping, sulfite pulping, organic solvent pulping, and biological pulping(Saijonkari-pahkala, 2001), (Rodrı, 2008)and (Biermann, 1996).

### 2.6.1. Alkaline pulping

In the process of alkaline pulping, the solution of alkaline agents would be formulated to treat fiber materials to form uniform solution most of the lignin and isolate the fibers from the fabric into pulp. Consistent with the range of pulping condition in the alkaline pulping process of non-wood pulping is often divided into oxygen alkali method, sulfate method, sodium hydroxide method, lime method, and so on base on the chemical used for delignification.

After the production of fiber, the digester would be wont to hold the good parameter material, which is followed by input cooking liquor into the digester. Then, the cooking reaction homogeneous, the digester is often idled firstly, which precedes the indirect heating or direct steam heat to the at critical temperature for cooking (general 150–170°C). Then this temperature should stay for a period to get rid of the lignin and isolate the fibers. When the

making pulp endpoint is reached, the pulp in digester should be blown or transferred into the blow tank (Biermann, 1996).

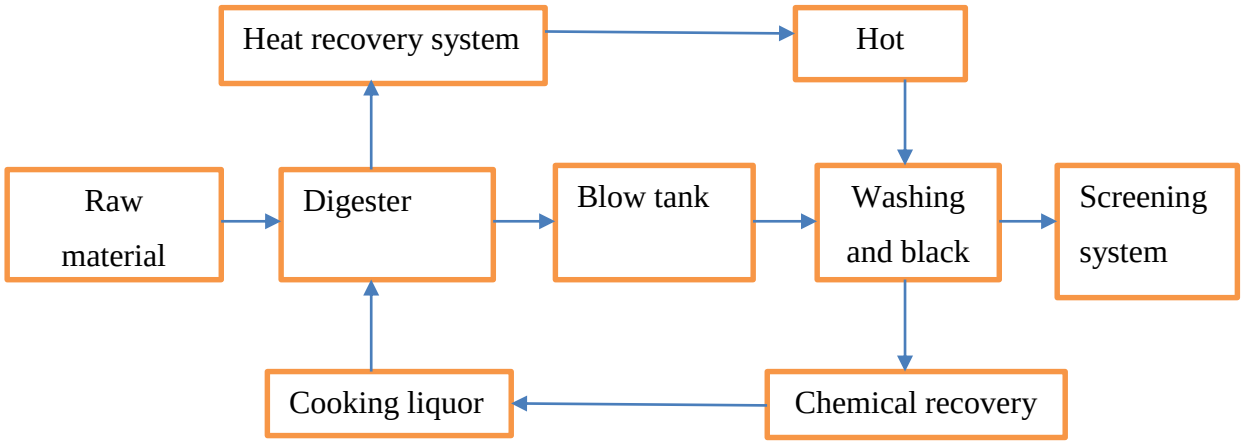



**Figure 2-1 Flow Diagram of Alkaline Pulping in Non-Wood Raw materials**

**Source** :- (Liu & Wang, n.d.)

### 2.6.2. Caustic soda pulping

The caustic soda pulping production process has been mostly used in the pulping of non-wood raw material. The main chemical used in the pulping process is NaOH, and sometimes used $Na_2CO_3$ to improve quality of pulp, the dosage of which depends on the fiber properties and raw material characterization. The cooking temperature in this condition used with the range of 140–170°C and the alkaline charge is almost 16%(Liu & Wang, n.d.) and (Biermann, 1996).

### 2.6.3. Kraft pulping

The Kraft pulping manufacturing process has become the common process for the production of full chemical pulp. The reasons are the strength of the pulp that produces stronger papers than the other methods, the versatility of the process in its ability to handle a wide range of raw materials, and the ready availability of a chemical recovery system.

Kraft process can obtain woods with high resin content, and in some cases modified to allow the removal and conversion of those and other organic materials into important by final output. The most cooking chemical is caustic soda, (NaOH) of a pH 12 or the active alkaline used 10 to 25% based on the types and nature of raw material. The wood, when cooked, will release acids into the cooking solution to scale back the pH during the making process. The caustic soda can use into several different reactions with the wood for the production of pulp, several of which can also contribute to the consumption of the NaOH and therefore the subsequent lowering of pH. If the pH is allowed to decrease during the cooking, the final output is going to be the degradation of the cellulose and loss of pulp quality. The loss of

quality in pulp may show up either in strength loss or colour development(Tran & Vakkilainen, 2016).

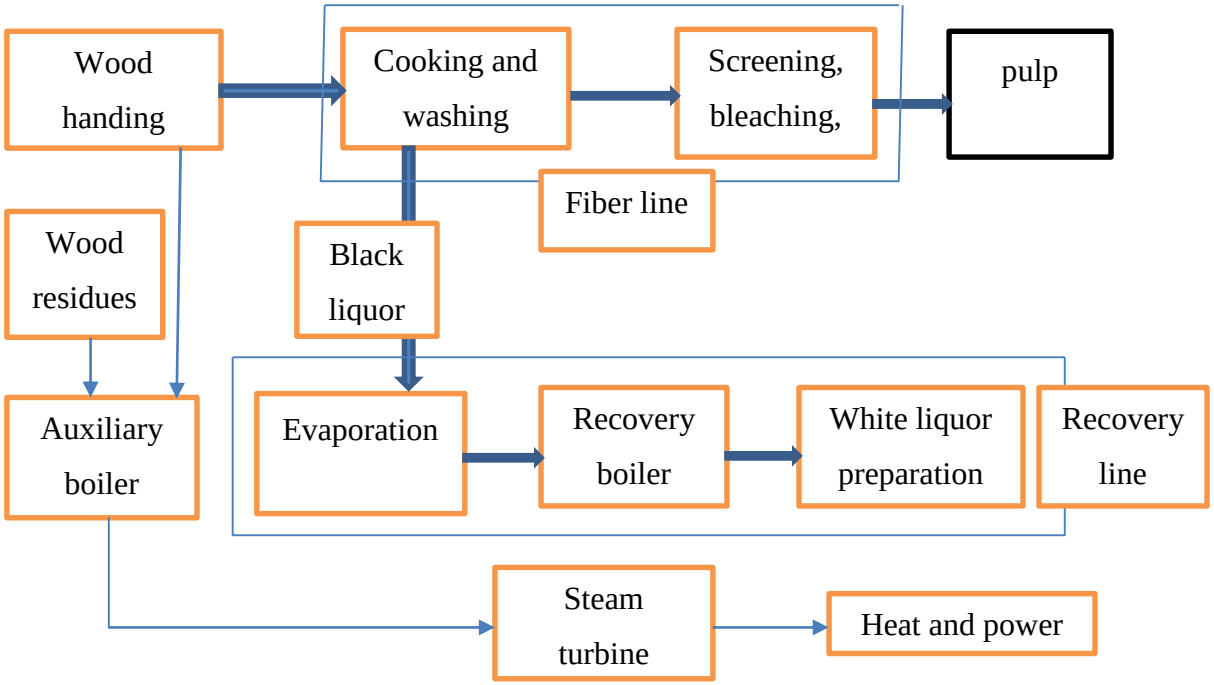



**Figure 2-2:Over View of Kraft Pulping Processes**

Source: (Biermann, 1996).

Additional, if the concentration of NaOH is just too high, it causes harm to the chips. The balance is maintained by the utilization of sodium sulfite, ($Na_2S$) which function as a buffer or caustic donor as shown within the equilibrium reaction below.

$$Na_2S + H_2O \leftrightarrow NaOH + NaHS \quad (2.1)$$

The controlling think about this equation is that the relative concentration of the compounds on either side of the equation. If the sodium hydroxide concentration is reduced, the reaction will proceed to the proper to replenish the NaOH concentration. The inclusion of the $Na_2S$ within the cooking liquor helps control the pH throughout the cook and thereby prevents, or a minimum of reduces the degradation or quality loss, of the resultant pulp. The equilibrium reaction in equation (2.1) shows that the caustic concentration remains suppressed as long because the pH is high, but the potential for regeneration or maintaining its concentration because the pH is lowered is out there until the $Na_2S$ is additionally expended.

The main reasons for the dominance of the Kraft process are its versatility in dealing with different raw materials coupled with superior pulp quality and a more efficient cooking

chemicals recovery method. Kraft pulping produces a stronger pulp, but it increases pressure on the environment by releasing sulfur-containing compounds known as total reduced sulfur compound (TRS), sulfur dioxide, suspended solids, and polluted wastewater (Biermann, 1996).

## 2.7. Overall Processes description of chemical pulping

In chemical pulping, chips and chemicals in preparation solution are cooked with then which is both chips and chemicals during a pressure vessel which may be maintained on a batch or continuous basis. Once the making is complete, the pressure is avoided to the vessels, blowing the delignified pulp out of the digester and into a holding tank. The sequence is then made more than one. In a continuous pulp making process pre-heated of chips are fed into the digester. Raw material and chemicals are mixed within the impregnation region to improve the good condition of the pulping condition at the highest of the digester then continue through the upper cooking part, the lower cooking part, and therefore the washing region before being sent into the blow tank for proper collection of the final output(Ross & Mazza, 2010). The fifth step is bleaching which separates the remaining lignin and therefore the final step is sheet making which spreads out the pulp into smooth, pressed sheets (often chemically added to supply particular properties the same as colour or water resistance). for a few papers the bleaching step makes no sense, but all white and coloured papers require bleaching for improving the quality of final output which is paper(Salmela, Alén, & Vu, 2008).

### 2.7.1. Raw material preparation

Wood is transferred to the Kraft mill in one of two ways: whole logs and sawmill chips (residuals from sawmills). The drum debarker is used to slightly inclined from the unwanted things, rotating drum is best suited to small diameter logs and good raw material preparation highly affected on the final output of the pulp and paper. Even if the material sorted but using type, quality and other basic parameter needed to improve the good quality of the paper. The raw material type and way of preparation directly related to the strength of paper.

### 2.7.2. Cooking

The pulping conditions consistency from 5% to 10% raw material to white liquor ratio. Typically, delignification/pulping process requires several hours from the range 60min to 180min based on the type of pulping process and raw material type if non-wood raw material used for pulping the temperature started from 130 to 160°C. Under these operation process, lignin and hemicellulose degrade to offer fragments that are soluble within the strongly basic

liquid. The solid pulp (about 50% by weight of the dry wood chips) is collected and washed. At now, the pulp is understood as brown stock due to its colour.

The cooking procedure is where the most a part of the delignification occurring. Here wood chips are heated in the solution of NaOH and $Na_2S$ take in the range from 10 to 30% and 20 to 25 % respectively during an autoclave, during which era tons of the lignin (the reinforcing substance that makes tree cells wood hard and woody instead of soft like those of other plants) is far away from the wood. In the cooking process, the sodium sulfide used to buffer and to sustain the cooking reaction due to the original caustic soda component is consumed through reaction with the lignin and carbohydrates within the wood. Small amounts of sulfide react with lignin within the wood, sharing arise to the odors identifying of Kraft mills for the production of pulp. These are thanks to the difference of evaporable compounds which allow methyl mercaptan and dimethyl sulfide (Gustavsson, 2006; Shahzad, 2012).

### 2.7.3. Pulp washing

It is necessary to get rid of the waste liquor from the stock to reclaim the liquor and also to supply top-quality pulp. The washer consists of rotary drums designed to scrub the stock into the tank below the washing drums. The water within the stock passes through the wire screen on the surface of the washing drum causing a pad of fibers to builds abreast of the drum surface. The pad of fibers is raised out of the tank by the rotation of the drum and washed further by showers located above the drum. The washed stock is often faraway from the drum and mixed with water and pumped to subsequent operation.

### 2.7.4. Pulp screening and bleaching

Bleaching is the treatment of cellulosic fiber with chemicals to increment the brightness of the pulp. Brightness may be achieved by either lignin separate (delignification) or lignin decolorization. Lignin remains a major constituent of pulp even after digestion by chemical pulping. For example, Kraft pulp may obtain up to 6% lignin obtained on its dry weight. The unbleached ground-wood spruce pulp may contain 27%. The strength of paper is largely due to the chemical bonds (hydrogen bonds) formulated between cellulose fibers. Although longer and more different pulping might separate more of the lignin, thus reducing the amount of bleaching needed, the cellulose molecules might be dissolved and their bonding power reduced. The isolation of lignin by bleaching is regarded as a continuation of the pulping process, although somewhat gentler and less destructive, bleaching too can degrade cellulose if done improperly(Biermann, 1996).

The isolation of unwanted also indicates the necessity for laundry as an integral part of the entire bleaching sequence. The pulp is subjected to washing immediately after bleaching to get rid of both the spent solution and then the impurities. Equipment used for bleaching processed consists primarily of closed tanks into which the pulp is pumped in water suspension after being mixed with bleaching chemicals (Zhong Liu, Pulping and Papermaking of Non-Wood Fibers, 2018).

### 2.7.5. Papermaking

Papermaking is the production process whereby pulp fibers are mechanically and chemically treated, formed into a dilute suspension, spread over a mesh surface, the water isolated by suction, and the final output pad of cellulose fibres pressed and dried to form paper. Paper capability is dependent on the individual fibre strength and the strength of the bonds between the fibres. It is usually the latter, which is the limiting factor. Refining increases, the inter fibre bonding at the expense of the individual fibre strength, but the net result will be an increase in paper strength. Pressing and calendaring (feeding through rollers) increase density and promote smoothness(Biermann, 1996).

## 2.8. Challenge in non-wood pulping processes

The principal problems identified with using industrially non-wood materials are the logistics of the bulky/huge raw material and its typically short harvesting time. Thus, the raw material must be stored between harvest seasons. If the raw material is stored outside some equipment under prevailing climate conditions, moisture and biological activity easily cause the material to decay and contaminate. In furthermore, non-wood plants usually have high silica content and the silicates soluble in alkaline cooking liquor which makes alkaline recovery difficult and in many cases places an excessive burden on the local environment(Leponiemi, 2011).

## 2.9. Gap analysis on the study

- Not clearly investigate the effect of time, temperature and active alkaline on the yield of pulp production from flax straw. In this study clearly investigate the effect of this pulping parameter.
- The ratio of white liquor to straw the past study mostly undertaking in 5:1 ratio. This follow highly develop color (black liquor). In this study the ratio white liquor to straw was kept 9:1 and compare to the past study on the effect ratio.
- In the past study pulp production from flax straw using retting (mechanical pulping) and the strength of pulp is poor and its required high energy. In this study used kraft pulping method and improved the strength of pulp.
- Other agricultural waste used kraft pulping for pulp production so in this study flax straw used for pulp production using kraft pulping process.
- In the past researcher flax straw used for especial paper production but in this study flax straw used for any printing and writing paper production from this straw.

# 3. MATERIAL AND METHOD

## 3.1. Material and equipment

The main raw material use in the experimental works was flax straw which is one of the most important agricultural residues.

Equipment used: -

Equipment's use to conduct this study was for the production of pulp from flax straw:- Autoclave for pulp cooking, Desiccators, Water bath, Drying oven, Soxhlet apparatus, Cellulose extraction Thimble, Spectrophotometer, Poly Ethylene Bag, Silica Crucible, Muffled Furnace, Digital weighing Balance, Weighing bottle, Stopper, Erlenmeyer flask, Heating mantle, Weighed Sintered Glass Crucible, Watt-man Filter paper, Measuring Cylinder, Rounded Bottom Flask, Cotton, Glove, Mask and Goggles, volumetric flask, Stopwatch, Pipettes, Burette, Reaction beaker, Spoon and magnetic stirrer, standard pulp beater machine equipped with a motor.

Chemical used: -

The chemicals and reagents used in this study was:-Analytical grade caustic soda (NaOH), sodium sulfide ($Na_2S$), distilled water, Potassium permanganate solution standardized 0.1000±0.0005N $KMnO_4$, Sulfuric acid 4.0N $H_2SO_4$, Acetone, Nitric acid, Aniline sulphate glycerin, hydrogen peroxide 5% ($H_2O_2$) etc.

## 3.2. Physicochemical characterization of flax straw

### 3.2.1. Raw material pre-treatment

Raw material treatment was conducted by sieve, and manual scan for removing unwanted material from pure flax straw at Addis Ababa University School of Chemical and Bio-Engineering laboratory (Addis Ababa, Ethiopia). Raw material, flax straw from Shewa agricultural research Centre was collected and cleaned from other unwanted things. 20kg of flax straw was transported to Addis Ababa Institute of Technology. Flax straw was cut into an average length of 2cm using the cutter and manual cutting in the Mechanical unit operation lab. Then the sample was ready for physicochemical characterization and pulping such as morphological analysis proximate and chemical composition of flax straw.

## 3.3. Morphological characteristics of flax straw

Morphological analysis of flax straw was performed by a calibrated motic-electron microscope at the Ethiopian agricultural research institute (Addis Ababa, Ethiopia). According to TAAPi T271 om-07, Ten samples randomly select of flax straw was taken from a storage bag for morphological analysis. In the morphological analysis of flax straw including fiber length, fiber diameter, lumen width, and cell wall thickness. For fiber length determination in the flax straw, small amount flax straw was taken, macerated with 50ml of $HNO_3$, 67% and distilled water with ratio 1:1 until the fiber separated in the solution and boiled in a water bath $100\pm2^oC$ for 20 min and wash with distilled water (O. Access, n.d.; Dhirhi, Shukla, Patel, Sahu, & Mehta, 2015) and (Engineering, Production, Stalks, & Pulping, 2015). The separated flax was then washed and cleaned, placed in small flasks, with 50ml of distilled water and the fiber bundles were isolated into individual fibers using a small mixer with a plastic end to removed fiber breaking. Finally, the fiber length was seen by a calibrated motic electron microscope. For fiber diameter, lumen width and cell wall thickness determination, cross-sections were cut on in small pieces in manually. This cross-section was stained with 1:1 aniline sulphate glycerin mixture to enhance cell wall visibility (cell walls retain a characteristic yellowish colour). Three derived values were also calculated using fiber dimensions: slenderness ratio as fiber length /fiber diameter, flexibility coefficient as fiber lumen width/fiber diameter) *100, and Runkel ratio as (2* cell wall thickness /lumen width). The results flax straw were compared with other agricultural waste according to (Saeed, Liu, Lucia, & Chen, 2017) as per TAPPI standard test methods (O. Access, n.d.; Dhirhi, Shukla, Patel, Sahu, & Mehta, 2015).

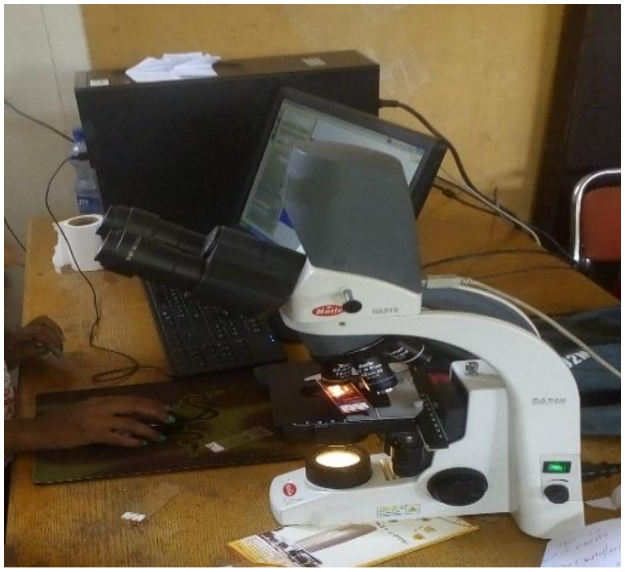


**Figure 3-1: Morphological Analysis of Flax Straw in Motic Microscopy**

## 3.4. Proximate analysis

### 3.4.1. Moisture content

The moisture content of flax straw was conducted by the oven and analytical balance at Addis Ababa University School of Chemical and Bioengineering laboratory (Addis Ababa, Ethiopia). The prepared flax straw was made free of moisture in an oven at 105±3℃ overnight and continue to stay in the oven until the constant weight of the prepared flax straw before cooking of pulp. Then the moisture content was calculated by using the following formula at every two hours' interval until a constant weight of flax straw was obtained.

$$Moisture\ content\ \% = \frac{M1 - M2}{M1} \times 100 \qquad (3.1)$$

Where:-

$M_1$ = Mass of flax straw before drying

$M_2$ = Mass of flax straw after drying

### 3.4.2. Ash content

Ash content of the flax straw was conducted by silica crucible, desiccators, muffle furnace at Addis Ababa University School of Chemical and Bioengineering laboratory (Addis Ababa, Ethiopia). The ash content of the residual lignin samples was determined under TAPPI Standard T 211 om-93 and T211om-02. Approximately 5g was burned in a muffle furnace at 525ºC. A separate test sample was used to find the moisture content of the specimen. The output weights of ash and moisture level in the sample was used to calculate the percentage ash present

at 525ºC on a moisture-free sample basis by the relationship shown below(Applications, 2008; Ragauskas, n.d.).

$$Ash\% = \frac{M1 \times 100}{M2} \quad (3.2)$$

Where: -

M1: is the weight of ash in grams

M2: is the weight of the moisture-free test sample in grams. The weight of crucible subtracts from both.

### 3.4.3. Extractive

Extractive conducted at Addis Ababa University School Chemical and Bio-Engineering laboratory (Addis Ababa, Ethiopia). According to (Ayeni et al., 2015) 5g of dried raw flax straw was loaded into the cellulose thimble and put within the Soxhlet extractor set up, 400 mL of acetone was used as a solvent for extraction. Residence times for the boiling and rising stages were carefully adjusted to 80 ºC and 25 min respectively on the heating mantle for a 4 h run period. After extraction, the constant weight of the extracted material was achieved in a convection oven at 105 ºC. The %(w/w) of the extractives content was evaluated as the difference in weight between the raw extractive-laden flax straw and extractive-free flax.

**Figure 3-2: Removal of Extractive with Oil Bath Soxhlet Extraction**

The following formula was used to obtain the alcohol-toluene solubility content of flax straw:

$$Extractive = \frac{M3 - M2}{M1} \times 100\% \quad (3.3)$$

Where:

$M_1$: Oven dry weight of sample, g

$M_2$: The oven-dry weight of flask, g and $M_3$: The oven-dry weight of extract and flask, g

## 3.5. Chemical composition

### 3.5.1. The lignin content of flax straw

Total lignin of flax straw was conducted by the Oven, Water Bath, Allihn Condenser, Fritted-Glass Crucible, And Desiccators at Addis Ababa University School of Chemical and Bio-Engineering laboratory (Addis Ababa, Ethiopia) and Debre Berhan University Chemical Engineering laboratory. According to (Ayeni et al., 2015) and TAPPi T222cm-99, 3 g of dried extracted raw flax straw was weighed in glass test tubes and 30 mL of 72% $H_2SO_4$ was added. The sample was kept at room temperature for 2h with carefully shaking at 30 min intervals to allow for complete hydrolysis. After the initial hydrolysis, 84 mL of distilled water was added. The second step of hydrolysis was made to occur in an autoclave for 1h at 121 °C. The slurry was then cooled at room temperature. Hydrolyzates were filtered through vacuum using a filtering crucible. The acid-insoluble lignin was determined by drying the residues at 105 $^oC$ and accounting for ash by incinerating the hydrolyzed samples at 575$^oC$ in a muffle furnace. The acid-soluble lignin fraction was determined by measuring the absorbance of the acid hydrolyzed samples at 320 nm in the spectrophotometer and used standard curve for acid-soluble lignin concentration. The lignin content was calculated as the summation of acid-insoluble lignin and acid-soluble lignin. Standard curve see at appendix A.


**Figure 3-3:Acid Soluble Lignin Content Determination using Spectrophotometer**

The following formula was used to obtain the lignin content of flax straw:

$$lignin\ content\ of\ flax\ straw = Acid\ souble\ lignin + acid\ insoluble\ lignin \quad (3.4)$$

### 3.5.2. Hemicellulose

Hemicellulose was conducted at Addis Ababa University School of Chemical and Bio-Engineering laboratory. (Ayeni et al., 2015) 6 g of extracted dried flax straw was transferred into a 500 mL Erlenmeyer flask. 300 mL of 1000 mol/$m^3$ NaOH was added. The mixture was boiled for 3.5h with distilled water. It was filtered after cooling through vacuum filtration and washed until neutral pH. The residue was dried to a constant weight at 105 $^oC$ in a convection oven. The difference between the sample weight before and after this treatment is the hemicellulose content (%w/w) of dry flax straw. Weighed until the variation between two successive measurements were not greater than 0.005 and record as W2. Finally, the Hemicellulose content was calculated as follow: -

$$Hemicellulose = \frac{W2}{W1} \times 100\% \quad (3.5)$$

Where,

W1: - is the oven-dried extractive free sample

W2: - is the weight of oven-dried hemicellulose

### 3.5.3. Cellulose

According to (Ayeni et al., 2015) Cellulose content of flax straw was determined simply by using calculation by assume the content of flax straw are cellulose, hemicellulose, ash, extractive and moisture. Cellulose was calculated by subtracting all other content from the initial weight of flax straw.

$$Cellulose = intial\ weight\ of\ flax\ straw - total\ lignin - hemicellulose - extractive - ash \quad (3.6)$$

$$Total\ weight\ of\ sample(dry\ basis) = ash + extractive + lignin + hemicelulose + celulose \quad (3.7)$$

## 3.6. Experimental set up for preparation of pulp from flax straw

### 3.6.1. Full factorial experimental design

In the production of pulp from flax straw, three number of a factor was controlled which is time, temperature, and active alkaline solution for each factor three-level was addressed. Therefor based on independent and dependent variable 27 total number of the experiment was obtained. For accuracy, the experiment was repeated once and the average value was recorded. Based on the below experimental arrangement 54 experiments were conducted. The coordination of each factor with its level as shown below: -

**Table 3-1: Number of Experiment with its Coordination**

| Factor | Level of experiment | | |
|---|---|---|---|
| | Minimum | Medium | Maximum |
| Time(min) | 60 | 90 | 120 |
| Temperature(℃) | 130 | 140 | 150 |
| Active alkaline (%) | 10 | 15 | 20 |
| Sulfidity (%) | 25 | 25 | 25 |

### 3.6.2. Pulp preparation from flax straw materials

Pulp was prepared from flax straw by autoclave, oven, heat resistant glass flask, and aluminum foil at Addis Ababa University School of Chemical and Bioengineering (Addis Ababa, Ethiopia).

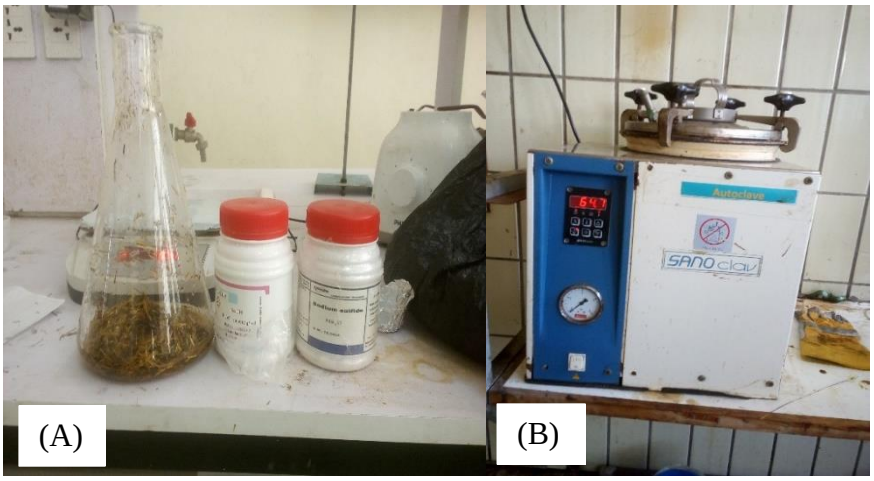



**Figure 3-4: Experimental framework (A): Chemical and Raw Material, (B): Autoclave Pulp Cooker**

The collected flax straw was cleaned and cut in a small size approximate 2cm. Once the flax straw material was prepared and the white liquor solution was prepared at the different pulping condition. The autoclave was cleaned and ready at required pulping parameter then the oven-dried flax straw was pulped using the Kraft method, by varying the cooking parameters as per the design and the Liquor to flax straw ratio was kept to 9:1. Then after each cook, 30minutes gas down period was allowed before the black liquor ejection. Each batch of produced pulps was disintegrated and washed with cold water on a standard size 220μm netted sieve. Then after washing and screening the produced pulp was dried in an oven (Zhong Liu, Pulping and Papermaking of Non-Wood Fibers, 2018) and (Engida, Kraft Pulping of Wheat Straw, 2017).

**Table 3-2: Pulping Conditions of Flax Straw**

| Parameter | Specifications |
|---|---|
| Liquor to flax straw ratio | 9:1 |
| Sulphidity | 25%, |
| Operating Pressure | 2 bar |
| Cooking temperature | 130,140 and $150^0$c |
| Sodium hydroxide | 10, 15 and 20% |
| Cooking time | 60, 90 and 120min |

### 3.6.3. Pulp bleaching

Water bath, beaker, filter paper, and aluminum foil was used for bleaching pulp at Addis Ababa university school of Chemical and BioEngineering (Addis Ababa, Ethiopia). Flax straw pulps were submitted to an oxidative delignification process using hydrogen peroxide. This bleaching process was done in three stages, using hydrogen peroxide during the two initial, and only a sodium hydroxide solution in the last one. Initially, pulp slurry of 10% consistency was mixed with the corresponding amount of 5% $H_2O_2$ and stirred at 80°C for 120 min. The pH of the bleaching solution was 12–12.5, but at the reaction end, it was reduced to approximately 11. Thus, the pulp was filtered in a Buckner funnel, extensively washed with distilled water, and dried at room temperature for 24 h. This procedure was performed for two consecutive times. In the third and last bleaching stage, the pulp was mixed with a 0.25 N NaOH aqueous solution inconsistency of 10% and stirred at 70 $^0$C for 60 min. Subsequently, the bleached pulp was washed with excess distilled water to remove the residual alkali and dried at room temperature until approximately 10% moisture content (Zhong Liu, Pulping and Papermaking of Non-Wood Fibers, 2018) and (Engida, Kraft Pulping of Wheat Straw, 2017).

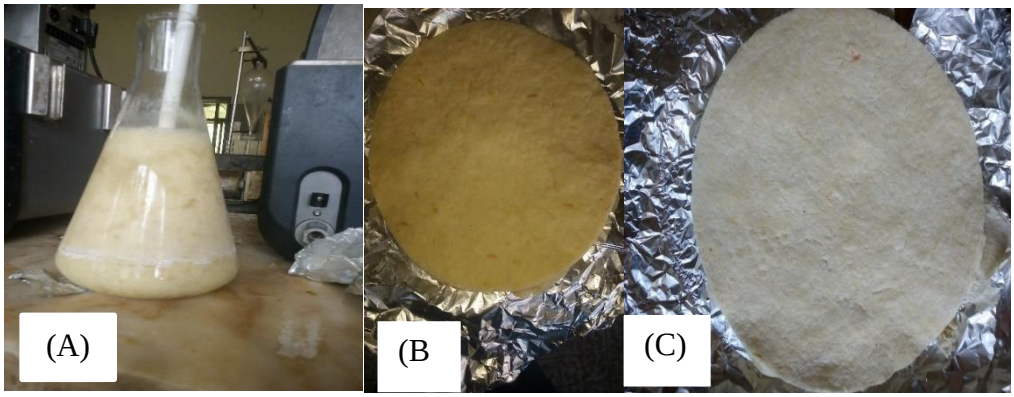



**Figure 3-5: Bleaching process (A): Pulp After Bleaching (B): Pulp Before Drying (C) Pulp After Drying**

## 3.7. Characterization of pulp

### 3.7.1. Pulp yield determination

Pulp yield was conducted by the oven to removing the moisture content of the pulp at Addis Ababa university school of chemical and BioEngineering (Addis Ababa, Ethiopia). Pulp yield expressed the quantity of lignin faraway from flax straw. When lignin was faraway from cooked chips fibers (flax straw) were obtained for papermaking and called the pulp. Since flax straws are made from many chemical components like other woody species. The expect the loss of pulp yield was get to cellulose degradation and fiber loss with rejects. Pulp yield which was expressed because the ratio of the moisture-free weight of screen pulp from digester with the oven-dry weight of the chips feeds for pulping was decided by the method as per TAPPI (Technical Association of Pulp and Paper Industries) standards (standard, 2012).

$$pulp\ yield(\%) = \frac{weight\ of\ oven\ dried\ pulp}{weight\ of\ oven\ dried\ flax\ straw} \quad (3.7)$$

### 3.7.2. Pulp kappa number

The spectrophotometer was used for the determination of kappa number of pulp at Addis Ababa University School of Chemical and BioEngineering in an analytical laboratory (Addis Ababa, Ethiopia) and Debre Berhan university at Chemical Engineering laboratory, Debre Brehan. The kappa number test was used to estimate the amount of lignin by measuring the oxidant demand of the pulp. Kappa numbers were performed on air-dried pulp samples, which was dried on a heated balance to acquire their oven-dried weight. The pulp was then treated with potassium permanganate ($KMnO_4$) under TAPPI standard(Chai, Luo, & Zhu, 2000; Lignin, n.d.; Muchorski, 2006; Ragauskas, n.d.).

This experiment was used due to the spectrophotometric method for the rapid determination of pulp kappa number through direct measurements of the permanganate concentrations in pulp-permanganate reaction solutions. As a result, the spectroscopic method was used to determine pulp kappa number in this work.

Mathematically pulp kappa number is defined as:

$$K = \frac{p}{w} \tag{3.8}$$

Where K is kappa number, P is the amount of 0.02 mole/L (0.1 N) permanganate solution consumed by the test sample in mL-pp, and w is the mass of moisture-free pulp sample in grams.

In a permanganate and pulp reaction experiment, the initial volume of 0.02 mole/L permanganate in the blank solution is **a** mL, and the amount of pulp used is **w** grams. At the end of the oxidation reactions, the excess volume of 0.02 mole/L permanganate is **b** ml. Therefore, the consumed volume, P, of 0.02 mole/L permanganate can be written as:

$$p = a - b = a\left(1 - \frac{b}{a}\right) \tag{3.9}$$

According to Beer's Law, the absorption is proportional to the concentration of the test sample, thus, we can have:

$$Ao = \varepsilon.l.Co = \varepsilon.l.\left(\frac{0.1a}{VT}\right) \tag{3.10}$$

And

$$Ae = \varepsilon.l.Ce = \varepsilon.l.\left(\frac{0.1b}{VT}\right) \tag{3.11}$$

Where:

*VT* is the total volume of the reaction solution, which includes the addition of sulfuric acid. **A0** and **Ae** are the permanganate absorbance (or spectral intensity) in the beginning blank solution and at end of the oxidation reactions in the solution, **ε** and **l** are the molar absorptivity of the solution and the optical path-length of the cell, respectively. We can determine the kappa number using the following expression:

$$K = \frac{a}{w}\left(1 - \frac{Ao}{Ae}\right) \tag{3.12}$$

From the equation, we can conclude that that kappa number can be calculated from the ratio of the permanganate absorption spectral intensities at a given wavelength at the beginning and end of the permanganate-pulp reaction. The percentages of remaining lignin content in the pulp can be estimated as:

$$lignin(\%) = kappa\ number\ \times 0.15 \quad (3.13)$$

**Experimental procedure for the determination of kappa number of pulp from flax straw using a spectrophotometer**

5ml of 0.1N concentration potassium permanganate solution was first measured for its spectral intensity at beginning $A_0$. Then 20ml of standardized sulfuric acid 2mol/L concentration added to the permanganate solution to make a strong acidic reaction solution. Then 1g oven-dry of pulp was added to the prepared reaction solution and stirred by a magnetic stirrer. After three minutes of reaction time filtration was done and the filtrate reaction solution measured for spectral intensity at the end, Ae. Then the kappa number was calculated based on the above formula.


**Figure 3-6: Kappa Number Determination using Spectrophotometer**

### 3.7.3. FTIR analysis of pulp from flax straw

Fourier Transform Infrared Spectroscopy was used to investigate changes that occur in the chemical structure of pulp from flax straw after was investigated using Fourier transform infrared spectroscopy(FTIR) equipped with origin JASCO. This technique was used to manipulate structural changes in samples and to examine the changes in functional groups induced by various treatments as a result of chemical modification by the identification of the functional group). Where the spectra are performed at room temperature in the range of 400 to

4000$cm^{-1}$with the resolution of change X cm-1 and a total of 3736 points for the sample(Lun, Anas, Gunny, & Kasim, 2017).

### 3.7.4. SEM analysis of pulp from flax straw

Scanning electron microscopy was performed to observe the morphology and surface structure by scanning the ruptured surface of pulp from flax straw(Rafiu, 2015). It was used to study the effects of various pulping condition and bleaching($H_2O_2$) on the morphology of the samples. The operation principle for SEM to cross-sectional morphology of the sample was done under vacuum at an accelerating voltage of 2500kV and x1806 magnification and also at different magnification. All the samples were firstly mounted on the surface of carbon tapes, loading on the top of aluminium stubs. The dirt was cleaned by the air jet and the samples were coated by a fine layer of gold with 20mA for 2 minutes to avoid charge(Chinga-carrasco, Miettinen, Hendriks, Gamstedt, & Kataja, 2011).

## 3.8. Paper hand sheet preparation and characterization

### 3.8.1. Hand sheet preparation

Pulp hand sheet physical strength was conducted by Beat machine and L-W AB Lorentz and wetter tearing tester in the laboratory of Ethiopian pulp and paper share company (Wonji, Ethiopia). Dry pulp produces from optimize pulping condition was used for sheet preparation. According to pulp and paper laboratory standard in wonji paper factory, 400g of oven-dry pulp was mixed with 2.3L water and pulp slurry with the consistency of 1.7% made. The prepared pulp slurry was added to the beating machine. Freeness of slurry was checked out at each ten minutes beating interval. Freeness was checked by taking 125 to 130ml of slurry from the freeness tester machine and diluted to 1000ml with distilled water and measured freeness value. When the freeness of pulp was 30CSF (Canadian standard of freeness), 1200ml of stock was taken from beater and diluted to 2000ml water (0.62% consistency) with 800ml wash. Then it was placed to the disintegrator with 500rpm for five minutes. Then the blade of the disintegrator was been wash with 250ml water and transferred to plastic vat and diluted with 2000ml water to a total volume of 6250ml and agitate well by hand. Materials from the dilute suspension were then taken and spread over the required paper sheet forming machine. Once the sheets shall prepare two-stage pressing was followed by applying 0.4MPa pressure for two minutes by pressing machine. Then the stock was removed from the press and attached to the drying plates to dry by oven at 100$^{o}$C for 45minutes according to wonji pulp and paper factory laboratory manual.

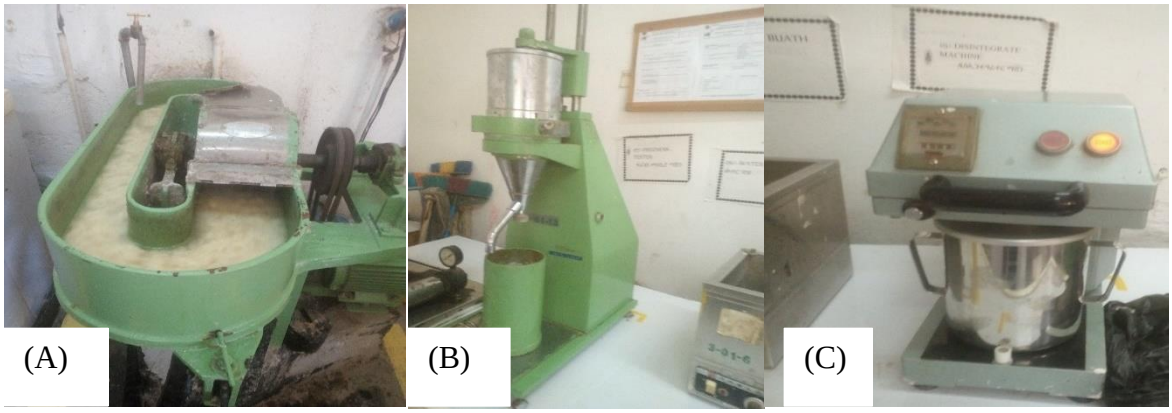



**Figure 3-7: Paper Hand-Sheet Making from flax straw A): Beating Machine B): Freeness Tester C): Disintegrator**

### 3.8.2. Bursting strength of paper

The test specimens were first prepared as 10 cm by 10 cm sheet and clamped in the tester tightly with bursting strength tester of model PN-BSM600 and the maximum reading pointer was set to zero position. The pump motor was then started and the pumping system and the test piece then wait to burst. The maximum read pointer was then recorded and allowed to rest gently to zero position and the broken sample was removed. Instrument reading = $Kg/cm^2$ according to wonji laboratory manual, TAAPi standards and (Karlsson, 2010).

**Figure 3-8: Bursting Tester Machine**

### 3.8.3. Tearing resistance of paper

The pendulum was raised to its initial position and 4 pieces of specimens (65*7.5cm) was clamped. According to (ISO, 2010) and (Engida, kraft pulping from wheat straw, 2017) Silt in the specimens were then made by completely pressed down the knife rocker arm. The pendulum was then stopped by quickly pressing down the releaser and the pendulum was broken softly after oscillation to the right. The scare value was recorded. The average of the

reading was then calculated and multiplied with the factor of the pendulum. So the product was equal to the tearing strength in millinewtons (mN) According to (ISO, 2012) and (Engineering et al., 2015).

**Figure 3-9:Tearing Tester Machine**

### 3.8.4. Tensile strength of paper

The result of paper from flax straw was checked tensile strength using tensile strength tester after the sheet specimens were cut into 15±0.1mm wide by 230mm long test pieces, it was then placed in the clamps of L-W AB Lorentz &Wetter tensile strength tester by making sure that any slacks were so eliminated. Any touch of the test area between the clamps with the fingers were avoided. All readings were then recorded except for test pieces that broke with in 2mm of clamming line according to TAAPi (T 494 om-01).

**Figure 3-10: Tensile Strength Tester**

# 4. RESULT AND DISCUSSION

The results of this study are presented and discussed the pulp and paper production parameter and optimization. The parameters investigated were chemical compositions including proximate properties of flax straw, pulp kappa number, lignin content, cooking time, pulp yield, fibre morphology, and strength properties of paper samples. Also, this study has conducted the effect of temperature, the effect of cooking time, and the concentration of active alkaline.

## 4.1. Proximate properties of flax straw and other biomass

Chemical compositions flax straw a great indication for pulp and paper production. Now from the experiment chemical characterization of flax straw and other biomass (wheat straw, rice straw, bamboo, and Enset) as shown below: -

**Table 4-1:Result on the Chemical Composition of Different Biomass**

| Biomass | Holocellulose (%) | Cellulose (%) | Hemicellulose (%) | Lignin (%) | Ash (%) | Extractive (%) |
|---|---|---|---|---|---|---|
| Flax straw [a] | 76.54 | 51.34 | 25.20 | 14.12 | 4.13 | 5.21 |
| Wheat straw b | 74.5 | 47.51 | 27 | 15.3 | 4.7 | 5.5 |
| Rice straw [c] | 64 | 44 | 20 | 19 | 9.8 | 7.2 |
| Bamboo [d] | 66.28 | 46 | 20.28 | 22.17 | 1.1 | 11.55 |
| Enset [e] | 87.87 | 59.6 | 28.27 | 8.22 | 3.8 | 1.11 |

**a**; current study **b**;(Ates, 2004) **c;**(Buranov & Mazza, 2008) **d;**(Antonio, Júnior, Lengowski, Andrade, & Venson, 2019) **e;**(Lemma, 2018)

From the above table the current study and the past research, Cellulose content of flax straw is higher than the other three biomasses (wheat straw, rice straw, and bamboo) except Enset. The cellulose content of flax straw is 51.43% greater than the other three (wheat straw, rice straw, and bamboo) crop except for Enset which has 59.6%(Lemma, 2018).

The holocellulose content of flax straw is 74.85% much higher than other biomass or agricultural waste which is wheat straw, rice straw, and bamboo(Antonio et al., 2019). This

indicated that flax straw was more preferable for the production of the pulp as input for the production of paper. As the above experimental data the higher cellulose content used for the production of pulp with its quality.

The lignin content of flax straw is slightly lower than wheat straw, bamboo, and rice straw this result indicated that the raw material which is flax straw more acceptable than other listed in the above table.

## 4.2. Morphological analysis of flax straw and other biomass

**Table 4-2:Morphological Analysis of Different Biomass**

| Parameters | Flax straw [a] | Wheat straw [b] | Cotton Stalk [c] | Bamboo[d] |
|---|---|---|---|---|
| Length(L),mm | 1.41 | 1.21 | 0.83 | 2.30 |
| Diameter (D),µm | 16.78 | 17.20 | 24.38 | 15.1 |
| Lumen width (d),µm | 9.45 | 8.40 | 15.65 | 6.9 |
| Cell wall thickness (W),µm | 3.77 | 3.80 | 4.37 | 4.17 |
| Slenderness ratio(L/D) | 84.03 | 70.34 | 34.04 | 152.3 |
| Flexibility coefficient,(d/D) *100 | 56.32 | 48.8 | 64.20 | 45.69 |
| Runkel ratio,(2w/d) | 0.8 | 0.9 | 0.54 | 1.21 |

**a**; current study **b**;(Ates, 2004) **c;**(Buranov & Mazza, 2008) **d;**(Antonio et al., 2019)

The fibre dimensions (fibre length, fibre diameter, lumen width and wall thickness) are essential parameters of lignocellulosic materials because they are associated with various structural, physical and chemical properties of the plant. So from the above table 4-2 the current student flax straw length(1.41mm) more preferable than wheat straw(1.21mm) (Ates, 2004) and cotton stalk(0.83mm) (Buranov & Mazza, 2008). Based on this result flax straw are also very good indicators to decide the material suitability for different end products. They affect much wood-product processing, like drying process, resistance to cutting and machining and pulpwood quality. Fibre dimensions are also related to different pulp quality indices like Runkel ratio, slenderness ratio, rigidity coefficient and flexibility coefficient. As a result of the experiment flax straw more flexibility coefficient than wheat straw(48.8%) and bamboo(45.69%)(Antonio et al., 2019). Fibre length has a positive correlation with burst strength, tensile strength and tear strength. Long fiber lengths are preferable for the production of a good quality of the paper. Long fibers give more drainable and less uniform sheet structure.

Thin cell walls positively affect flexibility, burst and tensile strength of paper based on these properties. The standard value for this ratio being one, satisfactory pulp strength is usually obtained when the Runkel ratio is below the standard value. Low Runkel ratio means thin fiber wall and larger fiber lumen width. Thin fiber wall is desirable for high quality, dense and well-formed paper. Paper manufactured from thick-walled fibers will be bulk with a coarse surface. Moreover, large lumen size positively affects the beating of pulp, which involves the penetration of liquid into spaces within the fiber. Thus, fiber with high Runkel ratio value will be stiff, less flexible and will form bulkier paper of low bounded area. The other important parameter is the slenderness ratio. If the value of slenderness ratio less than 70 the fibers are not used for a good quality pulp and paper production. The strength properties of paper such as tensile strength, bursting strength and tearing strength are highly affected the individual fibers are cross-linked together in the paper sheet. The degree of fiber cross-linked depends on the flexibility and compressibility of individual fibers in the pulp from the straw. The coefficient of flexibility, usually expressed in percentage, is derived from the ratio of lumen width to its fiber diameter

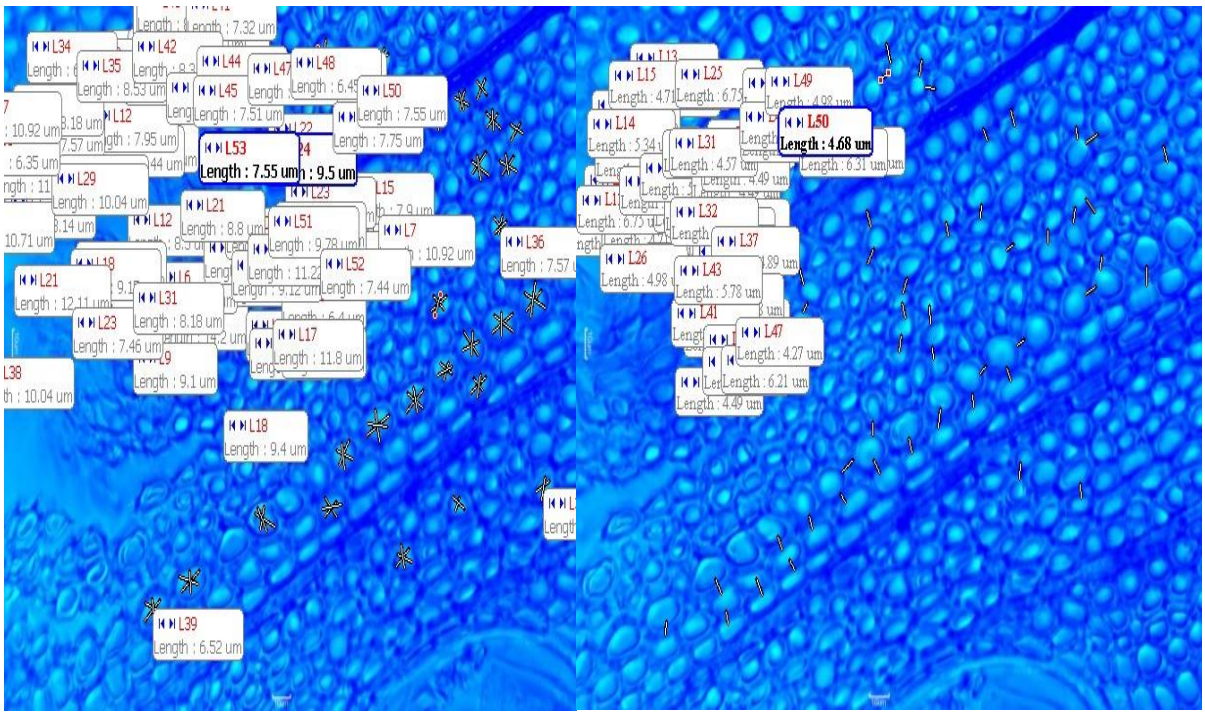



**Figure 4-1: Cell Wall Thickness and Diameter of Flax Straw from Motic Electroscope**

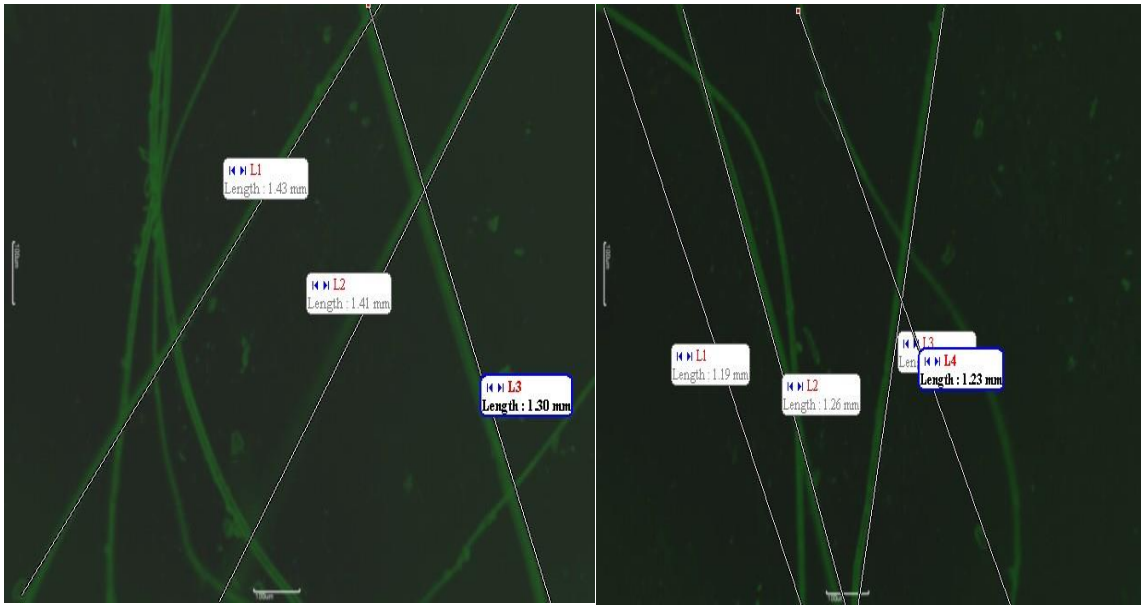



**Figure 4-2: Fiber Length of Flax Straw**

## 4.3. Scanning electron microscopy(SEM) analysis of pulp from flax straw

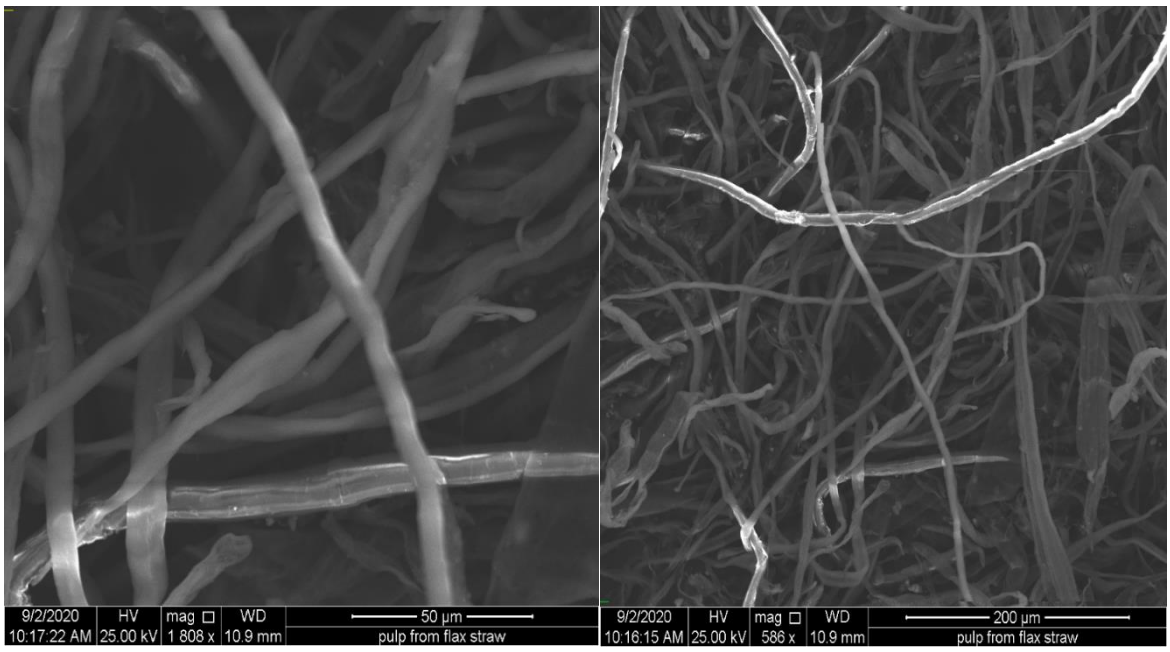



**Figure 4-3: SEM analysis of pulp fiber**

Scanning electron microscopy (SEM) analysis of the pulp produced from flax straw. Fibres were magnified at 200X and 50X are shown in figure 4-3. The analysis reveals the structure and arrangement of the fibre bundles inside the pulp fiber(Chinga-carrasco et al., 2011). However, the strength of the fibre can be explained according to the order and formation of the fibre pattern. Pulp fibres are parallel, aligned and closed to each other and the structure is crystalline and there is no contaminated fiber from them and This shows the higher fibre

content as well as long fibres in the sample to the other species. This fibre structure could increase the fibre mechanical properties and the quality of the paper produced. Moreover, the compactness and arrangement of fibres play an important role in the quality of the produced paper beside the other parameters such as cellulose content in the non-wood materials(Rafiu, 2015). As the pulp fiber as shown in the above figure 4-3 highly cross-linked and aligned to each other the final output of paper SEM structure highly cross-linked its give high strength of paper.

## 4.4. FTIR analysis of pulp from flax straw

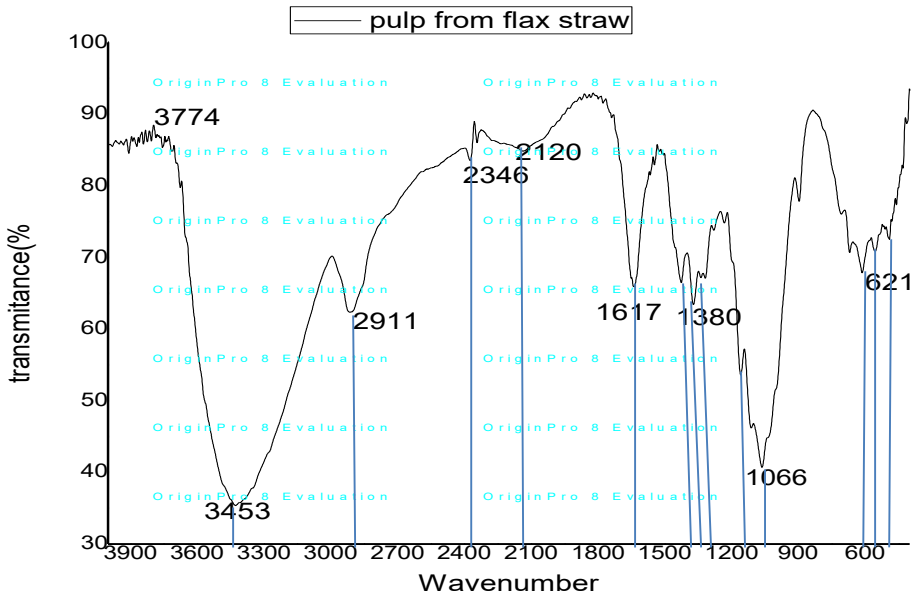



**Figure 4-4: FTIR Analysis of Pulp from Flax Straw**

FTIR spectra of cellulose fibers from flax straw pulp are 13 peaks as shown in figure 4-4. The absorption bands are observed in two wavenumber regions of 3500 - 2900 $cm^{-1}$ and 1617 - 400 $cm^{-1}$. The presence of peaks on the spectra of cellulose samples coming from flax pulp corresponds to bands of microcrystalline cellulose of pulp from flax straw as shown in figure 4-4, Identification of the absorption peaks in each wavenumber is following. The observed peaks in the wavenumber range of 3500 - 2900 $cm^{-1}$ are characteristic for stretching vibration of O-H and C-H bonds in polysaccharides(Hospodarova, Singovszka, & Stevulova, 2018). The broad peak at 3453 $cm^{-1}$ is characteristic for stretching vibration of the hydroxyl group in polysaccharides. This peak includes also inter-and intra-molecular hydrogen bond vibrations in cellulose. The band at 2911 $cm^{-1}$ is attributed to CH stretching vibration of all hydrocarbon

constituent in polysaccharides. Typical bands assigned to cellulose were observed in the region of 1617 - 700 $cm^{-1}$. The peaks located at 1617 $cm^{-1}$ correspond to the vibration of water molecules absorbed in cellulose. The absorption bands at 1380, 1230, 1066 $cm^{-1}$ and 900 $cm^{-1}$ belong to stretching and bending vibrations of -CH2 and -CH, -OH and C-O bonds in cellulose. The band at around 1420 - 1430 $cm^{-1}$ is associated with the amount of the crystalline structure of the cellulose, while the band at 700 $cm^{-1}$ is assigned to the amorphous region in cellulose(Bayu, Nandiyanto, Oktiani, & Ragadhita, 2019).

**Table 4-3: Wavelength Spectrum of Cellulose Standard and Pulp From Flax Straw**

| No. | Cellulose standard($cm^{-1}$)[a] | Flax straw pulp($cm^{-1}$)[b] |
|---|---|---|
| 1 | 3350.70 | 3453 |
| 2 | 2901.34 | 2911 |
| 3 | 2366.40 | |
| 4 | 2346.40 | 2346 |
| 5 | 2129.90 | 2120 |
| 6 | 1640.09 | 1617 |
| 7 | 1430.00 | |
| 8 | 1372.00 | 1380 |
| 9 | 1337.06 | |
| 10 | 1318.10 | |
| 11 | 1282.10 | |
| 12 | 1235.90 | 1230 |
| 13 | 1202.90 | |
| 14 | 1163.30 | |
| 15 | 1112.20 | |
| 16 | 1059.60 | 1066 |
| 17 | 1035.80 | |
| 18 | 898.50 | 900 |
| 19 | 670.20 | |
| 20 | 663.40 | 650 |
| 21 | 617.00 | 621 |
| 22 | 561.00 | 550.00 |

**Source: (a),** standard of cellulose spectrum interval(Zainal Abidin Nasution, 2016) **(b),** current study

## 4.5. Properties of paper

As a result, from the lab the properties of paper including three parameters which are tearing, bursting strength and tensile strength. The result of paper product from flax straw compare to the standard used at wonji paper factor. The standard compare to the base weight 60g which mean the initial weight of produced paper. The produced and the standard look in below table the calculation and formula part look in the appendix.

**Table 4-4: Properties of Paper**

| paper type | Basis weight ($gm/m^2$) | Burst ($kg/cm^2$) | Tear factor ($mm^2/g$) | Breaking length(m) | Ash content(%) | Moisture content(%) |
|---|---|---|---|---|---|---|
| Paper from flax straw (current study)[a] | 60 | 1.4 | 100 | 5200 | 7.2 | 6.9 |
| White bond( standard in wonji paper factory)[b](minimum value ) | 60 | 1.2 | 65 | 4000 | 6-10 | 6-8 |

**Source**: **(a),** current study **(b),** standard at wonji paper factor, wonji Ethiopia

From the above table basis weight of paper for both paper from flax straw and white bond standard in wonji paper factor used are 60($gm/m^2$). So with similar basis weight, the other parameter of paper compare to the standard one. The first one is the burst of paper from flax straw is 1.4$kg/cm^2$ greater than the standard value of the white bond (which the minimum value is 1.2$kg/cm^2$). The paper from flax straw is good bursting strength and fulfil the properties of paper regarding bursting strength. Other properties of paper tearing factor, the tearing factor of paper from flax straw is 100$mm^2/g$ which is greater than that of the standard. The breaking length of the paper from flax straw is 5200m this one also above the standard. Finally, the basic properties of paper which are ash and moisture content with the interval of the standard. Generally, the paper from flax straw is fulfilled all parameter/ properties of paper. This indicated that the production of paper from agricultural waste is important for fulfilling the demand for paper in our country(Ethiopia) and reduced the foreign currency used for the imported pulp from the aboard. Even if we used flax for production of paper there are side important for the production of linseed for production and extraction of oil the main product as the waste used for the paper production.

## 4.6. Pulp yield and kappa number

The experimental values of pulp yield and kappa number obtained under different pulping conditions are presented in the table below.

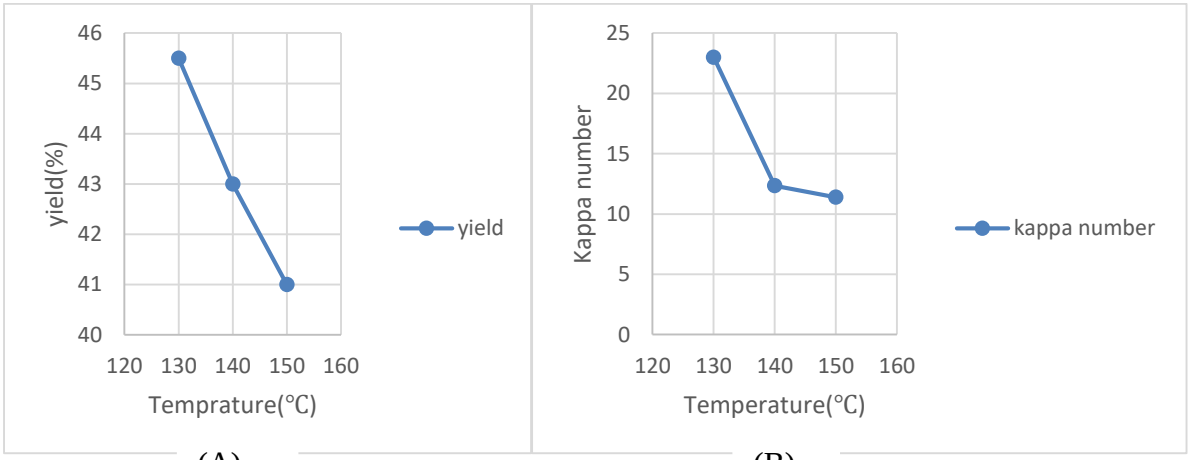
**Table 4-5: Kappa Number and Yield of Pulp on the Experimental Value**

| Std | Run order | Blocks | Time (min) | Temperature (℃) | Active alkaline(%) | Yield(%) | Kappa number |
|---|---|---|---|---|---|---|---|
| 27 | 1 | Block 1 | 120 | 150 | 20 | 29.78 | 5.74 |
| 25 | 2 | Block 1 | 60 | 150 | 20 | 37.98 | 9.42 |
| 1 | 3 | Block 1 | 60 | 130 | 10 | 45.5 | 23 |
| 7 | 4 | Block 1 | 60 | 150 | 10 | 41 | 11.39 |
| 26 | 5 | Block 1 | 90 | 150 | 20 | 32 | 6.04 |
| 19 | 6 | Block 1 | 60 | 130 | 20 | 42.78 | 19.18 |
| 2 | 7 | Block 1 | 90 | 130 | 10 | 43 | 15.55 |
| 20 | 8 | Block 1 | 90 | 130 | 20 | 37.75 | 13.01 |
| 17 | 9 | Block 1 | 90 | 150 | 15 | 33.11 | 8.3 |
| 3 | 10 | Block 1 | 120 | 130 | 10 | 42.1 | 10.39 |
| 14 | 11 | Block 1 | 90 | 140 | 15 | 37.6 | 9.45 |
| 23 | 12 | Block 1 | 90 | 140 | 20 | 35.01 | 7.89 |
| 16 | 13 | Block 1 | 60 | 150 | 15 | 39.35 | 10.39 |
| 12 | 14 | Block 1 | 120 | 130 | 15 | 40.13 | 9.64 |
| 10 | 15 | Block 1 | 60 | 130 | 15 | 44 | 21.2 |
| 24 | 16 | Block 1 | 120 | 140 | 20 | 32.95 | 4.75 |
| 22 | 17 | Block 1 | 60 | 140 | 20 | 41.01 | 10.86 |
| 9 | 18 | Block 1 | 120 | 150 | 10 | 34.34 | 8.34 |
| 11 | 19 | Block 1 | 90 | 130 | 15 | 39.59 | 14 |
| 18 | 20 | Block 1 | 120 | 150 | 15 | 31.09 | 6.4 |
| 5 | 21 | Block 1 | 90 | 140 | 10 | 38.76 | 11.2 |
| 13 | 22 | Block 1 | 60 | 140 | 15 | 42.13 | 11.98 |
| 21 | 23 | Block 1 | 120 | 130 | 20 | 38.03 | 6.77 |
| 8 | 24 | Block 1 | 90 | 150 | 10 | 35.07 | 9.25 |
| 6 | 25 | Block 1 | 120 | 140 | 10 | 37.55 | 8 |
| 4 | 26 | Block 1 | 60 | 140 | 10 | 43 | 13.89 |
| 15 | 27 | Block 1 | 120 | 140 | 15 | 37.25 | 6.1 |

### 4.6.1. The effect of an experimental variable on the pulping condition

#### *4.6.1.1. The effect of temperature on the yield of pulp and kappa number*

At constant active alkaline, time and sulfidity, (10%, 60min, and 25%) respectively. The cooking temperature increased from 130 to 150℃ the yield of pulp decreased from 45.5% to 41%. Similarly, the kappa number of pulp decreased from 25.50 to 11.39.




(A) (B)

**Figure 4-5: The Effect of Temperature on the (A): Yield of Pulp and (B): Kappa Number of Pulp**

At constant active alkaline, time and sulfidity (15%, 90min and 25%) respectively. The effect of temperature on the yield of pulp and kappa number directly related that of the lignin content of pulp indicated the quality of the paper and its strength. When the active alkaline at 10%, sulfidity constant throughout the experiment, the cooking time at 60min, and the cooking temperature increased from 130 to 150℃ the yield of pulp decreased from 44% to 39.35%. Similarly, the kappa number of pulp decreased from 23.71 to 10.39.

This implies that, high rate of degradation of cellulose and delignification occurs at elevated temperature. During pulping both lignin and cellulose are dissolved at different rates. This rate is much accelerated by increasing the temperature. There was a general decrease in the pulp yield and Kappa number due to increases in the pulping temperature at constant time.

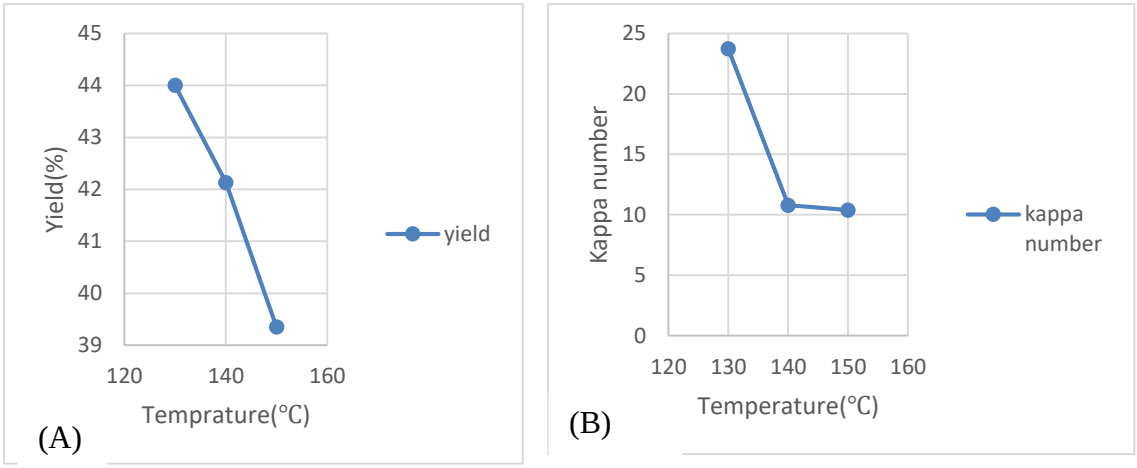



**Figure 4-6: The Effect of Temperature on the (A) Yield of Pulp: (B): Kappa number of Pulp**

### *4.6.1.2. The effect of time on the yield of pulp and kappa number*

Reaction time increase leads to completion of reaction. At constant temperature, active alkaline, and sulfidity (130$^{o}$c, 10%, and 25%) respectively. Based on the experimental result when the time at 60 min the pulp yield and kappa number is 45.5 and 25.50 respectively. Similarly, when the cooking time at 90min the pulp yield and kappa number is 43 and 15.55 respectively. Finally, when the time at 120min the pulp yield and kappa number is 42.1 and 10.39 respectively. From these expressions easily determined the effect of time. When the time increased from 60 to 90 min pulp yield decreased by 2.5% and the time increased from 90 to 120min pulp yield decreased by 0.9%.

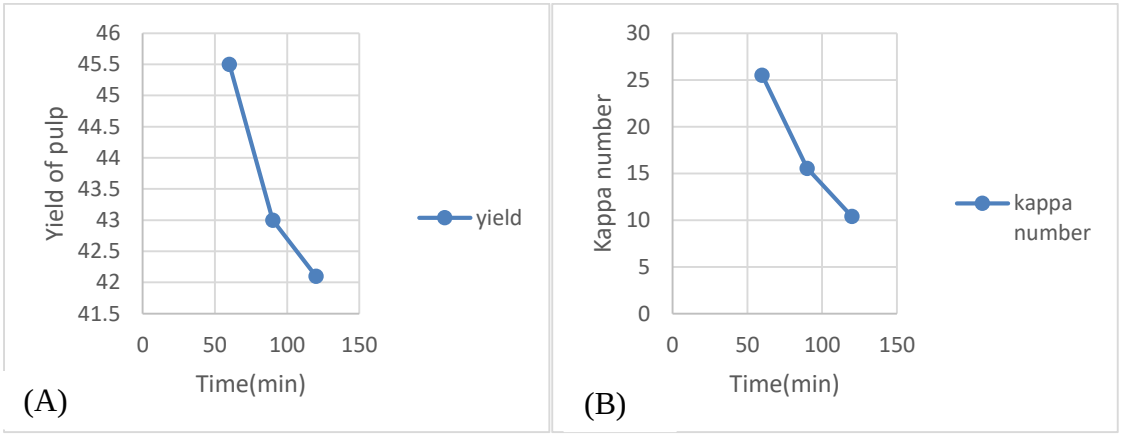



**Figure 4-7: The Effect of Time on the(A): Yield of Pulp (B): Kappa Number**

As figure 4-8 below, identified yield and kappa number respectively at a constant temperature, active alkaline and sulfidity (140℃, 15% and 25%) respectively. As observed from the experimental result when the time at 60 min the pulp yield and kappa number is 42.13 and 10.78 respectively. Similarly, when the cooking time at 90min the pulp yield and kappa number

is 37.60 and 9.45 respectively. Finally, when the time at 120min the pulp yield and kappa number is 37.25 and 7.00 respectively. From these expressions easily determined the effect of time. When the time increased from 60 to 90 min pulp yield decreased by 4.53% and the time increased from 90 to 120min pulp yield decreased by 0.35% and also time affected the pulp kappa number when the time increased from 60 to 90min kappa number decreased by 1.33% similarity when the time increased from 90 to120min the pulp kappa number decreased by 2.45%.

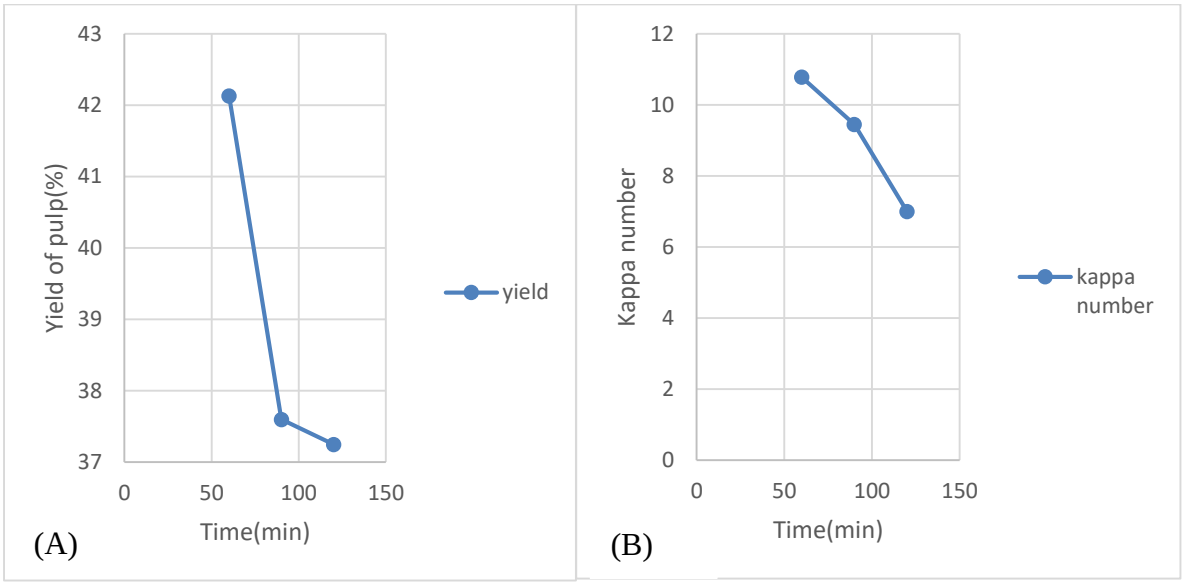



**Figure 4-8: The Effect of Time on the (A): Yield of Pulp and (B): Kappa Number of Pulp**

#### *4.6.1.3. The effect of active alkaline on the yield of pulp and kappa number*

The increase in concentration of caustic soda improves the delignification and provides better quality pulp with lower lignin content. Pulp yield decreases slowly with increase of caustic soda concentration in liquor due to increase of delignification and solubilization of hemicelluloses in caustic soda. But the quality of pulp obtained at higher pulp yield is not suitable for further processing in paper industry due to high kappa number and residual lignin in pulp. In flax straw chemical pulping, the increase in NaOH concentration affects the yield slightly and highly the kappa number.

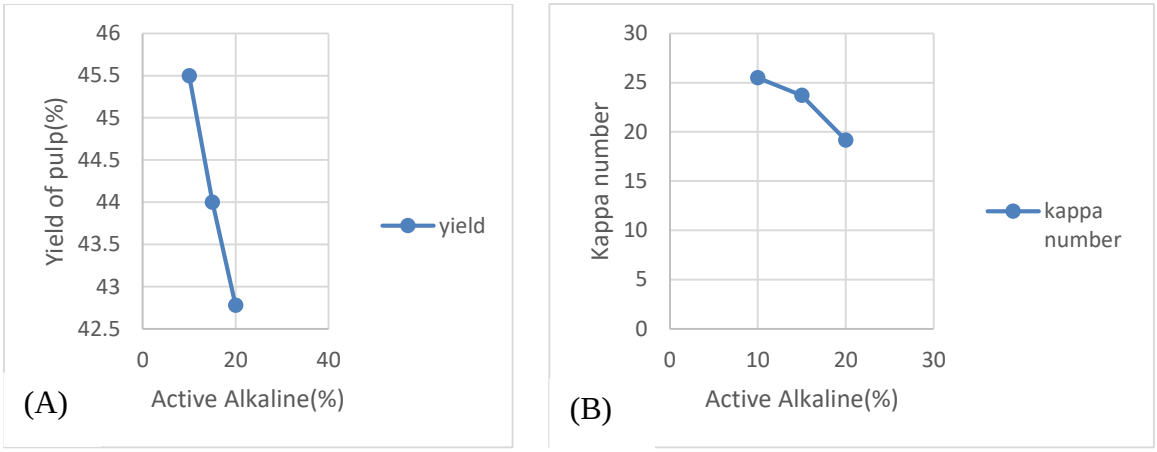



**Figure 4-9:The Effect of Active Alkaline on the (A) Yield of Pulp and (B) Kappa Number**

Based on the above graph it able observe each factors on the yield of pulp and kappa number separately. But there is an interaction effect on the response and find out the optimum parameter that gets the maximum yield at minimum cost. Then it is possible to determine the optimum temperature, time and active alkaline at a maximum yield of pulp. To determine the optimum value of a pulping parameter using a design expert in the next section.

## 4.7. Experimental analysis and adequacy check for full factorial models

The effect of temperature, time, and active alkaline on the kappa number and yield of pulp has been mainly effect of the quality of pulp. Then here, the resulted data is going to be analyzed to determine the significant factors of the experimental work by using DESIGN-EXPERT 6.08 software. Pulp yield and kappa number obtained from laboratory experiments result was an input to the software.

Pulp yield obtained from laboratory experiment result was analysed by design expert and obtained the general yield formula, model type, F value, P-value, $R^2$ and determine the significant effect of the factor on the yield of pulp.

**Table 4-6: Model Summary Statistics in Pulp Yield**

| Source | Sum of Squares | DF | mean squares | F value | Prob > F | |
|---|---|---|---|---|---|---|
| Mean | 39434.63 | 1 | 39434.63 | | | |
| Linear | 414.24 | 3 | 138.08 | 72.81 | < 0.0001 | |
| 2FI | 12.95 | 3 | 4.32 | 2.81 | 0.0654 | |
| Quadratic | 24.55 | 3 | 8.18 | 22.75 | < 0.0001 | Suggested |
| Cubic | 0.74 | 7 | 0.11 | 0.2 | 0.9786 | Aliased |

| | | | | | | |
|---|---|---|---|---|---|---|
| Residual | 5.37 | 10 | 0.54 | | | |
| Total | 39892.49 | 27 | 1477.5 | | | |

From the above table, the recommended mode is quadratic and cubic model is not good because the F value is 0.9786 which is greater than alpha. Then used the quadratic model to get the optimum yield and kappa number.

**Table 4-7: Analysis of Variance (ANOVA) for The Response Pulp Yield of Flax Straw**

| source | Sum of Squares | DF | Mean of Square | F- value | Prob>F | |
|---|---|---|---|---|---|---|
| Model | 451.74 | 9 | 50.19 | 139.4 | <0.0001 | Significant |
| A | 159.19 | 1 | 159.19 | 442.56 | < 0.0001 | |
| B | 194.44 | 1 | 194.44 | 540.54 | < 0.0001 | |
| C | 60.61 | 1 | 60.61 | 168.5 | < 0.0001 | |
| $A^2$ | 24.25 | 1 | 24.25 | 67.43 | < 0.0001 | |
| $B^2$ | 0.28 | 1 | 0.28 | 0.79 | 0.3862 | |
| $C^2$ | 0.015 | 1 | 0.015 | 0.041 | 0.8424 | |
| AB | 10.27 | 1 | 10.27 | 28.54 | < 0.0001 | |
| AC | 2.52 | 1 | 2.52 | 7.01 | 0.0169 | |
| BC | 0.16 | 1 | 0.16 | 0.45 | 0.5125 | |
| Residual | 6.12 | 17 | 0.36 | | | |
| Cor total | 457.86 | 26 | | | | |

Where:

A: Time

B: Temperature

C: Active alkaline

The Model F-value of 139.54 implies the model is significant. There is only a 0.01% chance that a "Model F-value" this large could occur due to noise. Values of "Prob > F" less than 0.0500 indicate model terms are significant. In this case, A, B, C, $A^2$, AB, AC are significant model terms. Values greater than 0.1000 indicate the model terms are not significant.

Based on the above software analysis $B^2$, $C^2$ and BC are no significant effects of the model this means there is no interaction effect. it can modify the model by ignoring the above three value which is $B^2$,$C^2$ and BC. After modified the value of R- square and mean value as shown below. Temperature more effect on the yield of pulp based on the F- value. Determine the exact value of cooking temperature more economical value.

**Table 4-8: Modified Analysis of Variance (ANOVA) for the Response Pulp Yield of Flax Straw**

| Source | Sum of Squares | DF | Mean of Square | F- value | Prob>F | |
|---|---|---|---|---|---|---|
| Model | 451.74 | 6 | 75.21 | 228.78 | <0.0001 | Significant |
| A | 159.19 | 1 | 159.19 | 484.21 | < 0.0001 | |
| B | 194.44 | 1 | 194.44 | 591.42 | < 0.0001 | |
| C | 60.61 | 1 | 60.61 | 184.36 | < 0.0001 | |
| $A^2$ | 24.25 | 1 | 24.25 | 73.77 | < 0.0001 | |
| AB | 10.27 | 1 | 10.27 | 31.23 | < 0.0001 | |
| AC | 2.52 | 1 | 2.52 | 7.67 | 0.0118 | |
| Residual | 6.12 | 20 | 0.36 | | | |
| cor total | 457.86 | 26 | | | | |

From the above two tables which is the one original quadratic model and modified model F value is 139.54 and 228.78 respectively this indicated the modified model which is best to analyze the data or the effect of the factor on the yield of pulp is minimum.

**Table 4-9: Model adequacy measures for pulp yield**

| Std. Dev. | 0.57 | R-Squared | 0.9856 |
|---|---|---|---|
| Mean | 38.22 | Adj R-Squared | 0.9813 |
| C.V. | 1.5 | Pred R-Squared | 0.9771 |
| PRESS | 10.49 | Adeq Precision | 55.458 |

Unmodified equation of yield

$$yield = +34.35037 - 0.023741 * A + 0.52386 * B - 0.35700 * C + +2.23395\text{E} - 003 * \text{A}^2 - 2.1778E - 0.003 * \text{B}^2 - 1.97778\text{E} - 003 * \text{C}^2 - 3.08333\text{E} - 003 * \text{A} * \text{B} - 3.05556\text{E} - 003 * \text{A} * \text{C} + 2.3166E - 003 * B * C \quad (4.1)$$

Modified yield equation

**Final Equation in Terms of Actual Factors:**

$$Yield = +72.43667 - 0.023741 * \text{A} - 0.051167 * \text{B} - 0.092 * \text{C} + 2.23395\text{E} - 0.003 * \text{A}^2 - 3.08333\text{E} - 003 * \text{A} * \text{B} - 3.0556\text{E} - 0.003 * \text{A} * \text{C} \quad (4.2)$$

**Kappa number analysis**

Under experimental investigation easily determined the optimum parameter or pulping condition, develop the design equation, determine the value of R-square, the interaction effect of the variable on the kappa number of pulp and develop the modified design equation finally

find out the best pulping condition with minimum kappa number at optimum yield at minimum cost and energy.

**Table 4-10: Model Summary Statistics in Pulp Kappa Number**

| Source | Sum of Squares | DF | Mean Square | F value | P value | |
|---|---|---|---|---|---|---|
| Mean | 3160.74 | 1 | 3160.74 | | | |
| Linear | 461.07 | 3 | 153.69 | 37.5 | < 0.0001 | |
| 2FI | 56.17 | 3 | 18.72 | 9.83 | 0.0003 | |
| Quadratic | 30.49 | 3 | 10.16 | 22.74 | < 0.0001 | Suggested |
| Cubic | 3.96 | 7 | 0.57 | 1.56 | 0.2537 | Aliased |
| Residual | 3.64 | 10 | 0.36 | | | |
| Total | 3716.07 | 27 | 137.63 | | | |

Based on the experimental result and the predicted value of kappa number, the recommended design equation is a quadratic equation but a cubic equation is aliased so quadratic equation select and modified the equation with ignoring the parameter no interaction effect on the value of kappa number.

**Table 4-11:Model Summary Statistics in the Pulp Kappa Number**

| Source | Std Dev. | R square | adjusted R Square | Predicted R square | Press | |
|---|---|---|---|---|---|---|
| Linear | 2.02 | 0.8303 | 0.8081 | 0.7519 | 137.77 | |
| 2FI | 1.38 | 0.9314 | 0.9108 | 0.8687 | 72.91 | |
| Quadratic | 0.67 | 0.9863 | 0.9791 | 0.965 | 19.45 | Suggested |
| Cubic | 0.6 | 0.9935 | 0.983 | 0.9465 | 29.73 | Aliased |

As the above table from model summary statistics in the kappa number of pulp from flax straw quadratic model is suggested and the cubic model is not recommended. The on this information select the quadratic model and see the significant terms which pulping condition on the kappa number of pulp.

**Table 4-12: Analysis of Variance (ANOVA) for the Response Pulp Kappa Number of Flax Straw**

| Source | Sum of Square | DF | Mean of Square | F Value | P-value | |
|---|---|---|---|---|---|---|
| Model | 547.73 | 9 | 60.86 | 136.17 | < 0.0001 | Significant |
| A | 236.02 | 1 | 236.02 | 528.11 | < 0.0001 | |
| B | 183.49 | 1 | 183.49 | 410.56 | < 0.0001 | |
| C | 41.56 | 1 | 41.56 | 92.98 | < 0.0001 | |

| | | | | | | |
|---|---|---|---|---|---|---|
| $A^2$ | 1.2 | 1 | 1.2 | 2.6 | 0.1192 | |
| $B^2$ | 29.29 | 1 | 29.29 | 65.54 | < 0.0001 | |
| $C^2$ | 1.16E-03 | 1 | 1.16E-03 | 2.59E-03 | 0.96 | |
| AB | 55.73 | 1 | 55.73 | 124.69 | < 0.0001 | |
| AC | 0.035 | 1 | 0.035 | 0.079 | 0.7823 | |
| BC | 0.4 | 1 | 0.4 | 0.9 | 0.3554 | |
| residual | 7.6 | 17 | 0.45 | | | |
| Cor total | 555.33 | 26 | | | | |

The Model F-value of 136.17 implies the model is significant. There is only a 0.01% chance that a "Model F-value" this large could occur due to noise. Values of "Prob > F" less than 0.0500 indicate model terms are significant. In this case, A, B, C, $B^2$, AB are significant model terms. Values greater than 0.1000 indicate the model terms are not significant.

Without modified the value of R- Squared in the selected quadratic model as the above-suggested model. When the probability value greater than 0.1 there is no significant effect so we can modify the model with ignoring the interaction effect of a variable.

**Table 4-13: The Value of R- Square on the Kappa Number of Pulp Under Modified the Model**

| | | | |
|---|---|---|---|
| Std. Dev. | 0.66852 | R-Squared | 0.986319 |
| Mean | 10.81963 | Adj R-Squared | 0.979076 |
| C.V. | 6.178774 | Pred R-Squared | 0.9<br>64973 |
| PRESS | 19.45168 | Adeq Precision | 44.29576 |

Based on the above model relation A, B, C, $B^2$, and AB are a significant model. This indicated that other factor which is no significant effect on the kappa number so the quadratic model becomes modified with ignoring the term which is $A^2$, $C^2$, AC and BC. This shows with the quadratic model the interaction effect of time and active alkaline and temperature and active alkaline not significant on the kappa number of pulp from flax straw. The modified model summary as shown below: -

**Table 4-14: Modified Analysis of Variance (ANOVA) for the Response Pulp Kappa Number of Flax Straw.**

| Source | Sum of Square | DF | Mean of Square | F- value | p-value | |
|---|---|---|---|---|---|---|
| Model | 546.09 | 5 | 109.22 | 248.21 | < 0.0001 | Significant |

| | | | | | | |
|---|---|---|---|---|---|---|
| A | 236.02 | 1 | 236.02 | 536.4 | < 0.0001 | |
| B | 183.49 | 1 | 183.49 | 417 | < 0.0001 | |
| C | 41.56 | 1 | 41.56 | 94.44 | < 0.0001 | |
| $B^2$ | 29.29 | 1 | 29.29 | 66.57 | < 0.0001 | |
| AB | 55.73 | 1 | 55.73 | 126.65 | < 0.0001 | |
| Residual | 9.24 | 21 | 0.44 | | | |
| Cor Total | 555.33 | 26 | | | | |

The Model F-value of 248.21 implies the model is significant. There is only a 0.01% chance that a "Model F-value" this large could occur due to noise. All the model in terms of pulping condition the value of p above 0.1 this means the model is significant and the pulping parameter have significant on the kappa number. Based on the F value in the above table cooking time is highly effect the value of kappa number.

**Table 4-15: Modified Value of R- Square on the Kappa Number of Pulp Under Modified the Model**

| | | | |
|---|---|---|---|
| Std. Dev. | 0.66 | R-Squared | 0.9834 |
| Mean | 10.82 | Adj R-Squared | 0.9794 |
| C.V. | 6.13 | Pred R-Squared | 0.9715 |
| PRESS | 15.8 | Adeq Precision | 57.046 |

**Final Equation in Terms of Actual Factors:**

$$Kappa\ number = +593.02833 - 1.12637 * A - 7.15222 * B - 0.3038 * C + 0.022098 * B^2 + 7.1833E003 * AB \quad (4.3)$$

Where:
A: Cooking time

B: Temperature

C: Active alkaline

As the above model equation of kappa number, we can get the value of it at different pulping variable and easily determine the optimum and economical feasible value related to cost.

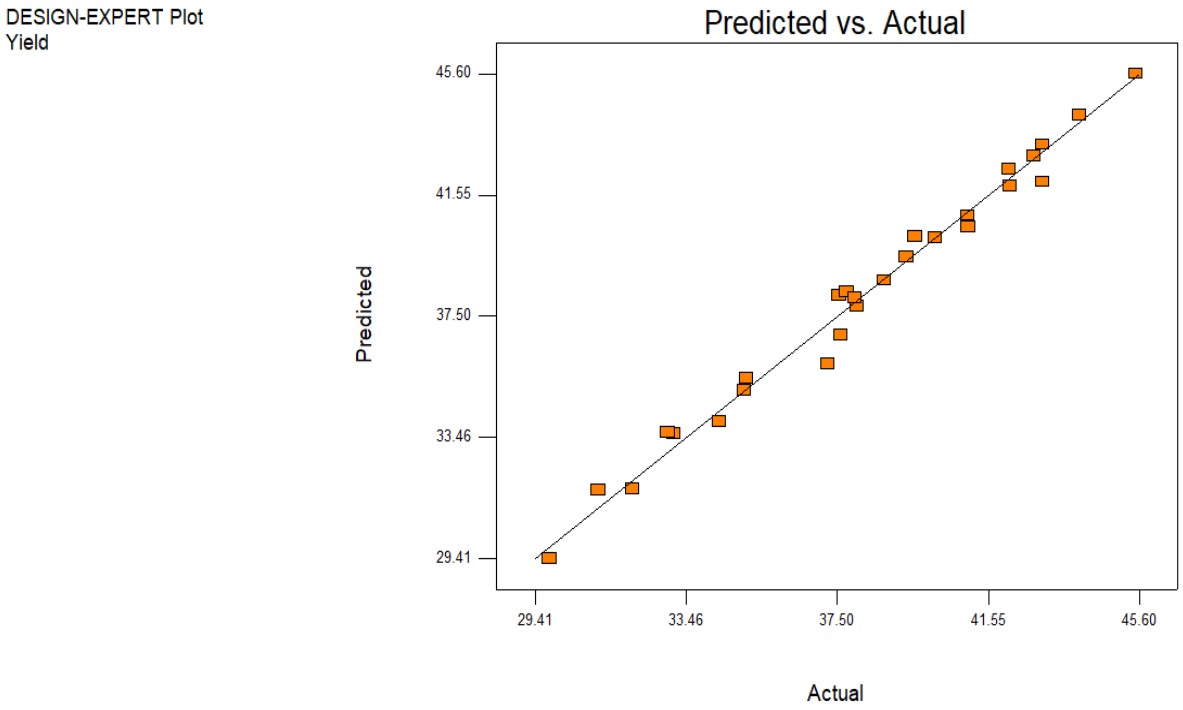



**Figure 4-10: Predicted Vs Actual Value of Yield**

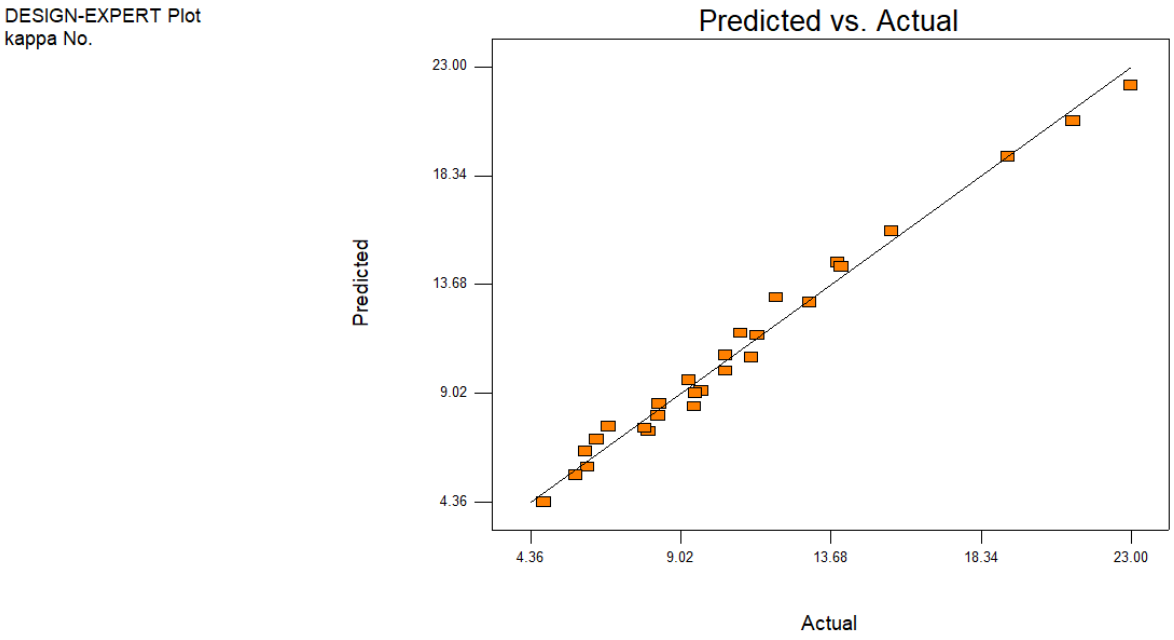



**Figure 4-11:Predicted Vs Actual Value of Kappa Number of Pulp**

From the above figure, 4-10 and 4-11 show the two value which is predicted Vs actual value lay on the same line this shows that the experiment performed properly and the pulping parameter (time, temperature and active alkaline) are fit to the experimental prediction value. The purpose is to detect a value, or group of values, that are not easily predicted by the model and easily compare to the actual value.

### 4.7.1. Interaction effect of time and temperature on the yield of pulp

The below graph indicated the interaction effect of cooking time and temperature and identified the pulping condition on the yield of pulp. The pulping conditions which are at time 90min, temperature 140°C and active alkaline 15% and yield of pulp at this pulping parameter 36.88%. Temperature is more effect on the yield of the pulp as shown the F value from the data temperature value is greater than other pulping parameters which is time and active alkaline. The interaction of both time and temperature as shown figure below 4-12.

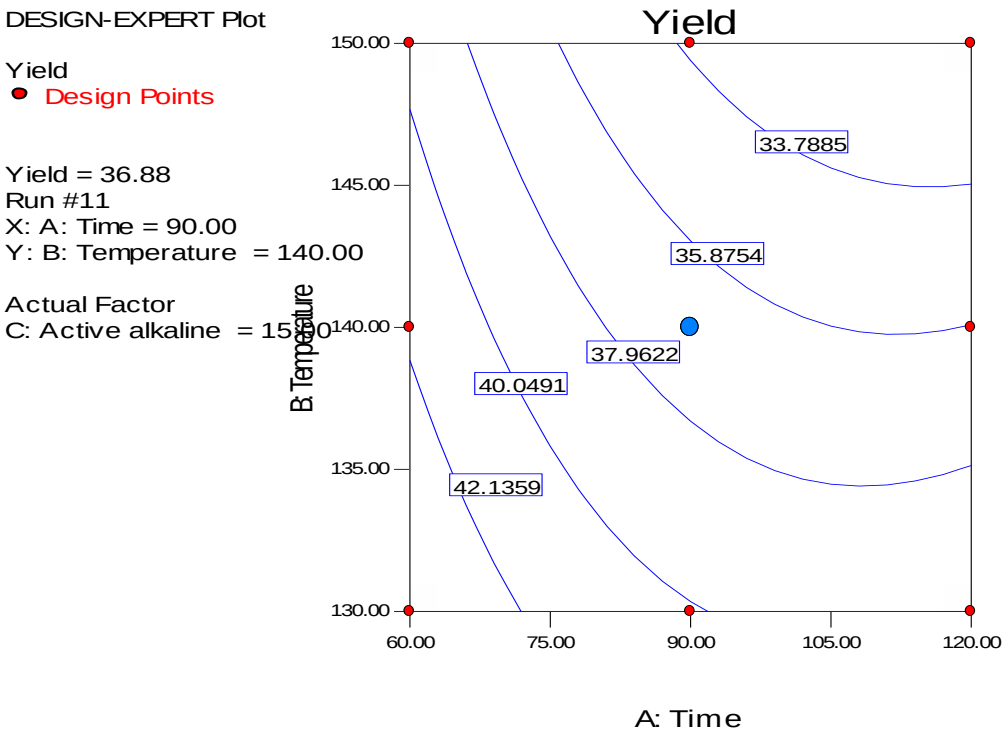



**Figure 4-12: Interaction Effect of Time and Cooking Temperature on the Yield of Pulp**

When the cooking temperature and cooking time increased total yield had decreased because high temperature and more cooking time helps the cooking liquor to dissolve more lignin and hemicellulose. Therefore, low total yield was obtained because better penetration and a higher rate of delignification were obtained. Pulp yield also depends on the degradation of carbohydrates and these carbohydrates are degraded by peeling, chain cleavage and the dissolution of short-chain carbohydrates. During cooking hemicelluloses which mainly consist of glucomannan and xylan are degraded. Both are degraded at specific conditions and reduce the pulp yield. As shown in figure 4-12, lower temperatures give high yield as compared to high temperature. When temperature increases from 130 to 150$^{o}$C pulp yield decreases from

40.2 % to 39.4%. At higher temperature, degradation of both hemicelluloses and celluloses occur which results in reducing the total yield.

### 4.7.2. Interaction effect of time and active alkaline on the yield of pulp

The effect of active alkaline and cooking time on the yield of pulp and find out the yield at the different pulping condition. The value of yield in these pulping condition as shown in the below figure 4-13.

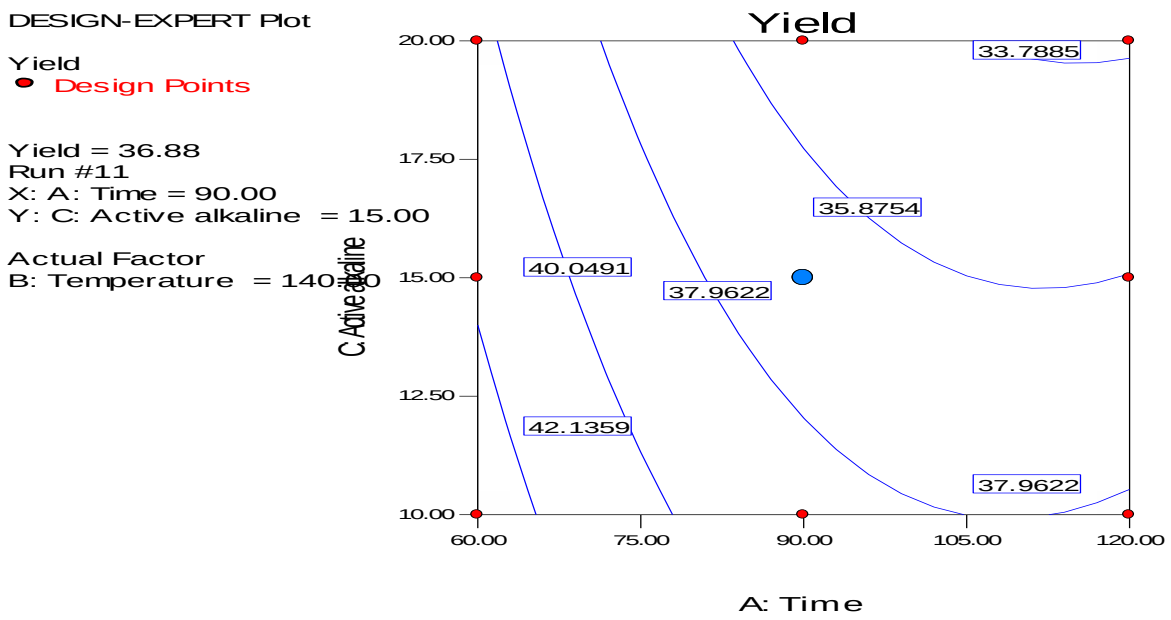



**Figure 4-13: Interaction Effect of Time and Active Alkaline on yield of pulp**

Based on the above graph the yield of pulp is 36.88% at 90min, 140℃ and 15% at this pulping condition time, temperature and active alkaline respectively. The interaction effect of time and active alkaline at a constant temperature when the time and active alkaline increased the yield of pulp is decreased but the effect of both pulping condition initially at the lower time the effect of active alkaline is strong on the yield of pulp and when the time above 110min the effect of active alkaline is weak.

### 4.7.3. Interaction effect of time and temperature on the kappa number of pulp

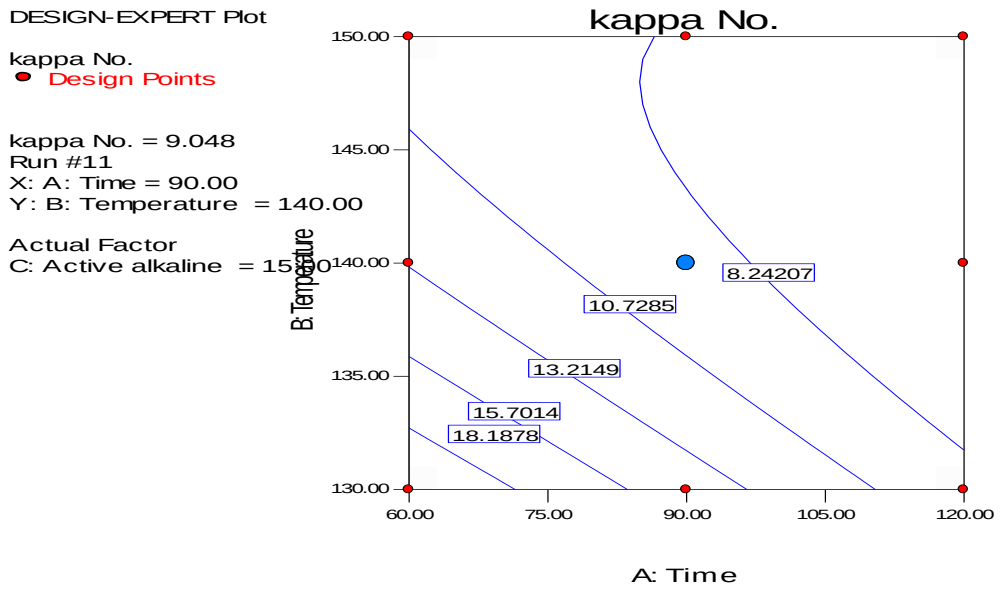



**Figure 4-14: Interaction Effect of Time and Cooking Temperature on the kappa number of pulp**

The kappa number of pulp is 9.048 at the pulping condition temperature, time and active alkaline 140℃, 90min and 15% respectively. Based on the above graph there is an interaction effect between time and cooking temperature. As the cooking time increase from 60 to 120min kappa number of pulp decreased and similarly when cooking temperature increased from 130 to 150℃ the pulp kappa number is decreased. The value of kappa number as mentioned from the above value is greatly important in the economy. The kappa number of pulp varies at the pulping conditions also vary. When the time and temperature is maximum kappa number of pulp become lower. Kappa number of pulp directly related to lignin of pulp. This shows the quality paper; minimum kappa number means a minimum amount of lignin.

## 4.8. Process variable and response factor optimization

As the objective of this study finds out the optimum pulping parameter or process variable with a maximum yield of pulp and minimum kappa number of yield this show maximum economical benefit as the production of pulp used as input material for the production of paper. Optimization allows generating predicted response(s) for any set of factors. The process variables such as cooking temperature, the concentration of active alkali and pulping time have been optimized. Since the goals of optimization were to maximize the economic benefit by minimizing process cost, the process variables need to set at their minimum value and the two

response variables pulp yield and kappa number were set to maximum and minimum levels respectively. Once the optimum pulping condition was obtained, flax straw pulp was produced.

**Table 4-16: Summary on Factors, Response(yield and kappa number) and Goals of Optimization**

| Name | Goal | Lower limit | Upper limit | Lower weight | Upper weight | Importance |
|---|---|---|---|---|---|---|
| A | In range | 60 | 120 | 1 | 1 | 3 |
| B | In range | 130 | 150 | 1 | 1 | 3 |
| C | In range | 10 | 20 | 1 | 1 | 3 |
| Yield | Maximize | 29.78 | 45.5 | 1 | 1 | 3 |
| Kappa | Minimize | 4.75 | 23 | 1 | 1 | 3 |

At maximum yield the pulping condition set at minimum economical consideration this means as the time of pulping condition increases the time value considered as cost and consumption of chemical directly related to cost. Finally, the experimental optimization set at the optimum pulping condition and related cost, minimum cost, maximum yield or maximum final output related to good quality.

In the above optimum goals, seven solutions are founding. The optimum pulping condition at maximum yield and minimum kappa number at good desirability as shown below table 4-17.

**Table 4-17: Solution of a Pulping Condition at Maximum Yield**

| Number | Time(min) | Temperature(℃) | Active alkaline(%) | Yield(%) | kappa No. | Desirability | |
|---|---|---|---|---|---|---|---|
| 1 | 120.00 | 131.74 | 10.00 | 41.6859 | 9.75942 | 0.741272 | Selected |
| 2 | 120.00 | 131.81 | 10.00 | 41.6544 | 9.72557 | 0.741236 | |
| 3 | 120.00 | 131.54 | 10.00 | 41.7679 | 9.85146 | 0.741228 | |
| 4 | 120.00 | 132.28 | 10.00 | 41.4571 | 9.51121 | 0.740962 | |
| 5 | 60.00 | 146.21 | 13.92 | 40.6911 | 10.9755 | 0.676255 | |
| 6 | 60.00 | 146.38 | 12.87 | 40.9391 | 11.25 | 0.676048 | |
| 7 | 60.00 | 145.34 | 17.37 | 39.9478 | 10.1717 | 0.67428 | |

In the above seven solutions, the maximum yield and minimum kappa number get based on the set value is aproximality 41.7% and 9.8 respectively with a good Desirability value at 0.741272. this optimum value gets at pulping parameter which is (time, temperature and active alkaline) 120min, 131.74℃ and 10% respectively.

To confirm the optimized model, the actual validation experiment was carried out at optimum conditions that were obtained in a design expert. To validate the optimum conditions predicted by the full factorial methodology model results, triplicate experiments were conducted at the above specified optimum process conditions predicted by the model.

After optimization, triplicate experiments were performed using these optimized process conditions. At this condition, the mean percentage of yield and kappa number obtained was 41.7% and 9.8 respectively. As shown in table 4.17 and which was then related to the data obtained from optimization analysis using the desirability function.

**Table 4-18: Result of optimization and model validation**

| Number | Cooking time(min) | Temperature(℃) | Active alkaline(%) | Yield(% | Kappa number |
|---|---|---|---|---|---|
| Predicated | 120 | 132 | 10 | 41.7 | 9.8 |
| Experimental | 129 | 132 | 10 | 40.56 | 10.45 |

The mean percentage of yield obtained by triplicate experiments 40.56% which is not significantly different from the predicted value of 41.7% yield and kappa number obtained from experiment 10.45 similar to the predicted value at the optimal conditions are time (120min), active alkaline (10%), and temperature (132℃).

Therefore, the model was valid and capable of predicting the maximum pulp yield i.e. numerical optimization can be taken as an optimal value because the predicted value was close enough to the experimental value. In summary, this study shows that active alkaline, temperature, and time could be used for the optimization of pulp produced from flax straw and the yield could be optimized by tuning concentration of active alkaline, temperature, and time parameters.

# 5. CONCLUSIONS AND RECOMMENDATIONS

## 5.1. Conclusions

The result from the experiment of proximate properties of flax straw contained ash content and extractive is 4.13 and 5.21 respectively this indicated that the lower ash content means the lower mineral content this range under the standard of biomass proximate properties and preferable for pulp production and used as input for paper production. Chemical compositions get from the experiment, the cellulose content of flax straw was found to be 51.34%, which is satisfactory for pulp production. In addition to this, the cellulose content of flax straw is comparable to the reported cellulose content of biomass (40-52%) and hardwoods (38-56 %). The lignin content of flax straw was comparable to other nonwood papermaking fiber resources and less than wood fiber sources. And it was also found that the flax straw contained low amounts of extractives and ash due to the presence of low silica content. It was found that the yield and kappa number of flax straw pulp were influenced by pulping variables such as concentrations of active alkali, cooking temperature and time. Pulp yield was slightly influenced by these process variables and a slight decrease in pulp yield was observed upon increasing the levels from the bottom to the next. But a rapid falling was observed in the case of kappa numbers when increasing levels of process variables from bottom to the next and most of the delignification process were carried out during this period. Generally, both the pulp yield and kappa numbers were inversely related to the processing variables.

The optimized flax straw pulping conditions that have been considered high pulp yield, low kappa number, low chemical and energy consumption easily related to cooking temperature with short pulping time chosen using numerical optimization as a combination of 10% active alkali, 131.74$^{o}$C temperature and 120 minutes while keeping Sulphidity 25% and liquor to straw ratio 9:1 is practically feasible. Because of the experimentally obtained results of pulp yield and kappa numbers 40.56% and 10.45 respectively. Properties of paper full fill the standard of paper in a white bond which is bursting, tearing and tensile strength are 1.4gm/m$^2$, 100mm2/g and 5200m respectively and basic properties paper basis weight, ash content and moisture content are 60gm/m$^2$, 7.2% and 6.9% respectively.

## 5.2. Recommendation

Based on the properties and nature of flax straw highly recommended for the production of textile with retted its fiber because the result from lab the fiber morphology analysis shows the fiber length of pulp is too high this shows it is preferably used for textile rather than paper production. The ratio of white liquor and raw material highly effected on the yield of pulp and quality pulp related to kappa number so it is possible to study their factor. It is also possible to study the effects on pulp yield and kappa number physical characteristics by using flax straw in combination with other widely available agricultural by-products which might be feasible environmentally and economically and the way of a collection of raw material from agricultural another critical study on another future study.

Production of pulp from flax straw at different cooking parameter and determine the yield pulp, kappa number, paper hand sheet making and its properties conducted in this study at the limited pulping condition used only kraft pulping but including another parameter may be used for large scale production of paper so I recommended for future study.

In this study, it was investigated the effects of the cooking parameter on the yields and kappa numbers of flax straw pulp at a different level the value may be varied due to personal and equipment error. Varieties of flax straw may be varied on the chemical composition and yield of pulp so future study needed to including the varieties of straw for an extract of pulp determination properties of straw. The brightness of paper did not perfect to the standard so future bleaching required to get the perfect white colour.

Finally, from this experiment I recommended, there is two advantage when flax straw used for manufacturing of pulp as input for the production of paper the main product also used for edible oil production. Therefore, a large amount of flaxseed/linseed is recommended for these two main large projects, Besides, the soil condition recommended for harvesting the linseed plant.

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*CHARACTERIZATION , VALORIZATION AND OPTIMIZATION OF ENSET / ENSETE VENTRICOSUM / FIBERS FOR PAPER PULP PRODUCTION HANNA BERHANU LEMMA A PhD Dissertation Submitted to the School of Chemical and Bio Engineering in Partial Fulfillment of the Requirements of the Degree of Doctor of Philosophy ( Process Engineering Stream ) PhD Candidate :*

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# APPENDICES

## Appendix A: - Experimental Framework




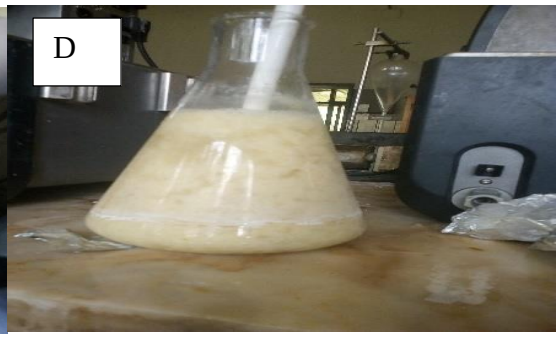






Figure A-1: Experimental frame work (A): Raw material, (B): Morphological analysis (C): Pulp washing after cooking (D): Pulp bleaching (E): Beating pulp using beating machine (F): Freeness tester (G): Burst tester (H): Tearing tester (I): Tensile strength test

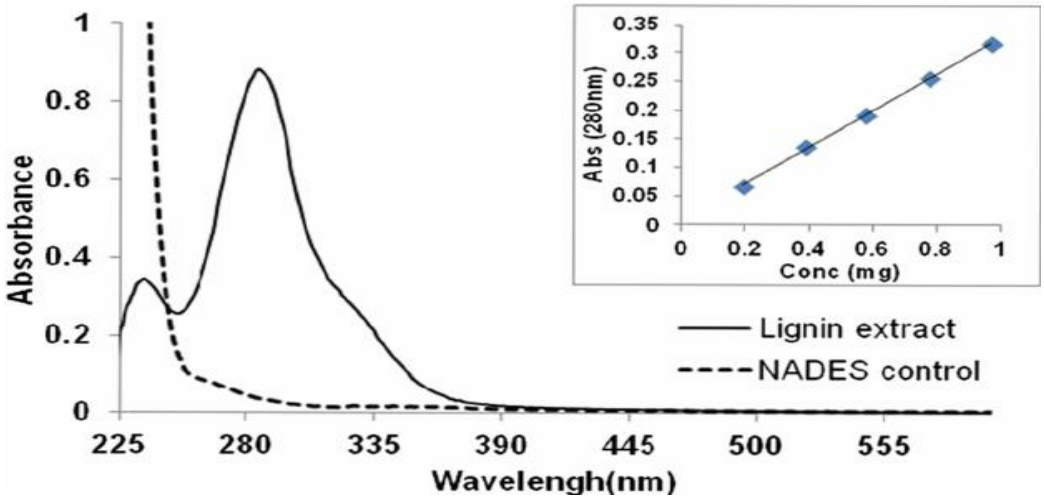


Figure A-2: Standard curve for acid soluble lignin content determination

**Appendix B: - The cooking liquor and the charge calculations**

Let white liquor be yL

Target sulfidity =A, in fraction

EA concentration =(target 75g/L) = z g/L*yL=xg

The calculation as following

$$sulfidity = A = \frac{Na_2S}{Na_2S + NaOH} \quad (B.1)$$

$$A * NaOH + A * Na_2S = Na_2S \quad (B.2)$$

$$NaOH = \frac{Na_2S(1 - A)}{A} \quad (B.3)$$

$$Conc.EA = NaOH + \frac{1}{2}Na_2s \quad (B.4)$$

$$NaOH = x - \frac{1}{2}Na_2S \quad (B.5)$$

$$Na_2s = \frac{2Ax}{2 - A} \quad (B.6)$$

## Appendix C:- Functional group properties with wavenumber interval

Table C-1: Functional group properties with wavenumber

| **Functional group/assignment** | **Wavenumber (cm-1)** |
|---|---|
| **1. Saturated Aliphatic (alkene/alkyl)** | |
| **a) Methyl (-CH3)** | |
| Methyl C-H asym./sym. Stretch | 2970–2950/2880–2860 |
| Methyl C-H asym./sym. Bend | 1470–1430/1380–1370 |
| gem-Dimethyl or ‘‘iso’’- (doublet) | 1385–1380/1370–1365 |
| Trimethyl or ‘‘tert-butyl’’ (multiplet) | 1395–1385/1365 |
| **b) Methylene (>CH2)** | |
| Methylene C-H asym./sym. Stretch | 2935–2915/2865–2845 |
| Methylene C-H bend | 1485–1445 |
| Methylene —(CH2)n— rocking (n ≥ 3) | 750–720 |
| Cyclohexane ring vibrations | 1055–1000/1005–925 |
| **c) Methyne (>CH-)** | |
| Methyne C-H stretch | 2900–2880 |
| Methyne C-H bend | 1350–1330 |
| Skeletal C-C vibrations | 1300–700 |
| **d) Special methyl (-CH3) frequencies** | |
| Methoxy, methyl ether O-CH3, C-H stretch | 2850–2815 |
| Methylamino, N-CH3, C-H stretch | 2820–2780 |
| **2. Olefinic (alkene)** | |
| Alkenyl C=C stretch | 1680–1620 |
| Aryl-substituted C=C | 1625 |
| Conjugated C=C | 1600 |
| Terminal (vinyl) C-H stretch | 3095–3075<br>3040–3010 |
| Pendant (vinylidene) C-H stretch | 3095–3075 |
| Medial, cis- or trans-C-H stretch | 3040–3010 |
| **Functional group/assignment** | **Wavenumber (cm-1)** |
| Vinyl C-H in-plane bend | 1420–1410 |
| Vinylidene C-H in-plane bend | 1310–1290 |
| Vinyl C-H out-of-plane bend | 995–985 + 915–890 |
| Vinylidene C-H out-of-plane bend | 895–885 |
| trans-C-H out-of-plane bend | 970–960 |
| cis-C-H out-of-plane bend | 700 (broad) |
| **3. Olefinic (alkene)** | |
| Alkenyl C=C stretch | 1680–1620 |
| Aryl-substituted C=C | 1625 |
| Conjugated C=C | 1600 |

| | |
|---|---|
| Terminal (vinyl) C-H stretch | 3095–3075<br>3040–3010 |
| Pendant (vinylidene) C-H stretch | 3095–3075 |
| Medial, cis- or trans-C-H stretch | 3040–3010 |
| Vinyl C-H in-plane bend | 1420–1410 |
| Vinylidene C-H in-plane bend | 1310–1290 |
| Vinyl C-H out-of-plane bend | 995–985 + 915–890 |
| Vinylidene C-H out-of-plane bend | 895–885 |
| trans-C-H out-of-plane bend | 970–960 |
| cis-C-H out-of-plane bend | 700 (broad) |
| **4. Aromatic ring (aryl)** | |
| C=C-C Aromatic ring stretch | 1615–1580<br>1510–1450 |
| Aromatic C-H stretch | 3130–3070 |
| Aromatic C-H in-plane bend | 1225–950 (several) |
| Aromatic C-H out-of-plane bend | 900–670 (several) |
| C-H Monosubstitution (phenyl) | 770–730 + 710–690 |
| C-H 1,2-Disubstitution (ortho) | 770–735 |
| C-H 1,3-Disubstitution (meta) | 810–750 + 900–860 |
| C-H 1,4-Disubstitution (para) | 860–800 |
| Aromatic combination bands | 2000–1660 (several) |
| **5. Acetylenic(alkyne)** | |
| C≡C Terminal alkyne (monosubstituted) | 2140–2100 |
| C≡C Medial alkyne (disubstituted) | 2260–2190 |
| Alkyne C-H stretch | 3320–3310 |
| Alkyne C-H bend | 680–610 |
| Alkyne C-H bend | 630 (typical) |
| **6. Aliphatic organohalogen compound** | |
| Aliphatic fluoro compounds, C-F stretch | 1150–1000 |
| Aliphatic chloro compounds, C-Cl stretch | 800–700 |
| Aliphatic bromo compounds, C-Br stretch | 700–600 |
| Aliphatic iodo compounds, C-I stretch | 600–500 |
| **7. Alcohol and hydroxy compound** | |
| Hydroxy group, H-bonded OH stretch | 3570–3200 (broad) |
| Normal ‘‘polymeric’’ OH stretch | 3400–3200 |
| Dimeric OH stretch | 3550–3450 |
| Internally bonded OH stretch | 3570–3540 |
| Nonbonded hydroxy group, OH stretch | 3645–3600 (narrow) |
| Primary alcohol, OH stretch | 3645–3630 |
| Secondary alcohol, OH stretch | 3635–3620 |
| Tertiary alcohol, OH stretch | 3620–3540 |
| Phenols, OH stretch | 3640–3530 |

## Appendix D: Paper properties calculation

### Tensile strength

$$X1 = \frac{a}{b} \quad (D.1)$$

Where,

X1 = tensile strength (KN/m)

a = maximum tensile force in (N) = instrument reading in kg to change in to (N) = kg * 9.807

b = initial width of the sample in (mm)

**Tensile index**

$$X2 = 1000 * \frac{X1}{W} \quad (D.2)$$

Where,

$X_2$ = tensile index (Nm/g)

$X_1$ = tensile strength (KN/m)

W = mean Grammage in ($g/m^2$)

**Breaking Length**

$$X3 = \frac{a * 102{,}000}{b} \quad (D.3)$$

Where

a = mean tensile strength in, KN/m

b = Grammage in, $g/m^2$

$X_3$ = breaking length in meter, m

**Burst Properties**

Bursting strength

It is the capacity of a material (such as a paper or textile) or object (such as a metal pipe) to maintain in continuity when subjected to pressure; broadly the pressure often expressed in pounds per square inch required to rupture such a material or object under rigidly controlled conditions.

The test specimens was first prepared as 10 cm by 10 cm sheet and clamped in the tester tightly with Bursting strength tester of model PN-BSM600 and the maximum reading pointer was set to zero position. The pump motor was then started and the pumping system and the test piece then wait to burst. The maximum read pointer was then recorded and allowed to rest gently to zero position and the broken sample was removed. Instrument reading =

Kg/cm2

To change Kg/cm2 in to Kpa (Kilo Pascal), Kpa = Kg/cm2 * 98.07

Where, Kpa -SI unit of bursting strength

Kg/cm$^2$ - instrument reading.

Burst factor

This factor, which has been called the bursting area, is equivalent to the number of square meter of paper, the weight of which, if applied to each square centimeter of the test sheet camped in the instrument cause a burst.

$$burst\ factor = \frac{burst\ strength\left(\frac{kg}{cm2}\right) * 1000}{basis\ weight(\frac{g}{cm2})} \qquad (D.4)$$

Burst Index

Burst index is bursting strength divided by basis weight

$$X = \frac{a}{W} \qquad (D.5)$$

Where

X- Burst index Kpa m$^2$/kg  A- Burst strength in Kpa  W- Basis weight in g/m$^2$

Tearing Properties

Tearing resistance

Tear resistance is a measure of how well a material can withstand the effects of tearing. More specifically, however it is how well a material resists the growth of any cuts when under tension using L-W AB Lorentz & Wetter tearing tester.

## Appendix E : Diagnostics Case Statistics of yield of pulp

Table E-1: Diagnostics Case Statistics of yield of pulp

| standard order | actual value | predicted value | residual | leverage | student residual | cook's distance | outilers | run order |
|---|---|---|---|---|---|---|---|---|
| 1 | 45.5 | 45.63 | -0.13 | 0.509 | -0.3 | 0.009 | -0.292 | 3 |
| 2 | 43 | 42.03 | 0.97 | 0.343 | 2.005 | 0.209 | 2.226 | 7 |
| 3 | 42.1 | 42.45 | -0.35 | 0.509 | -0.821 | 0.07 | -0.813 | 10 |
| 4 | 43 | 43.37 | -0.37 | 0.343 | -0.754 | 0.03 | -0.744 | 26 |
| 5 | 38.76 | 38.84 | -0.08 | 0.259 | -0.156 | 0.001 | -0.151 | 21 |
| 6 | 37.55 | 38.34 | -0.79 | 0.343 | -1.615 | 0.136 | -1.703 | 25 |
| 7 | 41 | 40.67 | 0.33 | 0.509 | 0.783 | 0.064 | 0.773 | 4 |
| 8 | 35.07 | 35.22 | -0.15 | 0.343 | -0.309 | 0.005 | -0.3 | 24 |
| 9 | 34.34 | 33.79 | 0.55 | 0.509 | 1.309 | 0.178 | 1.339 | 18 |
| 10 | 44 | 44.18 | -0.18 | 0.343 | -0.377 | 0.007 | -0.367 | 15 |
| 11 | 39.59 | 40.12 | -0.53 | 0.259 | -1.034 | 0.037 | -1.036 | 19 |
| 12 | 40.13 | 40.09 | 0.045 | 0.343 | 0.092 | 0 | 0.089 | 14 |
| 13 | 42.13 | 42.04 | 0.091 | 0.259 | 0.176 | 0.001 | 0.171 | 22 |
| 14 | 37.6 | 37.05 | 0.55 | 0.259 | 1.056 | 0.039 | 1.06 | 11 |
| 15 | 37.25 | 36.09 | 1.16 | 0.259 | 2.244 | 0.176 | 2.596 | 27 |
| 16 | 39.35 | 39.46 | -0.11 | 0.343 | -0.226 | 0.003 | -0.219 | 13 |
| 17 | 33.11 | 33.55 | -0.44 | 0.259 | -0.853 | 0.025 | -0.846 | 9 |
| 18 | 31.09 | 31.66 | -0.57 | 0.343 | -1.176 | 0.072 | -1.191 | 20 |
| 19 | 42.78 | 42.64 | 0.14 | 0.509 | 0.33 | 0.011 | 0.322 | 6 |
| 20 | 37.75 | 38.12 | -0.37 | 0.343 | -0.768 | 0.031 | -0.758 | 8 |
| 21 | 38.03 | 37.63 | 0.4 | 0.509 | 0.96 | 0.096 | 0.957 | 23 |
| 22 | 41.01 | 40.61 | 0.4 | 0.343 | 0.816 | 0.035 | 0.808 | 17 |
| 23 | 35.01 | 35.17 | -0.16 | 0.259 | -0.311 | 0.003 | -0.302 | 12 |
| 24 | 32.95 | 33.75 | -0.8 | 0.343 | -1.642 | 0.141 | -1.737 | 16 |
| 25 | 37.98 | 38.15 | -0.17 | 0.509 | -0.404 | 0.017 | -0.393 | 2 |
| 26 | 32 | 31.78 | 0.22 | 0.343 | 0.449 | 0.01 | 0.438 | 5 |
| 27 | 29.78 | 29.44 | 0.34 | 0.509 | 0.821 | 0.07 | 0.813 | 1 |

Table E-2: Diagnostics Case Statistics of kappa number of pulp

| standard order | actual value | predicted value | residual | levereage | student residual | cook's distance | outiller t | run order |
|---|---|---|---|---|---|---|---|---|
| 1 | 23 | 22.04 | 0.96 | 0.306 | 1.729 | 0.219 | 1.822 | 3 |
| 2 | 15.55 | 16.27 | -0.72 | 0.167 | -1.186 | 0.047 | -1.199 | 7 |
| 3 | 10.39 | 10.49 | -0.1 | 0.306 | -0.185 | 0.003 | -0.181 | 10 |
| 4 | 13.89 | 14.49 | -0.6 | 0.222 | -1.021 | 0.05 | -1.022 | 26 |
| 5 | 11.2 | 10.87 | 0.33 | 0.167 | 0.551 | 0.01 | 0.542 | 21 |
| 6 | 8 | 7.24 | 0.76 | 0.222 | 1.291 | 0.079 | 1.313 | 25 |
| 7 | 11.39 | 11.35 | 0.041 | 0.306 | 0.074 | 0 | 0.073 | 4 |
| 8 | 9.25 | 9.88 | -0.63 | 0.167 | -1.045 | 0.036 | -1.047 | 24 |
| 9 | 8.34 | 8.42 | -0.077 | 0.306 | -0.139 | 0.001 | -0.135 | 18 |
| 10 | 21.2 | 20.52 | 0.68 | 0.25 | 1.175 | 0.077 | 1.186 | 15 |
| 11 | 14 | 14.75 | -0.75 | 0.111 | -1.197 | 0.03 | -1.211 | 19 |
| 12 | 9.64 | 8.97 | 0.67 | 0.25 | 1.161 | 0.075 | 1.172 | 14 |
| 13 | 11.98 | 12.97 | -0.99 | 0.167 | -1.631 | 0.089 | -1.703 | 22 |
| 14 | 9.45 | 9.35 | 0.1 | 0.111 | 0.165 | 0.001 | 0.161 | 11 |
| 15 | 6.1 | 5.73 | 0.37 | 0.167 | 0.618 | 0.013 | 0.609 | 27 |
| 16 | 10.39 | 9.83 | 0.56 | 0.25 | 0.976 | 0.053 | 0.975 | 13 |
| 17 | 8.3 | 8.36 | -0.063 | 0.111 | -0.101 | 0 | -0.099 | 9 |
| 18 | 6.4 | 6.9 | -0.5 | 0.25 | -0.866 | 0.042 | -0.86 | 20 |
| 19 | 19.18 | 19.01 | 0.17 | 0.306 | 0.316 | 0.007 | 0.309 | 6 |
| 20 | 13.01 | 13.23 | -0.22 | 0.167 | -0.362 | 0.004 | -0.355 | 8 |
| 21 | 6.77 | 7.45 | -0.68 | 0.306 | -1.236 | 0.112 | -1.253 | 23 |
| 22 | 10.86 | 11.45 | -0.59 | 0.222 | -1.006 | 0.048 | -1.006 | 17 |
| 23 | 7.89 | 7.83 | 0.063 | 0.167 | 0.104 | 0 | 0.101 | 12 |
| 24 | 4.75 | 4.21 | 0.54 | 0.222 | 0.93 | 0.041 | 0.927 | 16 |
| 25 | 9.42 | 8.31 | 1.11 | 0.306 | 2.008 | 0.296 | 2.18 | 2 |
| 26 | 6.04 | 6.84 | -0.8 | 0.167 | -1.328 | 0.059 | -1.354 | 5 |
| 27 | 5.74 | 5.38 | 0.36 | 0.306 | 0.655 | 0.031 | 0.646 | 1 |