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Characterization and Optimization of Soda-Anthraquinone Pulping of Teff Straw for Paper Making Process

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A Thesis submitted to the School of Chemical and Bio Engineering

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in Chemical Engineering (Process Engineering Stream)

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This is to certify that the thesis prepared by Kebede Alemu entitled "*Characterization and Optimization of Soda-Anthraquinone Pulping of Teff Straw for Paper Making Process*" and submitted in partial fulfillment of the requirements for the degree of master of sciences in Chemical Engineering (Process Engineering Stream) complies with the regulations of the university and meets the accepted standards with respect to originality and quality.

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DECLARATION

I declare that this thesis entitled "*Characterization and Optimization of Soda-Anthraquinone Pulping of Teff Straw for Paper Making Process*" for the M.Sc. degree at the university of Addis Ababa, hereby submitted by me, is my original work and has not previously been submitted for degree at this or any other university, and that all resources of materials used for this thesis have been duly acknowledged.

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ABSTRACT

The aim of this research was to investigate the important features of teff straw and its utilization in the pulp and paper industry via soda-anthraquinone pulping process. Morphological characterization indicated that the average length of teff straw fibers (1230µm), average fibers width (15.28µm), cell wall thickness (3.83µm), lumen diameter (21.28µm) and acceptable derived indices of slenderness ratio (80.78), Runkle ratio (0.36), flexibility coefficient (138.7) and wall rigidity coefficient (25) which were comparable to the most non-wood plants and Eucalyptus. The chemical composition of teff straw showed that the cellulose content (39.4%), hemicellulose (29.6%), lignin (14%), extractives (7.2%) and ash content (6.78%). It contained lower lignin and higher hemicellulose contents than most of non-wood plants which reflected that teff straw requires mild cooking conditions. For experimental design, Response Surface Methodology/Central Composite Design was used to compare the effects of cooking temperature (130, 140 and 150℃), cooking time (60, 90, and 120 minutes) and active alkali concentration (10, 15, and 20%) on pulp yield and Kappa number. The results indicated that sodium hydroxide concentration had a higher significant influence on both pulp yield and Kappa number followed by cooking time and temperature respectively. Greater interaction effects (temperature-time, temperature-active alkali concentration and time-alkali concentration) of factors were also seen on pulp yield and Kappa number both positively and negatively. Over cooking, extended time pulping and high active alkali concentration gave the lower pulp yield. The optimization results of pulping processes gave the optimal operating condition of 13.76% active alkali at 145.13℃ for 71.5 minutes and 33.15% pulp yield (based on oven dried teff straw) of 25.85 Kappa number. The paper hand sheets of 60 g/m^2 were prepared from the pulps produced at optimum conditions and tested for its mechanical properties that showed breaking length (4294 m), tensile strength (11.6 kN/m), tensile index (42.1 Nm/g), tear index (5.2 mN.m^2/g) and burst index (1.41 kPa.m^2/g), and porosity (19.5 se/100 air). The results indicated that the tested strength properties were acceptable and make teff straw an alternative material for pulp and paper application.

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ACRONYMS

AFPA	American Forest & Paper Association
ANOVA	Analysis of variance
AQ	Anthraquinone
COD	Chemical Oxygen Demand
CSA	Central Statistical Agency
CSF	Canadian standard of freeness
CV	Coefficient of Variation
DRS	Diffuse reflectance system
ECF	Elemental chlorine-free
EPPSC	Ethiopian Pulp and paper Share Company
FTIR	Fourier-transformed infrared spectroscopy
ISO	International Organization for Standardization
OD	Oven dried
PRESS	Predicted residual error sum of squares
RMP	Refiner mechanical pulp
RSM	Response Surface Method
TAPPI	Technical Association of Pulp and Paper Industries
TCF	Totally chlorine free
TMP	Thermo-mechanical pulping

1. INTRODUCTION

1.1. Background

Pulp and paper production is one of the high demand sectors in the world of industrial production. The total global consumption from paper-making was projected to increase from 316 million tons in 1999 and to about 425 million tons by 2010 (García *et al.*, 2008) and to over 490 tons by the year 2020 (John, 2006) with an average rate of 2.8 per annum. Progress in pulp and paper technology has overcome most of the related environmental problems. The environmental problems have brought forth the cleaner technology now involved in paper making. New raw materials have replaced traditional wood raw materials with non-wood and residual materials, and less polluting cooking and pulp bleaching processes have been evolved.

In recent years, non-wood fibers and agricultural residues have been considered as a potential source of papermaking raw material since demand for pulp cannot be fulfilled only by classic raw materials such as hard and soft woods (Ferrer *et al*. 2011 a, b; Gonzalez *et al*. 2011; Hou *et al*; 2011). Non-wood fibers (bamboo, straw, bagasse etc.), as agricultural residues and annual plants, are low-cost raw materials and, therefore, interesting as sources of alternative fibers to wood cellulose fibers (Sirdach, 2010). The benefit of non-wood plants as fiber sources, with straw being a by–product in the process, is their fast annual growth. Therefore, these non-wood plants, and their straw, represent an annually renewable fiber resource available in abundant quantities in many regions all over the world. In line with this, remarkable advantages are provided by the use of non – woody raw materials (Haung *et al*. 2006; Rodriguez *et al*. 2008).

- Deforestation and replanting can be alleviated; since wood raw materials are saved for other uses different from paper making.
- The wood cellulose fiber import can be reduced in countries where there is a lack of wood raw materials.
- The increasing demand of paper that is produced through clean technologies or from non-wood materials can be helped and fulfilled.

Just like in wood materials, straw contains carbohydrate and lignin as two major complex and polymeric chemical components. Lower amounts of extraneous materials, mostly in the form of organic extractives and inorganic minerals (ash), are present in straw as well. It is known that all non-wood materials, if compared against wood materials, consist of the same or lower content.

On the other hand, they have in general higher nutrient and silicon content (Hunter, 1988). As cereals are annual plants, their chemical composition is considerably more variable than the chemical composition of wood species. Chemical composition varies not only based on the type and cultivar of cereals but also in respect to the geographic location of cereals, climate and soil conditions (Han, 1998). The proportion of cellulose, hemicelluloses, and lignin in agricultural residue is an important criterion when determining both, its suitability as an economically sustainable raw material and the optimum pathway of its conversion for paper industry. Large quantities of cellulose do not necessarily mean that fibers are appropriate for further processing in paper industry; however, they are the first of many criteria in the selection of raw materials for further processing.

Several investigations have been focused on the application of farming to get potential agricultural residues and pulping techniques (Khristova *et al*., 1998; Villar *et al*., 2001). The results of previous studies strongly implied that pulp delignification, yield and cellulose protection were increased by addition of small amount of organic compounds that act as catalysts. Among these anthraquinone is used as an oxidant that is often used in chemical pulping for carbohydrate stabilization and delignification improvement (Borrega et al., 2013). Anthraquinone react with aldehyde end groups of the carbohydrates, oxidizing them to carboxylic acid (Azizi *et al*., 2010). This oxidation of aldehyde to carboxylic acid inhibits the alkaline de-polymerization reaction that occurs with the reducing end groups which results in an increased yield. The interaction of these conditions allowed for the attainment of pulps with similar cooking times at much different yields and Kappa number. The environmentally friendly Soda-AQ trials gave good results in terms of strength and yield (Khristova et al., 1998; Azizi et al., 2010).

Ethiopia has abundance of agro-waste materials that have not been utilized for pulp and paper production and dependence on import to fulfill the current demand of paper and paper products. Examples of such agro-waste materials are teff straw, coffee husk, wheat straw, barley straw, corn stalks, bagasse, etc. Teff straw is one of most important agricultural residue. Its annually renewable fiber resources that is available and produced in most of the regions of higher land coverage. It occupies about 28% of the total crop area allocated to cereals (Anonymous, 2010a) and 17% of cereal crop residues production annually (Anonymous, 2010b; FAO, 1987). Moreover, teff straw from threshed grains is considered to be animals’ forage and superior to straws from other cereal species in Ethiopia. It is also utilized to reinforce the mud used for covering the wooden materials, during construction of houses, mainly in the countryside. In the year 2017/18, teff was grown on about 3,023,283.5 hectares of crop area of Ethiopia (CSA). Taking the straw yield of 5000 kg/ha (FAO, 1980), the annual teff straw yield can be estimated to be about 15.12 million tones/year.

In this study, attempts have been made to investigate the possibility of using teff straw as raw material of agricultural biomass for pulp and paper making process by applying Soda-anthraquinone pulping method. The morphological properties and their derived values, chemical composition and proximate analysis were also performed. The influences operating variables affecting cooking conditions in the pulping process were studied by simulating the model through a polynomial model obtained from Response surface methodology/CCD (Design-Expert ® version 7.0.0) and optimum operating condition of process variables also found.

1.2. Statement of the problem

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. The availability of conventional and forest-based raw materials used in fiber isolation became limited due to the increasing demand for pulp and paper products. Agricultural residues can meet the problem of increasing cost of pulp and paper; and environmental concerns as alternative sources of raw materials and use to alleviate the shortage in wood raw materials mostly because they are annually renewable and economically feasible.

Numerous researches conducted on a global scale are focused on identifying alternative non-wood raw materials as a source of cellulose fibers. Some types of non-wood fibers have already been used in some paper grade productions, although the paper quality varies based on the source of the fibers. In Ethiopia, one of highly produced cereal crop is teff; estimated land area in hectares is more than 3.1 million (CSA, 2017/18) and it has good adaptation to prevailing climatic conditions that enable it to grows in most parts of the country. Taking the straw yield of 5000 kg/ha (5ton/ha) (FAO, 1980), the annual teff straw yield can be estimated to be about 15.12 million tones. Consequently, large quantity of teff straw, which could contain huge quantity of lignocellulosic compounds, is also being produced and has been used as cattle food of poor roughage (Andualem T. *et al.*, 2015; Chalchissa *et al.*, 2014) and open land dispose.

Despite large number of studies on biomass characterization and application, teff straw has not been studied much for its potential usages. One of the modern applications of such largely produced agro-residues is in pulp and paper production process. Ethiopia has been importing higher tons of pulps and papers, corrugated and non-corrugated packaging, exercise books and sanitary napkins, books and other printed items with high costs and there is no pulp producing factory. In order to overcome the dependence of the country on pulp import and substitute with pulp obtained from agricultural biomass of sustainable source, this study was aimed to provides essential baseline information and gives emphasis about the potential of teff straw for production of pulps and papers.

1.3. Objective

1.3.1. General Objective

The main objective of this study was characterization and optimization of soda-anthraquinone (Soda-AQ) pulping of teff straw for paper production process.

1.3.2. Specific objectives

The specific objectives of this study were:

- To characterize the morphological structure and chemical composition of teff straw and their effects on pulp and paper properties.
- To make and characterize the pulps from teff straw through soda-AQ pulping process.
- To study the individual and interaction effects of pulping parameters (cooking temperature, cooking time and alkali amount) on pulp yield and kappa number; and determine the optimal pulping conditions of soda-AQ pulping of teff straw
- To prepare hand sheets at optimum pulping conditions and analyses some strength properties of the sheets.

1.4. Significance of the study

This study gives insight for teff straw as alternative raw material for pulp and paper production and paves the way for further study in the future based on emphasis of environmental concern, sustainable availability and its inexpensiveness. It also provides the information and highlights our country's industrial sector to focus on highly abundant and promising agricultural biomass and to be independent from importing pulps and papers. In general, it was aimed to provide the possibilities of:

- Finding raw materials which have promising fibers, easy pulping and bleaching capability for the production of pulp and paper.
- Increasing the utility value of domestic raw material.
- Reducing environmental load emissions by replacing forests with agricultural residues.
- Using agricultural residues particularly teff straw, as raw material for the pulp and paper production.
- Providing useful baseline for re-planning of experiment in search for pulping process and optimization of this agro-residue.

1.5. Scope of the study

This study was limited to the raw material collected from specific farming area (Tulu Bollo, South Western of Addis Ababa). Teff (Eragrostis tef) straw that has been used for the study was also obtained from brown teff species. Since the mineral contents of the soil, geographical area and variety of the teff have an impact on morphological structure and chemical compositions; it would have been a deeper and extensive coverage if the samples collection were from different parts of country and different species of teff.

2. LITERATURE REVIEW

2.1. Historical Background of Pulp and Paper Production

The manufacture of pulp, paper and paper products ranks among the world's largest industries. 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 total consumption of 179.6 million tons. Whereas the global production of paper and paper board in 2014 was 406 million tons, with 407.6 million tons consumed. Asia is the leader in both production and consumption with about 45% in both categories (Susanna *et al.*, 2016). In 2015, the regional distribution of pulp and paper production was as follows: Asia-Pacific, 195 million tons (48%); Europe, 104 million tons (26%); Northern America 83 million tons (21%); Latin America and the Caribbean, 21 million tons (5%); and Africa, 4 million tons (1%) (FAO, 2015).

Pulp is one of the most abundant raw material worldwide which is used predominantly as a major component in the manufacture of paper and paper board, and with increasing importance also in the form of a wide variety of cellulose products in the textile, food, and pharmaceutical industries (Kumar *et al.*, 2013). The increasing demands and the requirements of these paper and products are in line with the increasing of human population, their quality of life and the country's rapid development and progress. Paper can be defined as the crossing network of cellulose fibers bonded to each other. Until recently, there are various criteria for paper produced in accordance with the requirements of the users. To fulfill the user's product specifications, there are various types of fiber, cooking methods as well as treatments that can be used (Ai and Tschirner, 2010).

Paper is an evolution of various other materials used as a medium for recording, storing and conveying information from ancient times. Among these are pieces of clay, pottery, stone, metal, bone, wood, bamboo, papyrus and vellum. Asia has been using pieces of wood or bamboo as information media. Meanwhile, the Sumerian, Babylonian and Mesopotamian have been using pieces of clay as their media. As for the Egyptian, Greek and Roman, they use papyrus scrolls and the Persians, Arabs and Jews use animal skin scrolls (Atchison and McGovern, 1987).

A.D. 105 often cited as the year which papermaking was invented. Early Chinese paper have been made from a suspension of mashed pieces of mulberry bark, cloth and hemp waste in water, washed, soaked and beaten to a pulp with wooden mallet. A paper mold, probably a sieve of coarsely woven sloth stretched in a four-sided bamboo frame, was used to dip up the fiber slurry from the vat and hold it for drying (Ai and Tschirner, 2010).

2.2. Fiber sources for pulp and paper production

Normally, fiber resources for pulp and paper are obtained from trees or agricultural crops residues. These resources include plant materials harvested directly from the land (wood, straw and bamboo), plant material by products or residual from other manufacturing processes (wood chips from sawmills, bagasse and cotton linear) and fiber recovered from recycled paper or paperboard. Forest resources have important value in producing a range of different wood resources for pulp and paper-based industries (Aripin, 2014).

Nowadays, many countries are looking for non-wood plants fiber resources as alternative fibers in pulp and paper based industries. This is due to the depletion and rising prices of wood resources and readily available non-wood fiber resources in these countries (Atchison, 1992).

2.2.1. Non-wood fiber sources

Non-wood plant can be divided into several groups depending on the location of the fibers in the plant. Iivessalo-Pfaffili (1995) has described four fiber types: grass fibers, bast fibers, leaf fibers and fruit fibers. Grass fibers are also termed stalk or culm fibers (Hurter 1988, Judt 1993). Generally, non-wood plant fiber pulps can be grouped into two broad categories.

Common non-woods or hardwood substitutes such as cereal straws, sugarcane bagasse, bamboo (shorter fiber species), reeds and grasses, esparto, kenaf (whole stalk or core fiber), corn stalks, sorghum stalks etc. Specialty non-woods or softwood substitutes such as cotton staple and linters; flax, hemp and kenaf bast fibers; sisal; abaca; bamboo (longer fibers species) (Robert *et al* 1997). Grass fibers currently used in papermaking are obtained mainly from cereal straw, sugarcane, reeds and bamboo (Atchison 1988).

The total of non-wood plants (8-10%) pulping capacity worldwide is increasing faster than the wood pulping capacity (González *et al*., 2008 and Rodríquez *et al*., 2008). This is made up of 44% straw, 18% bagasse, 14% reeds, 13% bamboo and 11% others.

Several studies examined the viability of substituting wood based materials with crops residues from annual plants; such as rye straw (Usta, 1985), cereal straw (Wong, 1995), wheat straw (Moore, 1996), okra stalks (Atik, 2002) and licorice (Copur et al., 2007) to produce pulp and paper. Moreover, bagasse and straw are best at contributing excellent formation to papers and can replace hardwood chemical pulps for printing and writing paper (Sridach, 2010b). Agricultural residues have higher cellulose and lower lignin content than annual plants and non-wood crops. These contents generally provide the higher mechanical properties of hand sheet. The chemical and physical properties of non-wood fibers also affect their mechanical properties.

2.3. Properties of non-wood fiber

Non-woods have large differences in their physical and chemical characteristics, and they all contain to varying degrees a wide variety of fiber and cell types. Monocots such as cereal straws, sugarcane bagasse and corn stalks are more similar to hardwoods as the fiber fraction is in the same order; but, they are much more heterogeneous and contain a large proportion of very thin-walled cells, barrel-shaped parenchymous cells, and vessel and fine epidermal cells in a wide range of dimensions (Insaf Galal Eldin Karar, 2004).

2.3.1. Morphological properties of non-wood fiber

Fiber morphology is important in deciding the techno-commercial suitability as well as the method of pulping. Fibers are elements with the length varying between 100 and 10000µm and width between 5 and 75µm (Ana moral *et al*., 2009). The rigidity and mechanical resistance of the fiber will vary according to the process it undergoes.

Morphological characteristics, such as fiber length and width, are important in estimating pulp quality of fibers (Wood 1981). The Average fiber length ranges from 1 mm to 30 mm, being shortest in grasses and longest in cotton. The ratio of fiber length to fiber diameter determines the suitability of fibers for paper application. Larger ratios will give pulps with higher mechanical properties, such as strength and toughness (B. Lauke and S. Fu., 1999). In fibers suitable for paper production, the ratio fiber length to width is about 100:1 (Hurter, 1988; Hunssigi, 1989; McDougall *et. al*., 1993). The average ratios of fiber length to diameter range from 50:1 to 150:1 in non-wood species (Hurter 1988). Fiber length and width of non-woody species vary depending on plant and the plant part from which the fiber is derived (Iivessa and Pfaffli, 1995).

Lumen size and cell wall thickness affect the rigidity and strength of the papers (Hurter, 1988; Fengel and Wegener, 1989; McDougall *et al.*, 1993). Fibers with large lumen and thin walls tend to flatten to ribbons during paper making with enhanced inter-finer bonding between fibers and consequently having good strength characteristics. The smaller fiber lumen width results the poorer pulp beating because of liquids cannot penetrate into empty spaces of the fibers. The larger the fiber lumen width, the better will be the beating of pulp, because of penetration of liquid into empty space between the fibers. Thin walled cells on the other hand, collapse readily to form dense, well-boded paper, low in tear but high in other strength properties.

Flexibility coefficient influences tensile strength and to some extent the burst strength while the relative fiber length influences tearing resistance (Siddique and Chowdhury, 1982). The Runkel ratio (cell wall thickness to lumen diameter) gives an indication of suitability of fibers for paper making (Runkel 1949). Fiber length is an exceedingly important index of fiber quality, but it is subordinate to the wetting or fibrillating qualities, since adequate sheet strength can be obtained only by means of a high degree of fiber-to-fiber bonding, which prevents the fibers from slipping past one another (Casey, 1967).

Generally, the successful conversion of pulp into a marketable product depends on the original fiber characteristics and the response of the fiber to the processing variables. Thus, analysis of fiber characteristics such as fiber length, fiber diameter, lumen width, cell-wall thickness and their derived morphological factors like Runkle ratio, flexibility coefficient, slenderness ratio, coefficient of rigidity and wall coverage ratio became important in estimating pulp quality of fiber (Oluwafemi and Sotannde, 2007).

Table 2.1 Physical properties of some non-woods used for Papermaking

Properties	Unit	Rice straw	Wheat straw	Bagasse	Reed grass	Bamboo	Jute	Hemp (bast)	Kenaf (bast)
Avg. fiber length	mm	1.41	1.48	1.7	1.5	1.36-4.03	2.5	20	2.74
Avg. fiber width	mm	8	13	20	20	8-30	18	22	20
L/D		175:1	110:1	85:1	75:1	135-175:1	139:1	1000:1	135:1

Source, (Chen *et al.*, 1987; Hurter, 1988; Rodríguez *et al.*, 2008).

Short fiber length (< 2 mm), high content of fines and low bulk density are the most important physical features of non-wood raw materials (Oinonen and Koskivirta, 1999; Paavilainen, 2000). The large amount of fines and the short fiber length especially affect the drainage properties of pulp. Apart from the operation of the pulp mill itself, these properties also affect dewatering in the paper machine. Due to the wide range of different non-wood species and their different physical properties, substantial differences in dewatering behavior may arise (Cheng and Paulapuro, 1996a, b). The low bulk density affects the logistics of non-wood raw materials. This would make the amount of cellulose handled comparable to wood.

2.3.2. Chemical composition of non-wood fiber

Wood and other lingo-cellulosic are three-dimensional, naturally occurring, polymeric composites which primarily made up of cellulose, hemicelluloses, lignin and small amounts of extractives and ash. Most agricultural lignocellulose biomass is composed of 10-25% lignin, 20-30% hemicellulose and 40-50% cellulose (Kumar et al., 2009). The cellulose content of a plant depends on the cell wall of plant species (Hartley, 1987; Hurter, 1988), the varieties of the plants (Khan *et al.,* 1977), the age of the plants (Gill *et al*., 1989; Grabber *et al.,* 1991) and plants part (Grabber *et al*., 1991, Theander 1991). The amount and composition of cell wall components differ among plant species and even among plant parts and they affect the pulping properties of the plant material (McDougall *et al.,* 1993).

Annual plants generally have about the same cellulose content as woody species (wood, 1981), but higher content of hemicellulose exists. Non-wood fibers are high in ash content, low in lignin, and rich in pentosans compared to coniferous wood. Silica (a major portion of the ash content) is present to the extent of 12 to 18% in rice straw, 6 to 7% in esparto, 4 to 6% in wheat straw, 4 to 5% in reeds, 2 to 3% in bamboo, 1.5 to 2% in well- depithed bagasse, and 2 to 2.5% in upgraded bast and leafy fibers. A high portion of the silica is dissolved in alkaline pulping and appears in the spent liquor; where it creates sever operating problems at various stages of the recovery operation (Rydholm, 1965).

Some of the non-woody fiber plants contain more pentosans (over 20%), holocellulose (over 70%) and less lignin content (about 15%) as compared with hardwoods (Hunsigi 1989). They have also high hot water solubility, which is apparent from the easy accessibility of cooking liquors. The low lignin content in grasses and annuals reduces the requirement of chemicals for cooking and bleaching (Hunsigi, 1989). Except for the fibrous material, plants also contain mineral compounds, while the inorganic compounds are essential for plant growth (Mitscherlich, 1954; Epstein, 1965; Marschner, 1995); they are undesirable in pulping and papermaking (Keitaanniemi andVirkola 1982; Keitaanniemi and Virkola, 1978; Jeyasingam, 1985).

Cellulose: - is the β-1, 4-polyacetal of cellobiose (4-O-β-D-glucopyranosyl-D-glucose). Approximately 65 percent of the cellulose is highly oriented, crystalline, and not accessible to water or other solvents. The remaining cellulose, composed of less oriented chains, is only partially accessible to water and other solvents as a result of its association with hemicellulose and lignin. None of the cellulose is in direct contact with the lignin in the cell wall (Rowell, 1992). Cellulose is the principal component in the cell wall and in the fibers. The non-cellulose components of the cell wall include hemicelluloses, pectins, lignin and proteins (Hartly, 1987; Taiz and Zeiger, 1991).

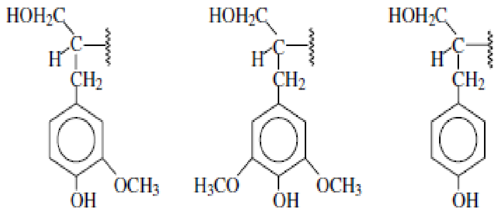
Many properties of cellulose depend on its degree of polymerization (DP), i.e. the number of glucose units that make up one polymer molecule. The nature of bond between the glucose molecules (β-1, 4 glucosidic) allows the polymer to be arranged in long straight chains. The latter arrangement of the molecule, together with the fact that the hydroxides are evenly distributed on both sides of the monomers, allows for the formation of hydrogen bonds between the molecules of cellulose. The hydrogen bonds in turn result in the formation of a compound that is comprised of several parallel chains attached to each other (Faulon *et al.*, 1994).

Cellulose is insoluble in water, where it swells. It is also insoluble in dilute acid solutions at low temperature. At higher temperatures it becomes soluble, as the energy provided is enough to break the hydrogen bonds that hold the crystalline structure of the molecule. It is also soluble in concentrated acids, but severe degradation of the polymer by hydrolysis is caused. In alkaline solutions extensive swelling of cellulose takes place as well as dissolution of the low molecular weight fractions of the polymer (DP < 200) (Krassig and Schurz, 2002). Additionally, aqueous salt solutions, such as zinc chloride, dissolve limited amounts of cellulose (Kirk Otmer, 2001). Cellulose does not melt with temperature, but its decomposition starts at 180^{o}C (Thermo-wood handbook, 2003).

Like all carbohydrates, the cellulose molecule is capable of reactions at its functional groups. The hydroxyl groups react with addition, substitution and oxidation agents and the acetal groups undergo hydrolysis in both acid and alkaline media. The aldehydic end groups can be reduced to alcoholic groups, oxidized to carboxyl groups or rearranged under the influence of alkali to form either alcohol or carboxyl end groups (Rydholm, 1965).

Hemicellulose: - is a collective term that represents a family of polysaccharides such as arabino-xylans, gluco-mannans, galactans, and others that are found in the plant cell wall and have different composition and structure depending on their source and the extraction method. Important aspects of the structure and composition of hemicellulose are the lack of crystalline structure (much lower degree of polymerization than cellulose), mainly due to the highly branched structure, and the presence of acetyl groups connected to the polymer chain. The specific constitution of the hemicellulose polymer depends on the particular plant species and on the tissue. Glucose, xylose and mannose often predominate in the structure of the hemicellulose (Philip 1992). Hemicellulose is insoluble in water at low temperature. However, its hydrolysis starts at a temperature lower than that of cellulose, which renders it soluble at elevated temperatures (Thermo-wood handbook, 2003).

Lignin: - is the most complex natural polymer. It is an amorphous three-dimensional polymer with phenyl propane units as the predominant building blocks. It behaves as an insoluble three-dimensional network. It acts as binder between cells creating a composite material that has a remarkable resistance to impact, compression and bending. Solvents that have been identified to significantly dissolve lignin include low molecular alcohols, dioxane, acetone, pyridine, and dimethyl sulfoxide. Furthermore, it has been observed that at elevated temperatures, thermal softening of lignin takes place, which allows depolymeristation reactions of acidic or alkaline nature to accelerate (O’Connor *et al.*, 2007). Great variation in lignin structure and amount exists also among cell types of different age within a single plant (Albrecht *et al.*, 1987; Buxton and Russel ,1988; Jung, 1989), and even between different parts of the wall of a single cell (whetten *et al.*, 1998). Gymnosperm lignin contains guaiacyl units, which are polymerized from coniferyl alcohol, and a small proportion of phydroxyphenyl units (H-units) formed from p-coumaryl alcohol. Angiosperm lignin are formed from both syringyl units (S-units), polymerized from sinapyl alcohol, and G-units with a small pro- portion of H-units (Sarkanen and Hergert, 1971; whetten *et al.*; 1998). Syringyl lignin increases in proportion relative to guaiacyl and phydroxyphenyl lignins during maturation of some grasses (Carpita, 1996).



Guaiacyl (G) Syringyl (S) P-hydroxyphenyl propane (P-H)

Figure 2.1: Schematic representation of the structural units of lignin (A. Tejado et al., 2007)

In grass species, the total lignin content varies from 15 to 26% (Higuchi *et al.*, 1967) and predominantly formed from coniferyl and sinapyl alcohol (Buxton and Russel, 1988).

Lignins are considered to contribute to the compressive strength of plant tissue and water impermeability of the cell wall. It also aids cells in resistance to microbial attack (Taiz and Zeiger, 1991; Whetten *et al.*, 1998), but they do not influence the tensile properties of the cell wall (Grisebach, 1981). The lignin may be separated from an associated wood component either by preferentially dissolving lignin or by preferentially dissolving non-lignin components.

Isolated lignins, in general, are amorphous and non-crystalline. Isolation procedure of lignin may be divided into procedures which depend upon the removal of cellulose and the other constituents of wood by chemical treatment leaving the lignin as insoluble residue, or procedures which selectively dissolve the lignin away from cellulose and other substances with which it is associated. Reactions of lignin include sulphonation, hydrolysis, alcoholysis and oxidation. Other reactions include nitration, gelation of lignosulphonates, reactions with diazo compounds, as well as methylation and degradation under pressure (Pearl, 1967).

Extractives and ash: - The extractive materials are primarily composed of cyclic hydrocarbons. These vary in structure depending on the source and play a major role in natural decay and insect resistance and combustion properties of lignocellulosic. The inorganic portion (ash content) of lignocellulosic can vary from a few percent to over 15 percent, depending on the source.

The significance of extractives to pulp and paper industry can be:-

- Reducing penetrability of pulping liquor; lignin solubility and some cause liquor decomposition,
- Accelerating digesters corrosion, i. e polyphenols and organic acids,
- Affecting pulp properties,

Difficulties associated with the high extractives content of wood have been encountered in the digesters and in the spent liquor heat and chemical recovery sections (Hillis, 1962).

Table 2.2 Composition of various lignocellulosic materials

Lignocellulosic Material	Lignin (%)	Hemicellulose (%)	Cellulose (%)	Reference
Sugarcane bagasse	20	25	42	Kim & Day, 2011
Sweet sorghum	21	27	45	Kim & Day, 2011
Hard wood	18-25	24-40	40-55	Malherbe & Cloete, 2002
Soft wood	25-35	25-35	45-50	Malherbe & Cloete, 2002
Wheat straw	16-21	26-32	29-35	McKindry, 2002
Barley Straw	22	38	46	Plazonic *et al.*, 2016
Teff straw	9.4±3.2	32.4±0.5	36.7±3.2	Akiber Chufo *et al.*, 2015
Rice straw	18	24	32	Prassad *et al.*, 2007
Corn cobs	15	35	45	Prassad *et al.*, 2007
Corn Stover	19	26	38	Zhu *et al.*, 2005

The chemical compositions of non-wood materials have tremendous variations in chemical and physical properties compared to wood fibers (Gümuüşkaya and Usta, 2002; Rezayati-Charani e*t al.*, 2006). They vary, depending on the non-wood species and the local conditions, such as soil and climate (Bicho *et al.*, 1999; Jacobs *et al.*, 1999). The non-wood materials generally have higher silicon, nutrient and hemicellulose contents than wood (Hurter, 1988).

2.3.3. Composition and morphology of straw

Similar to wood, straw is considered a natural composite material because of its composition of polysaccharides (cellulose and hemicelluloses) and lignin. The former two components are hydrophilic while the lateral is hydrophobic. However, they are practically insoluble in water due to hydrogen bonding and covalent bonding with lignin (Xiao B. *et al.*, 2001). Different fractions across the straw vary in chemical composition which is also affected by soil type and fertilizer treatment. Overall, there is a higher concentration of cellulose in internode; ash in leaf and leaf base; and lignin in the node cored compared to the other parts of straw (Harper S and Lynch J., 1981, Theander O., 1985). The high silica content introduces some problems in straw pulping, such as difficulties in utilizing straw for rayon pulps and regeneration of kraft pulping chemicals (Rydholm 1965).

The anatomical structure of straw, normally the sclerenchyma cells in the bundle itself have a small diameter and a thick fiber wall while the extra vascular fiber often have a much larger diameter and a very variable wall thickness.

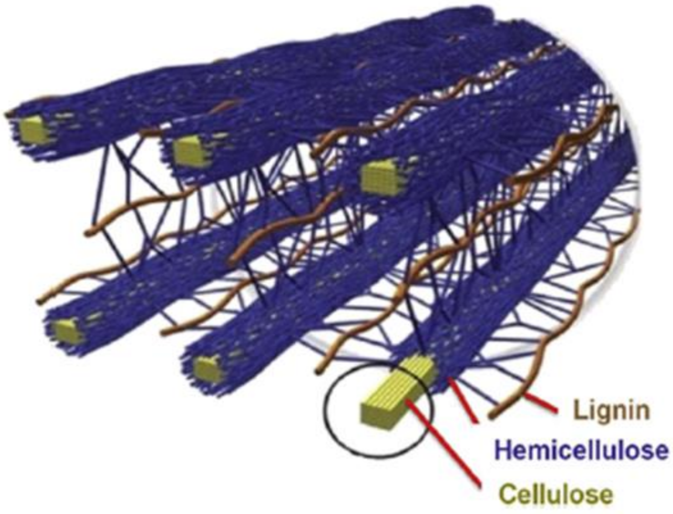


Figure 2.2: Cellulose strands surrounded by hemicellulose and lignin (Doherty W., *et al.*, 2011)

2.4. Non-wood Pulping

Traditionally, non-wood material is cooked with hybrid chemi-mechanical and alkali-based chemicals (Goyal *et al.*, 1992; Jahan *et al.*, 2007). Hybrid chemi-mechanical pulps, which were once thought of as a logical replacement for chemical pulps, simply do not provide the purity necessary for high grade and dissolving pulps. Chemi-mechanical pulps cannot be used in grades that do not allow fiber-containing furnishes due to brightness reversion, brightness levels, or simply customer insistence.

The production of pulp from non-wood resources has many advantages such as easy pulping capability, excellent fibers for the special types of paper and high-quality bleached pulp. They can be used as an effective substitute for the forever decreasing forest wood resources (El-Sakhawy *et al.*, 1995; 1996; Jiménez *et al.*, 2007). These allow the production of high-quality bleached pulp by a less polluting process than hardwood pulps (Johnson, 1999) and the reduced energy requirements (Rezayati-Charani *et al.*, 2006). However, some mineral substances in their composition, including K, Ca, Mn, Cu, Pb, and Fe, may have negative effects on the different steps of pulp and paper manufacturing, especially the bleaching process. Metals may interfere during the bleaching with hydrogen peroxide or ozone. The transition elements form radicals that react unselectively with the pulp when the pulp is bleached without chlorine chemicals (Gierer, 1997). Furthermore, bleaching is accompanied by the formation of oxalic acid. Calcium reacts with oxalic acid to form calcium oxalate, which deposits easily. Thus, effluent-free bleaching will obviously be difficult to achieve in the bleaching plant (Dexter and Wang, 1998). Non-wood pulping processes generate large volumes of black liquor as by-products and wastes. Black liquor wastewater is a mixture of organic and inorganic materials, with very high amounts of total dissolved solids (TDS). The total dissolved solids in the black liquor are composed of lignin derivatives, low molecular weight organics, and the rest being made up of chemicals from the digesting liquor (Huang *et al*., 2007). In delignification, the relatively high amount of silicon present in non-wood material is dissolved together with lignin into cooking liquor; this has led to difficulties in the recovery of cooking chemicals.

This situation makes black liquor one of the most difficult materials to handle in wastewater treatment processes. Generally, alkaline non-wood pulps contain much hemicellulose while their fibers are short. This impairs the dewatering properties in different unit processes, the adhesive forces in the paper machine, and paper quality. Then the hemicellulose content of the pulp should be controlled to avoid these problems. However, when using the alkaline pulping processes, the hemicellulose content of the pulp cannot be easily controlled without losses in pulp quality (Rousu *et al*., 2002).

2.5. Reviews on Teff Production and Distribution

Teff is thought to have originated in Ethiopia, where it started to be used as a food grain between 4000 and 1000 BC. It is mainly cultivated in its native range (Ethiopia and the highlands of Eritrea) and in neighboring northern Kenya. It has been introduced into South Africa, the USA, Canada, Australia, the Netherlands and Yemen for small-scale production of gluten-free grain (Tefera *et al*., 2006). In Ethiopia, teff grows where annual rainfall ranges between 950-1500 mm with a growing season rainfall of about 450-550 mm. Teff is mainly grown on sandy loams, but it can grow on black, heavy clay soils (black cotton soils) provided they are well drained and have sufficient nitrogen fertility; but, neutral or slightly acidic soils are preferred. It can also grow in places prone to drought after short rains (Tefera *et al*., 2006). It is a leafy species; selfpollinated, chasmogamous cereal annual plant. It has a fibrous roots mostly erect stem; although some cultivars are bending or elbowing types. The sheaths of the teff are smooth, glabrous, linear; 25-45 cm long x 0.1-0.5 cm wide, open and distinctly shorter than internodes. Its ligule is very shorter and ciliated while its lamina is slender, narrow and nearly linear with elongated acute tips. It has panicle type of inflorescence showing different forms- from loose to compact; the latter appearing like a spike. Its spikelet's have 2-12 florets. Each floret has a lemma, plea, three stamens and an ovary mostly two in exceptional cases three, feathery stigmas. The caryopsis is 0.9-1.7 mm in length and 0.7-1 mm in diameter; which is very small and its colour varies from white to darky brown (Tadesse, 1975).

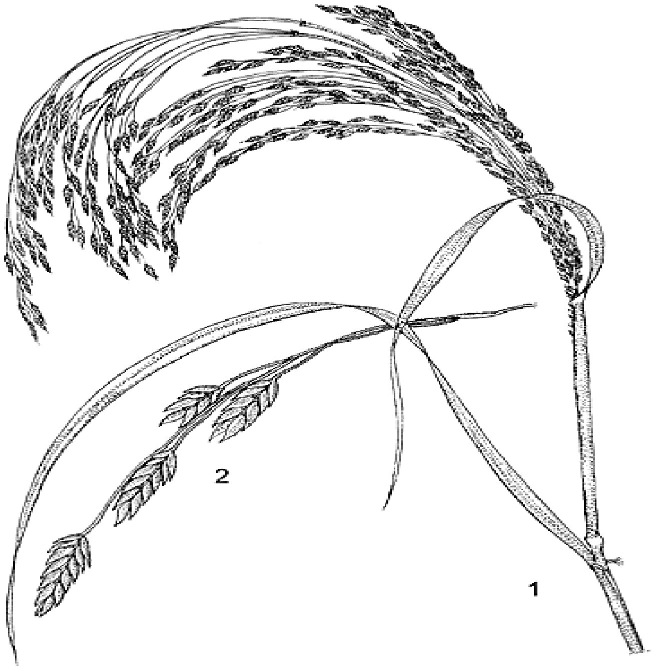


Figure 2.3: Eragrostis tef (Zuccagni) Trotter; 1, upper part of flowering culm; 2, part of inflorescence with spikelets (Protabase Record, 2014).

Teff leads all the grains by a wide margin in its calcium content, and also an excellent source of vitamin C, a nutrient not commonly found in grains. Currently teff is introduced in some part of the world and is getting good acceptance as high fiber content and gluten free grain.

In Ethiopia, it occupies about 28% of the total crop area allocated to cereals (Anonymous, 2010a), delivering about 20% of the total cereal grain production and 17% of cereal crop residues production annually (Anonymous, 2010b; FAO, 1987).

Table 2.3: Estimated land area (ha) of cereal crop production, from the year 2015 to 2018.

Cereal Crop	Land area in hectares	
	2015/16	2017/18
Teff	3,017,914.36	3,023,283.5
Wheat	1,696,082.59	1,696,907.05
Barley	959,273.36	951,993.15
Maize	2,135,571.85	2,128,948.91
Oats	24,040.94	24,040.94
Rice	24,040.94	25,896.22

Source; Central Statistical Agency (CSA)

Teff accounts for the largest share of cereal crops under cultivation in Ethiopia. Worldwide distribution of the crop was for its use as a food grain and animal forage (Davison, 2010). Moreover, teff straw from threshed grains is considered to be animals' forage and superior to straws from other cereal species in Ethiopia. It is also utilized to reinforce the mud used for covering the wooden materials, during construction of houses, mainly in the countryside. In the year 2017/18, teff was grown on about 3,023,283.5 hectares of crop area of Ethiopia. Taking the straw yield of 5000 kg/ha (5ton/ha) (FAO, 1980), the annual teff straw yield can be estimated to be about 15.12 million tones/year.

2.4: The annual dry matter of teff straw and some plant species

Plant species	DM yield (ton/ha)	Pulp yield (ton/ha)	Reference
Wheat straw	2.5	a)1.1	FAO, 1995; Pahkala et al., 1994
Barley straw	2.1	a)1.9	FAO, 1995; Pahkala et al., 1994
Teff straw	5	na	FAO, 1980
Oat straw	1.6	a)0.7	FAO, 1995; Pahkala et al., 1994
Rice straw	3	b)1.2	Paavilainen & Torgilsson, 1994
Bagasse	9	b)4.2	Paavilainen & Torgilsson, 1994
Bamboo	4	b)1.6	Paavilainen & Torgilsson, 1994
Eucalyptus	15	b)7.4	Paavilainen & Torgilsson, 1994

a: soda-anthraquinone pulping process; b: pulping method unmentioned; na: not avialable

2.5.1. Traditional uses of Teff straw and its Chemical Composition

Currently, teff straw has no commercial value in Ethiopia except its traditional uses as animals' forage, mud mix for house making mainly in rural area and open air burning for release of nutrients for the next cultivation which could cause air pollution.

Like other poor quality roughages, teff straw is deficient in nitrogen, sulphur, phosphorous and readily available carbohydrate. Low rumen ammonia concentration, as a result of low crude protein contents, observed when roughages are fed to ruminants is probably the first constraint to the productivity of much of Africa's ruminant population (Preston, 1986). Consequently, teff straw is neither digested fast nor to an appreciable extent that could allow adequate intake of nutrients to maintain body weight. Tough texture, poor digestibility and nutrient deficiency all contribute to the low level of consumption (El-Naga, 1989).

According to Andualem T. *et al.* (2015) crude protein (CP) of teff straw was 4.26% on dry matter basis. This result is lower than the range of FAO's (1984) recommendation, that the threshold value of feedstuffs for crude protein is between 7% and 8%, which is adequate for maintenance of livestock and it should be above the minimum requirement for optimum rumen function (7.5%) suggested by Van Soest (1982).

Table 2.5: Dry matter chemical composition of teff straw

Content	Dry matter	Ash	Crude Protein	NDF	ADF	ADL	IVDMD
Chem. composition % (Dry matter)	92	7.89	4.26	71.10	46.25	5.24	50.68

Journal home page: http://www.starjournal.org/

Where, NDF: Neutral detergent fiber

ADF: Acid detergent fiber

ADL: Acid detergent lignin

IVDMD: In vitro dry matter digestibility

Roughage feeds with NDF content of less than 45% are categorized as high quality, 45-65% as medium quality and those with more than 65% as low quality roughages (Singh and Oosting, 1992). Therefore, teff straw is categorized as low quality roughages that may inflict limitations on animal performance. The higher NDF content could be a limiting factor on feed intake, since voluntary feed intake and NDF content are negatively correlated (Ensminger *et al*., 1990).

ADF is widely used for measuring the fiber in feeds, often substituting for crude fiber, which is used in the proximate analysis of feeds. The acid soluble fraction included primarily hemicelluloses and cell wall proteins, while the residue recovers cellulose and the list digestible non-carbohydrate fractions. Acid detergent has the advantage of removing substances that interfere with the estimation of refractory components so that ADF residue is useful for the sequential estimation of lignin, cut in, cellulose, indigestible Nitrogen and Silica (Van Soest, 1982). High ADF content in crop residues might be associated with lower digestibility since digestibility of feed and its ADF are negatively correlated (McDonald *et al*., 2002). Generally, Kellems and Church (1998) categorized roughages with less than 40% ADF as high quality and above 40% as low quality.

Lignin is completely indigestible and forms lignin-cellulose/hemicelluloses complexes (Kellems and Church, 1998) due to physical encrustation of the plant fiber and making it unavailable to microbial enzymes (McDonald *et al*., 1995). However, the ADL content of teff straw was lower than the maximum level of 7% that limits DM intake and livestock production (Reed *et al*., 1986); but still it prevents fast digestion.

The mean *in vitro* digestible dry matter in the dry matter (IVDMD) for crop residues should be higher in order to be considered as quality roughage for the ruminants. Due to long lag times and slow fermentation, straws and stovers limit intake and utilization (Van Soest, 1982).

2.5.2. Previous studies on Teff Straw

Several studies have been reported in literature which used teff straw as raw material: adsorbent for textile metal ions/teff straw char for Cr(VI) removal (Mulu, 2013), an adsorbent for the chromium removal (Bizuayehu *et al*., 2014), bio-methane production (Chufo *et al*., 2015), wastewater treatment (Wassie and Srivastava 2016a, 2016b), preparation and characterisation of nano-silica (Bageru nd Srivastava, 2017), and epoxy-based composites reinforced material for lightweight applications (GL D. and Shishir S., 2018).

Chufo *et al*., 2015, reported teff straw degradation up on treatment with different sodium hydroxide concentrations; more specifically, as NaOH concentration used in the pretreatment stage increases from 1% to 6%, lignin degradation was significantly increased from 6.4% to

27.7%. The loss in hemicellulose was also following similar trend like lignin with increased NaOH concentrations. However, the highest percentage for cellulose removal was 15.0% in all NaOH concentrations. As a result, lignin network destruction from its complex structures and swelling of carbohydrate fibers could occur due to both physical and chemical interactions between the biomass and alkali in the pretreatment process. Before the pretreatment of teff straw by NaOH, lignin, cellulose and hemicellulose, accounting nearly 78.5% in dry matter of 91.6 ± 0.4% the total solids (TS).

Chufo *et al*. (2015) also reported the composition of teff straw as cellulose was 36.7 ± 3.2%; hemicellulose, 32.4 ± 0.5% and lignin, 9.4 ± 3.2% respectively. Additionally, morphological structure of untreated and NaOH-treated teff straw was done by SEM image analysis and showed the external scanned surfaces of the untreated teff straw was not broken into pieced surface and all hemicelluloses and the fibers of carbohydrate were not visible, being shielded by lignin in a possible structure. Comparison results between the two structures have indicated that NaOH pretreated teff straw has more porous surface and has evidenced the exposed fibers than untreated teff straw; which elucidated that the NaOH pretreatment could result in the destruction of some lignin structures from teff straw.

Comparison of raw teff straw SEM image with that of NaOH-soaked teff straw was made and image analysis showed clear difference in the surface morphology; NaOH-treated teff straw structure failure, cellulose dominant biomass was seen and, removal of lignin and hemicelluloses with cellulose swelling from sodium hydroxide treatment (Wassie and Srivastava 2016). They also identified that SEM image of teff straw has cracks on its surface and that it is porous in nature. This crack and porosity comes from oven heating effect after washing. EDX analysis was done to determine elemental composition of the straw and it was found to possess 49% carbon, 45% oxygen and rest minor percentage of calcium, magnesium and iron. The internal structure and structure heterogeneity of teff straw was also observed in terms of pore size distribution; and hence, pore diameter showed mesoporous nature of the teff straw.

Generally, NaOH pretreatment resulted in the partial hydrolysis of functional groups like ester, decomposition of aliphatic side chains from the structure of lignin such as methyl and methylene groups, and carbonyl functional groups. The value of these changes in structural composition of lignin gives an opportunity to expose physically hindered substrates such as cellulose and hemicellulose for different purposes (Zheng *et al*., 2009).

2.6. Production and Consumption of Pulp and Paper in Ethiopia

The demand for pulp and paper in general is increasing progressively with the growth of population, urbanization, education and expansion of other social and economic activities. Ethiopia does not produce its own pulp, but only paper. The paper producing factory in Ethiopia, which is located in Wonji uses imported pulp and waste paper as its raw material. The mills produce some 12,500 metric tons per annum of different qualities of finished paper and 10,250 metric tons of corrugated paper. However, the paper demand of the country cannot be satisfied by domestic production only. Therefore, Ethiopia imports not only pulp but also finished papers and corrugated papers too. According to Ethiopian central statistical authority, pulp wood used by the mill is imported at an annual cost of about 200 million Birr, and about 2.2 billon Birr is needed to import finished paper products per year.

Currently, paper & paper products including printing, writing, duplicating, packaging and for other industrial and economical use is supplied both from local production and imports. Ethiopian Pulp and Paper Share Company (EPPSC) and Anmol Products Ethiopia Private Limited Company are producers of paper for writing, printing and other purposes in the country. However, there are a number of medium and small scale industries that are engaged in paper converting. They produce a wide range of papers and paper products either by taking the paper from the local paper manufacturers or by directly importing from abroad.

Yekatit Pulp and Paper Factory and China CEC Corp. has agreed to construct the largest paper mill in Ethiopia which will start operation by mid-2019 and produce (annually) 70,000 tons of paper for packaging purposes and 15,000 tons of tissue paper pulp the production of toilet papers, table napkins and kitchen towels. The current demand of Ethiopia for paper products will rise from the 200,000 tons per year to 400,000 tons per year within the next five years. To this end, Ethiopia will pump an equivalent of 2.6 billion ETB or 130 million USD into this industry (www.miac.info).

2.7. Pulping/De-lignification Processes Classification

Pulping is a process where the wood chips or other fibrous raw materials are ruptured mechanically, thermally, chemically or combinations of these treatments into a fibrous mass which known is as pulp. Several types of pretreatment including physical (milling and grinding); chemical (acid, alkaline, oxidizing agent and organic solvent treatment); and combination of physical and chemical techniques (steam pretreatment or auto hydrolysis, hydro-thermolysis and wet oxidation) can be used for this purpose. Chemical pretreatment is one of the more efficient and cost-effective methods (Limayem and Ricke, 2012; Agbor *et al*., 2011; Mosier *et al*., 2005). Acid hydrolysis, alkaline hydrolysis, use of oxidation agent, organosolv method and ionic liquids can be used for chemical treatment depending upon the end-use. Acid pretreatment solubilizes hemicellulose and cellulose via hydrolysis reaction. Lignin is not hydrolyzed by acid, but it can be made soluble by alkali treatment, while organosolv treatment mainly focuses on solubilization of carbohydrates, and ionic liquid can dissolve both carbohydrates and lignin.

In general, all the major pulping processes are based on the reactions between nucleophiles and lignin structures, which results in lignin fragmentation by cleaving linkages between lignin units and by increasing lignin hydrophilicity (Sixta; Potthast *et al*., 2005). Sulphite ion (SO_3^{2-}), hydrogen sulphide ion (HS^-), hydroxyl ion (OH^-), and the reduced form of anthraquinone, anthrahydroquinone, are all strong nucleophiles that are able to degrade lignin (Sixta, Potthast *et al.,* 2005; Dahlblom, Olm *et al*., 1989).The aim of delignification is to remove lignin with the least amount of degradation and depolymerisation of carbohydrates, mainly cellulose and hemicelluloses (Sjöström, 1981). The damage of carbohydrates cannot be totally avoided but the nature and the extent of the reactions can be affected by cooking, pH and temperature (Ingruper, Kocurek *et al*., 1985). In strong alkaline conditions carbohydrates are degraded to monomeric hydroxyl carboxylic acids through mechanism known as a peeling reaction and by the cleavage of glycosidic bonds. In acidic conditions the hydrolysis of glycosidic bonds is the most important reaction cutting carbohydrate chains (Sjöström, 1981).

2.7.1. Mechanical Pulping

Mechanical pulping is a process of shredding and de-fibring the wood chips or fibrous raw materials into shorter and stronger fiber (Smook, 1992; Casey, 1980). It is the least environmental hazardous process and has the advantages of producing a very high pulp yield compared to other processes, causes lower level of water pollution and less consumption (45, 000 - 68, 000 liters/ ton) compared to chemical pulping (159,000 - 204, 000 liters/ ton). In other words, low level water usage means less effluent discharge that contains degraded lignin, organic compounds and inorganic compounds but indeed effluent from mechanical pulping contains very little of these substances. However, mechanical pulping has the disadvantages of being a major user of electrical energy and producing generally lower grade pulp (Stanley, 1996).

Pulp is made either by pressing the wood against a revolving grinding stone or by passing chips through a mill, while water is sprayed. Many methods are used in mechanical pulping, the initial process is called ground wood process, where the sample is inserted and pressed lengthwise against a rugged rotating grinding stone. This process has a high yield, around 95% (which is greater than that produced by chemical pulping because both lignin and cellulose fibers remain intact), but the resulting paper has lower strength properties, high color reversion, and low brightness. It gives nearly quantitative yield but causes rupture to the fiber walls and gives pulp which contains substances of little value for many purposes (Rydholm, 1965).

2.7.2. Chemical pulping

Chemical pulping is a process where the wood chips or fibrous raw materials are cooked in an aqueous solution at elevated temperatures and pressure with appropriate chemicals. It is chemically separating the fibrous fiber into pulps by degrading about 90% of the lignin from the materials and retaining most of the cellulose and hemicelluloses while the pulp yield is around 50%. Chemical pulping is more expensive than mechanical pulping but it has better strength and brightness properties. In this process, extracted fibers are washed, filtered and sent to the paper making process. The filtrate, separated out in the cooking process, is called black liquor which is further processed in a recovery boiler for recovering inorganic chemicals and organics in the form of heat energy. The chemical pulping methods can be classified into two major principles namely; alkaline such as kraft process and soda process, and acidic such as sulfite and bisulfite.

Kraft or sulfate pulping: - Kraft process is commonly utilized pulping method in the pulp and paper industry. The main reasons for the application of kraft pulping compared to other processes, are the excellent pulp strength properties, low demand of wood or wood quality, well established recovery of cooking chemicals, energy, and by-products, and short cooking time; but, with disadvantage of odoriferous pollution through of sulfur compounds generation. In this process, wood chips are cooked with sufficient chemicals in an aqueous solution at adequate temperature and pressure in order to remove and dissolve away the lignin component and maintain most of the celluloses and hemicelluloses. The kraft process is a modification of the soda process which utilizes sodium hydroxide with the addition of sodium sulfate (Na_2SO_4) into the cooking liquor system (Sjostrom, 1993; Smook, 1992). It is always associated with severe environment pollution especially the air pollution. The air pollution from the kraft pulping is a major concern with the emission of sulphur gases into the atmosphere with a rate of 0.3-3 kilograms per metric ton of air-dried pulp (ADP) (World Bank Group, 1998). The four reduced sulphur gases are hydrogen sulfide, methyl mercaptan, dimethyl sulfide and dimethyl disulfide. The obnoxious odour of the gases even released from the advanced kraft mills. All the gases have extremely low odor thresholds, which indicated that long term exposure to these gases, the balance of ecosystem and even human health will be seriously interfered (Smook, 1992; Casey, 1980; Biermann, 1996). Both kraft and sulfite pulping processes emit the gas of sulfur oxides (SO_2) but the amount of emission from kraft pulping is not as much as sulfite pulping. More sulfur oxides are generated from sulfite mills at about 5 kg of SO_2/ ton than 1-3 kg SO_2/ tonne from kraft mills (Smook, 1992; Stanley, 1996). Other pollutants include such as particulate matter, nitrogen oxides and volatile organic compounds (VOCs) from the black liquor oxidation process (World Bank Group, 1998).

Sulphite pulping process: - Sulfite pulping is a solubilization of lignin which has removed from cellulose as salts of lignosulfonic acid using mixtures of sulfurous acid (H_2SO_3) while bisulfite pulping using bisulfite ion (HSO_3) (Casey, 1980; Smook, 1992). Besides, sulfite pulping also can be carried in neutral and alkali medium and known as neutral sulfite process and alkaline sulfite process (Smook, 1992).

Sulfite pulping is generally used only for special purposes given that the yield of sulfite pulp is much lower than that of Kraft pulp. In this process, a solution of sulfurous acid (H_2SO_3) and calcium bisulfite $Ca(HSO_3)_2$ is used to cook wood chips in order to dissolve lignin. The resulting pulp is usually moderately strong, soft, and flexible. The active sulfur containing species in the sulfite process are sulfur dioxide (SO_2), hydrogen sulfite ions (HSO^-_3), and sulfite ions (SO_3^-) in proportions depending on the actual pH of the cooking liquor.

Soda pulping process: - It is an alternative method for producing sulfur-free pulp. By using a high alkali charge associated with high temperature, the soda pulp viscosity is damaged, thereby the quality and paper strength as well. Therefore, pulping additives are added as an option for improving these parameters. Soda pulping does not involve the use of sulfur compounds to facilitate delignification, thus the emission of total reduced sulphur (TRS) related odour problem associated with kraft pulping does not occur. In other words, soda mills do not have to install the extensive TRS control system which is generally required by kraft mills to reduce the TRS emission (Green et al., 1992).

2.8. Soda-Anthraquinone Pulping

Kraft is the dominant pulp making process in the world. However, the sulfur compounds formed during the craft process can cause odor problems already at extremely low concentrations (Martinez *et al.*, 1970; Bordado and Gomes, 2002, 2003). Alternative pulping processes mainly compromise sulfur free alkaline processes, usually in the presence of some catalysts, such as soda cooking combined with anthraquinone catalyst (Biermann, 1996; Feng *et al.*, 2002a, b; Ban *et al.*, 2009; Prinsen *et al.*, 2013; Ikeda and Magara, 2015). Without catalyst, sulfur free alkaline cooking has some disadvantages. When NaOH is the only cooking chemicals, the pulping process is slower and yields less and weaker pulp due to alkaline degradation of carbohydrates, as strongly cooking conditions decomposes carbohydrates by peeling reaction and alkaline hydrolysis. Soda - AQ pulping was mainly used for delignification of non - wood materials, such as straws, reed canary grass, various agricultural residues and annual plants (Alen and Feng 2001; Finell and Nilsson 2004; Hedjazi *et al.*, 2009). Anthraquinone is an oxidant that is often used in chemical pulping for carbohydrates stabilization and delignification improvements (Borrega *et al.*, 2013); an additive really effective for both industrial and commercial for alkaline pulping and work as a redox catalyst, transferring electrons from wood carbohydrates to intermediate structures in lignin degradation, which results in higher yields and lower kappa number. Due to the electron transfer, the anthraquinone passes into its reduced form, anthrax-hydro-anthraquinone. The acceleration mechanism of delignification with anthraquinone involves the attack of the anthrax-hydro-anthraquinone transitional and reactive structures of lignin (Rodríquez *et al.*, 2010).

For soda pulping, AQ addition has increased pulp yields and strengths to levels similar to those of kraft without the use of troublesome sulphur compounds (Farrington *et al.*, 1911; Fossum *et al.*, 1980; Holton, 1977). Under alkaline conditions, peeling reactions occur as sugar units in polymeric chain are removed one by from the reducing end group and transformed into a carboxylic acid. This removal is accompanied by formation of new reducing end group (Borrega *et al.*, 2013). So, addition of anthraquinone reduces the peeling reaction; hence preserving cellulose while enhancing de-lignification process.

2.8.1. Soda-Anthraquinone pulping parameters

In recent years, the influences of pulping variables were extensively investigated by previous studies in order to obtain the optimum quality of non-wood based pulp and paper. The common pulping variables that usually been investigated in pulping process are active alkali concentration (%), AQ charge (%), time to reach pulping temperature (minute), pulping temperature (°C) and liquor to material ratio.

Cooking temperature: - The purpose of cooking is to liberate fibers by removing lignin. However, it is not only the reaction rates of desired reactions that increase with the temperature; the reaction rates of undesired carbohydrate-degrading reactions that reduce pulp yield also increase. The higher temperature (usually 130°C-170°C) speeds up the chemical reactions, so cooking time decreases. How far the cook has proceeded is measured as the kappa number; which quantifies the amount of lignin remaining in the pulp. A pulp without lignin should have a kappa number of zero; however, this is not always the case, as other structures can be oxidized, giving a false positive in the analysis (Sixta and Schild, 2009). As the reaction rate increases much faster than does the temperature, even a small temperature change will affect the time needed to achieve a certain cooking result, or kappa number. As the relative reaction rate varies greatly with temperature, 1 min at 170°C corresponds to 15 h at 100°C (Tavast, 2015). Pulping of agricultural residues require mild cooking condition as compared to hard wood and soft wood pulping which is usually 135-145°C.

Cooking time: - It has been found that increased time in the impregnation stage will improve cooking conditions in chips by providing more homogenous conditions in the chips. An increased impregnation time results in a more complete impregnation; causing improved cooking conditions and a more homogeneous cook (Ban *et al.*, 2003).

Catalyst (Anthraquinone): - It is considered an additive really effective for both industrial and commercial for alkaline pulping and work as a redox catalyst, transferring electrons from wood carbohydrates to intermediate structures in lignin degradation, which results in higher yields and lower kappa number (Gomide *et al.*, 1980a, b). These process modifications change the chemistry of the pulping process in order to improve the selectivity with respect to lignin removal without significant carbohydrates degradation (SILVA JÚNIOR *et al*., 2002). AQ has been used by pulp industry, focusing an increase yield, lower production of solids in the black liquor and reduction of kappa number. These applications generally aim to eliminate bottlenecks, with the major areas involved recovery boilers, caustification, the digesters and bleaching plant (SILVA JÚNIOR *et al*., 2002). It was observed that a significant reduction in pulp rejects was obtained when 0.2% AQ was used in cotton stalk-soda pulping. On the other hand addition of AQ in soda pulping resulted in higher viscosity compared to the soda pulp. Addition of AQ in soda pulp can be used to reach a certain kappa number in a shorter cooking time resulting in advantages of shorter process and reduced energy consumption (Atik, 2002; Copur *et al*., 2007; Lowendahl and Samuelson, 1978; Nelson and Irvine, 1992).

It was determined that AQ could be used for incremental pulp production (Leu, J.D. *et al*., 1980; Renard, J.J. *et al*., 1980; Mortimer *et al*., 1985; Blain, T.J., *et al*., 1983; Ringley, M.B., 1991; Blain, T.J., 1993) , environmental improvement (Renard, J.J. *et al*., 1981; McDonough *et al*., 1982; Parthasarathy *et al*., 1995), cost reduction (Renard, J.J. *et al*., 1980; Virkola and N.E., 1981; Andrews, J.D and Hart, P.W., 2013), and for non-conventional alkaline pulping processes (Virkola *et al*., 1981; Kettunen *et al*., 1982; Gumuskaya et al., 2011; Andrews, J.D, Hart, P.W., 2013). AQ was also found to be beneficial in the pulping of multiple non-wood species (Chen, J. et al., 1987; Feng *et al*., 2001; Hart, P.W. *et al*., 1993; Sridach *et al*., 2010).

Alkali Concentration: - The increment in concentration of active cooking chemical improves the delignification and provides better quality pulp with lower lignin content. But a higher concentration of active cooking chemicals increased the polysaccharide degradation and also demonstrated to cause higher dissolution of organic matter in the liquor (Tavast, 2015).

Cooking temperature, AQ concentration, reaction time and soda concentration was used according to the results of other researchers, industrial parameters and those available in the literature as 130-170°C, 0.1-0.5% (on dried raw material), 30-150 min and 10-34%, respectively (Smook, 1982; Khristova *et al*, 2004; Vasconcelos, 2005; Sixta, 2006; Khiari *et al*, 2009; Rodríguez *et al*, 2010).

2.9. Process Descriptions of Chemical Pulping

Pulp and paper making process involves: - Raw material collection and treatment, Pulping, Washing, Screening, and Recovery of chemicals, Bleaching and Paper making process. Pulping involves separation of fiber for chemical or mechanical pulping, removal of knots, washing of pulp for recovery of chemical, rejects/uncooked material, sand and other foreign material. Bleaching of pulp involves bleaching of washed and screened pulp with bleaching chemicals – chlorine, caustic, hypochlorite, chlorine dioxide, ozone, hydrogen peroxide, sodium hydrosulfite with different sequences of bleaching.

2.9.1. Raw Material Collection and Preparation

The collected material is firstly chipped and screened to required size. Chipping quality plays important role in the overall quality of pulp. Efficiency of chip size-length, thickness, uniformity of size, removal of dust and fines are important factors affecting pulping efficiency and quality of pulp. In case of agricultural residue, size of the straw sand and removal of dust also is important.

2.9.2. Pulping/Cooking Process

The "cooking process" is where the main part of the delignification takes place. Here, non-wood chips are heated in a solution of NaOH and AQ in a pressure cooker for modified soda process, during which time a lot of the lignin is removed. Other cooking processes such as Kraft and Sulfite are there having the same procedures. The quality of pulp produced is closely related to the concentration of sodium hydroxide in the cooking liquor as well as the cooking parameters. In chemical pulping, chips and chemicals in aqueous solution are cooked together in a pressure vessel which can be operated on a batch or continuous basis. In batch cooking, the digester is filled with chips through a top opening, the digestion chemicals are added, and the contents cooked at elevated temperature and pressure. Once the cook is complete, the pressure is released, “blowing” the de-lignified pulp out of the digester and into a holding tank. The sequence is then repeated. In continuous digesting, pre-steamed chips are fed into the digester at a continuous rate. Chips and chemicals are mixed together in the impregnation zone at the top of the digester and then proceed through the upper cooking zone, the lower cooking zone, and the washing zone before being blown into the blow tank (Herbert, 2006).

2.9.3. Pulp Washing

The process where the chemicals are separated from the cooked pulp is called pulp washing. The pulp and spent cooking liquor are subsequently separated in a series of brown stock washers. There are many types of machinery used for pulp washing. Most of them rely on displacing the dissolved solids (inorganic and organic) in a pulp mat by hot water, but some use pressing to squeeze out the chemicals with the liquid. An old, but still common method is to use a drum, covered by a wire mesh, which rotates in a diluted suspension of the fibers. The fibers form a mat on the drum and showers of hot water are then sprayed onto the fiber mat.

A good removal and recovery of chemicals (inorganic and organic) is necessary for several reasons such as prevention of the dissolved chemicals interfere with the downstream processing of the pulp, replacement of chemicals are expensive and the removal of chemicals (especially the dissolved lignin) are detrimental to the environment.

2.9.4. Pulp Screening

Apart from fibers, the cooked pulp also contains partially uncooked fiber bundles and knots. Modern cooking processes (together with good chip screening to achieve consistent chip thickness) have good control over the delignification and produce less "rejects". Knots andshaves are removed by passing the pulp over pulp screens equipped with fine holes or slots.

2.9.5. Chemical recovery

Non-wood pulping processes generate large volumes of black liquor as by-products and wastes. Black liquor wastewater is a mixture of organic and inorganic materials, with very high amounts of total dissolved solids (TDS) that is released from pulp washing process. The total dissolved solids in the black liquor are composed of lignin derivatives, low molecular weight organics, and the rest being made up of chemicals from the digesting liquor (Huang *et al.*, 2007). In delignification, the relatively high amount of silicon present in non-wood material is dissolved together with lignin into cooking liquor. This has led to difficulties in the recovery of cooking (sodium hydroxide and anthraquinone) chemicals. This situation makes black liquor one of the most difficult materials to handle in wastewater treatment processes.

2.9.6. Pulp Bleaching

Bleaching is a pulp purification process to remove the residual lignin with maximum cellulosic protection. The process efficiency and pulp bleaching responses may vary with pulp composition, bleaching chemicals, sequence of addition and reaction conditions. Therefore, many different bleaching technologies are being practiced and/or researched around the globe. Depending upon the chemistry of the process, bleaching can be of two types i.e., lignin retaining bleaching and de-lignifying bleaching. During the lignin retaining process, bleaching chemicals brighten the pulp (~ 5-15% increase in brightness) with insignificant losses in pulp residual lignin. Single stage hydrogen peroxide bleaching and sodium dithionite are the examples of lignin retaining bleach chemicals. De-lignifying bleaching process (lignin removing bleaching) is preferred over lignin retaining process as fiber strength and interlocking along with brightness stability of pulp increases with the removal of lignin constituents. Chlorine, ozone and peroxides etc. are some of the de-lignifying bleaching chemicals.

Bleaching is required for the production of the high grade paper which the whiteness or brightness of the paper is necessary. Brightness is a test of its paper ability to reflect monochromatic light in comparison to a known standard, magnesium oxide which has 96% brightness by the reflectance of blue light (Casey, 1980; Biermann, 1996). In order to produce high brightness chemical pulps, bleaching is required to eliminate the residual lignin with chemical agents. The de-lignifying bleaching process produces pulps with highly stable or permanent brightness (Sjostrom, 1993; Biermann, 1996). Bleaching process usually performs in a sequence of several stages due to the complexity of lignin nature which reacts differently with different bleaching chemicals. Thus, the employment of different bleaching agents in a sequence enable to reduce the amount of chemical required and also enhance the delignification of lignins while minimizes the cellulose degradation (Smook, 1992; Biermann, 1996).

Increasing concern about the environmental impact of bleaching processes with chlorine and chlorine based compounds have provided motivation for the use of elemental chlorine free (ECF) and total chlorine free (TCF) bleaching sequences (Shatalov and Pereira 2005; Abrantes *et al.*, 2007). These bleaching processes are based oxygen derived compounds, among which, hydrogen peroxide has provided to be a highly efficient and competitive bleaching chemical in terms of delignification efficiency, low cost and reducing ecological impact (Walsh, 1991;

Abrantes *et al.*, 2007). As the result, it has gained increasing importance in industrial applications (Zeronian and Englesby 1995). The basic purpose of bleaching is to selectively wash away the residual chromophoric lignin groups without causing damage to pulp cellulose. Peroxide primary works under alkaline conditions when perhydroxy ion, OOH^-, is formed as the following reactions (Zeronian and Englesby 1995; Johnson *et al*, 2002).

$$H_2O_2 + OH^- \longrightarrow OOH^- \text{ (bleaching agent) } + H_2O$$

$$OOH^- + \text{chromophore} \longrightarrow \text{bleaching (chromophore destroyed).}$$

An alkaline environment is needed to form an active hydro peroxide anion. Also, alkaline conditions lead to fiber swelling, which causes both improving of bleach liquor penetration and accessibility of the chromophore groups. The milder alkalinity of the $Mg(OH)_2$ system is believed to be the cause of more effects of this alkali source on pulp and bleaching process properties, such as the lower COD (load of bleaching effluent) formation. The higher COD values of NaOH were attributed to its strong alkalinity; with creating a high-pH environment, the longer chain molecules in the pulp hydrolyze to smaller and soluble ones (Z. He. *et al.*, 2004). Another advantage of the $Mg(OH)_2$ alkali is its low solubility, which results in a lower pH (M. Nystrom *et al.*, 1993). The low solubility of $Mg(OH)_2$ allows it to provide a constant alkalinity at various alkali charges, and also pH values are approximately constant during the bleaching, while initial and final pH values mark a significant difference in NaOH-based process. However, high concentration of the hydro peroxide anions causes decomposition of hydrogen peroxide, especially at elevated temperatures. Therefore, it is common practice to add stabilizing agents (i.e. sodium silicate) and the initial and final pH in the pulp bleaching process must be kept at an ideal value, which for the pH in bleaching at 65°C to 70°C is typically between 8.5 and 9.0 (H. U. Suess, 2010).

Alkaline hydrogen peroxide can change the chemical, physical, and optical properties of pulp significantly; therefore, adjusting condition of bleaching properly appears fairly essential to meet specific requirements of different paper grades (Johnson *et al.*, 2002; Ni *et al.*, 2007). Attack of bleaching chemical at certain specified sites either stabilizes the conjugated aromatic rings of residual lignin resulting in the loss of lignin chromaticity (lignin preserving bleaching) or depolymerize the lignin molecule (delignification) to be washed away during subsequent water washing. The bleaching reaction should be selective. Although the bleaching agents differ in their de-polymerization reaction on pulp cellulose or lignin, due to difference in oxidation potentials (Johnson, 1975); changes in pH and/or other reaction conditions may deteriorate the selectivity of the process resulting in the decrease of degree of polymerization (DP). The loss in DP or cellulosic content may lead to poor fiber bonding and thus poor strength of the product.

In ECF- bleaching only minor amounts of chlorine dioxide are used. During the pulp bleaching process, chlorine tends to combine with lignin to create chlorinated organics that end up in waste water. In contrast, chlorine dioxide breaks apart the lignin, leaving behind organic compounds that are water soluble and very similar to those occurring naturally in the environment (Dahlman *et al.*, 1994). Due to stricter pollution regulations, new non-pollutant bleaching processes are highly desired and the totally chlorine free bleaching technology based on the action of oxygen, ozone, hydrogen, peroxide and peracid appears to fulfill the condition for a closed cycle mill (Nelson ,1998).The delignification performed in the TCF bleaching is mainly based on redox reactions (Gierer,1997). ECF bleached pulp on other hand have a higher tear and fiber strength than TCF pulps (Ek *et al.*, 1994). ECF bleaching allows production of kraft pulps that meet the highest requirements with respect to strength , brightness, brightness stability, cleanliness, etc. (Jan Rennel and Jaaklo, 1995).

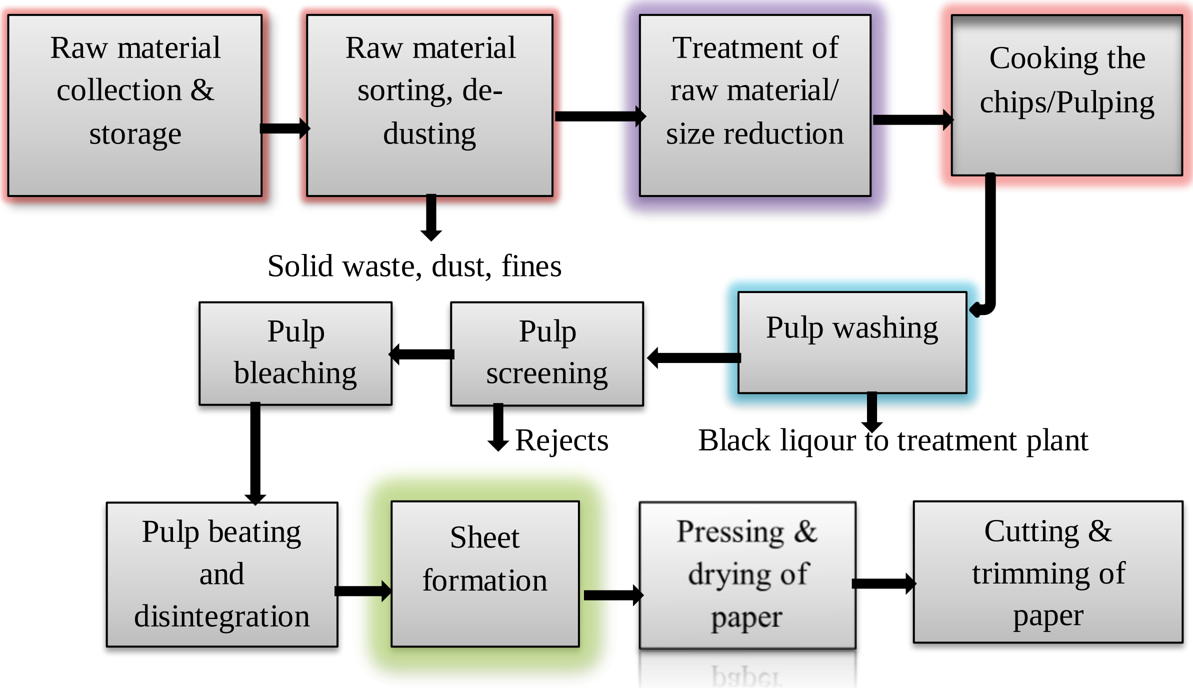


Figure 2.4: Flow chart of production process of paper from non-wood raw material

2.9.7. Paper Making Process

Paper making is the process whereby pulp fibers are mechanically and chemically treated, formed into a dilute suspension, spread over a mesh surface, the water removed by suction, and the resulting pad of cellulose fibers pressed and dried to form paper. The appearance of typical paper sheet is as a function of its detailed structure, presence and absence of light-absorbing groups (chromophores), the refractive indices of its components, its basic weights and its surface reflective characteristics.

Paper strength is dependent on the individual fiber strength and the strength of the bonds between the fibers. It is usually the latter, which is the limiting factor. Refining increases the inter fiber bonding at the expense of the individual fiber strength, but the net result will be an increase in paper strength. Pressing and calendaring (feeding through rollers) increase density and promote smoothness. Various chemicals are added, e.g. to give water resistance, to give increased strength, to produce colored paper, or to serve as inorganic fillers.

2.10. Properties of Pulp and Paper

The pulp is a complex system that can be given different properties and the resulting paper can be used for a broad verity of applications. Every application has its own specific demands. The selection of what properties the fiber should have to give the right paper properties, along with the type of processes used. Fibers in the pulp are rarely straight and fiber curl, deformations and damages can originate from several steps in the process, such as chipping, de-fiberization, and medium-consistency unit operations. This may in the end lead to lower strength of the paper

2.10.1. Basic Pulp Properties

Pulp Viscosity: - It is indirect measure of degree of polymerization of cellulose chains in fibers. Longer polymer chains mean thicker solution and higher viscosity and longer flow time. It also indicates degree of chemical damage to fibers.

Pulp yield: - is the main concern of pulp milling industry and it is mainly governed by the pulping processes. The pulp ideally needs to be pure fiber. That is the reason to remove lignin and solvent extractives. When lignin was removed from cooked chips, fibers were obtained for paper making and called pulp. Among all the pulping process, mechanical pulping provides high pulp yield, which retains almost all constituents of wood including lignin. Lignin which is second highest to cellulose, does not bond to itself or cellulose as fibers do. Therefore pulps with high yield results in weak pulp.

Pulp Kappa number: - It is volume (ml) of 0.1N potassium permanganate consumed by 1g (oven dried) of pulp. Estimate of lignin content can be given as,

$$\text{Kappa no. x } 0.15 \cong \% \text{ lignin}$$

Kappa number of the pulp is one of the important parameters in pulp manufacturing because it relates to the bleach ability or degree of delignification of the pulp. As lignin is removed from the sample, the Kappa number is reduced. Low Kappa pulps are easier to bleach but high kappa pulps usually require more energy in refining, and often produce stronger paper or board (particularly with regard to tear strength).

Pulp beating: - It increases the surface area and flexibility of the fibers. The flexible fibers are more bendable to conform around each other. This, together with the liberation of a lot of fines, will improve the contact between the fibers which in turn leads to an increased strength of the fiber joints and therefore also the strength of paper. The increased flexibility is probably due to an increase of porosity or delamination of the fiber wall. All the strength properties accept for the tear index will increase during beating. This is because the tear strength depends on the individual strength of the fibers and the other properties rely on the fiber joints. The increase of fiber joints will lead to an increase of the density of the paper and the light scattering coefficient will decrease. The bulk, opacity and porosity are other properties decreased by the refining.

The most important effects of beating are:-

- Cutting or shortening of fibers.
- Production of fines and complex removal of parts of the fiber wall, creating fragments in the suspension.
- External fibrillation and partial removal of the fiber wall
- Internal changes in the wall structure. This is described by delamination, internal fibrillation or swelling.
- Curling/Straightening of fibers.
- Inducing/Removal of kinks, nodes, slip planes and micro compressions in the fiber-wall.
- Dissolving or leaching out colloidal material into the external liquor.
- Redistribution of hemicelluloses from the interior of the fiber to the exterior parts.
- Scrub the surface at the molecular level to produce surface with a gel consistency of the surface.

Pulp Freeness: - It measures drain ability of a pulp suspension and can be analyzed by two different systems. These are Canadian Standard Freeness-CSF (N. America) and Schopper Riegler-SR (Europe) when CSF is higher numbers it is to mean faster draining and SR-higher numbers mean slower draining.

Pulp consistency: - It is the term used to describe solid content of pulp during pulp processing. In pulp and paper making process, all equipments are designed to handle a consistency of certain percent (Gravity thickeners, 6-8%; Vacuum washers, 10-15%; Bleaching plants, 10-12%; Screening plant, 2-4%; Refining, 1.6-2.2% pulp consistency respectively). Pulp consistency is roughly divided in to three ranges: Low Consistency: <5%, Medium Consistency: 5-15% and High Consistency: >15%. Oven dried pulp at 105°C is 100% consistency while air dried pulp is about 92% pulp consistency.

2.10.2. Paper Properties

Typical hand sheet physical and optical properties are: - Basis weight (grammage), calipers (thickness), tear strength, tensile strength, burst strength, brightness and whiteness.

Grammage: - the basis weight is the most fundamental property of paper and paperboard. The Basis weight of paper is the weight per unit area which is expressed by the weight in grams per square meter (g/m^2). Grammage of news print is about 40-50; paper for printing and writing, 60-90; and paperboard, 120-300 g/m^2 respectively.

Caliper: - the thickness that determines how bulky or dense the paper is. Thickness or Caliper of paper is measured with a micrometer as the perpendicular distance between two circular plane parallel surfaces under a pressure of $1kg/cm^2$. Uniform caliper is good for good roll building and subsequent printing while variation in caliper affects many aspects of paper properties.

Tensile strength: - is the force required to produce a rupture in a strip of paper or paperboard, measured by tensile tester and expressed in kN/m. This tensile strength gives an indication of the maximum possible strength of pulp beaten under ideal condition and shows the extent of fiber strength, fiber bonding and fiber length. The tensile breaking strength is measured by TAPPI method T-404 and measurement of elongation of paper and paperboard is done by using a pendulum type tester, and T-494 measures tensile breaking properties of paper and paperboard using constant rate of elongation apparatus (Caulfield and Gunderson, 1988).

Tearing strength: -is a measure of how well a material can withstand the effects of tearing under any applied tension and it indicates the behavior of paper in various end use situations; such as evaluating web run ability, controlling the quality of newsprint and characterizing the toughness of packaging papers where the ability to absorb shocks is essential. Fiber length and inter-fiber bonding are both important factors in tearing strength. Internal tearing resistance is a measure of the force perpendicular to the plane of the paper necessary to tear a single sheet through a specified distance after the tear has already been started. Edge tearing strength (T-470) is a measure of the force needed to initiate a tear. The papers and other film materials that exhibit high tensile stretch or elongation to break also exhibit high edge tearing strength (Caulfield and Gunderson, 1988).

Bursting strength: - is the capacity of a material to maintain in continuity when subjected to pressure under rigidly controlled conditions. It is a pressure measured at which a pulp sheet will burst, used as a measure of resistance to rupture. TAPPI method T-403 is the official test used for measuring the bursting strength of papers pressure applied through a rubber diaphragm on a sample with thicknesses up to 0.6 mm and diameter 30.5mm (Anon, 1987).

Whiteness and brightness: - they are sometimes used interchangeably when comparing the relative whiteness of different papers or when defining how white a specific paper is. However, while these two terms are related, their scientific definitions differ (Bureau, W.H., 1975).
Papers having the same degree of brightness, in fact, may differ greatly in visual appearance (Technidyne Corporation, 1996).

TAPPI brightness is based on the filter chosen to measure the reflectance of the pulp in the region most sensitive to the effects of bleaching (Bristow *et al.*, 1990).
Whiteness of paper is measured by the reflectance of a paper's surface for all wavelengths of the visible spectrum. Brightness of paper is measured by comparing the amount of light, of a prescribed single wavelength (457 nm) in the blue region of the spectrum, reflected by a pad of that paper to the amount that is reflected by an arbitrary standard having 100 reflectance at this same wavelength. The method is defined by TAPPI method T452. The selected standard is magnesium carbonate. This method states that this procedure is applicable to all naturally colored pulps, papers and paperboard. The TAPPI brightness measurement can be deceptive when the papers that contain dyes because the TAPPI brightness measurement technique ignores more than two-thirds of the visible light spectrum.

Laboratory sheet forming versus paper machine: - Laboratory sheet formers give isotropic sheets i.e. the fibers are randomly oriented in the paper. In a paper made on a paper machine, the fibers align themselves in the machine direction and this paper will be anisotropic. This results in different properties between the machine direction and in the cross direction for machine made paper. There is also a difference in formation between machine made paper and laboratory sheets (hand sheets). In the laboratory sheets the fibers will be evenly distributed and the formation will be almost ideal. On the paper machine, the fibers will catch on to each other and this leads to flocculation. Due to the fact that formation affects the strength properties of the paper, it can be misleading to give judgment on paper strength based on laboratory sheets.

In a paper machine, the pressing section differs a lot from the one used in the laboratory. The laboratory wet pressing is accomplished by pressing the sheets in a flat plate pressing machine in one or two quite long steps. In a paper machine the press section consists of two to three sets of pressing rolls which will press the paper web for only a short time each but at much higher load.

3. METHODOLOGY

3.1. Determination of Morphological Properties and Chemical Compositions of Teff Straw

3.1.1. Determination of Morphological Properties of Teff Straw

3.1.1.1. Materials and Chemicals

Materials: - Teff (*Eragrostis tef*) straw, Test tubes (100-250mL), Whatman Grade 1 filter paper (125μm), slides, round bottom flasks (250mL), ink/medicine dropper , Motic microscope (40-400X) and Razor blade.

Chemicals: - Chromic Acid, Nitric Acid, Safaranin and Canada balsam, Xylene and Ethanol

3.1.1.2. Methods

Fiber length and Fiber width: - Pre-treated teff straw samples were taken in test tubes; dipped them in Jeffrey's solution (10g chromic acid dissolved in 190mL distilled water, to which 15mL nitric acid was added) at room temperature for 24 hours. After maceration, chromic acid and nitric acid was drained and macerated fibers were washed three times with distilled water and filtered using Whatman Grade 1 filter paper for separation of fibers. For slide preparation fibers was stained with 20% safranin solution and again washed with distilled water for distaining of excess safranin and placed some amount of fiber suspension on glass slide with the help of ink/medicine dropper and allowed for air drying and mounting by using Canada balsam (Ogbonnaya *et al*., 1997). Two slides were prepared per sample and images were taken with a total magnification of 40xs using camera attached motic BA210 compound stereo microscope. Finally, the length of 100 fibers was measured using Motic Advanced 3.2 software.

Lumen diameter and Cell wall thickness: - Teff straw was cut by razor blade cross-sectionally. The samples were placed into safranin solution (1gm of safranin was added into 100mL of distilled water) and immersed into ethanol (30%, 50%, 70%, 90% and 100%) and xylene for one minute each respectively. In this process safranin is used as staining, alcohol for dehydration of water and xylene to enhance contrast between cells.

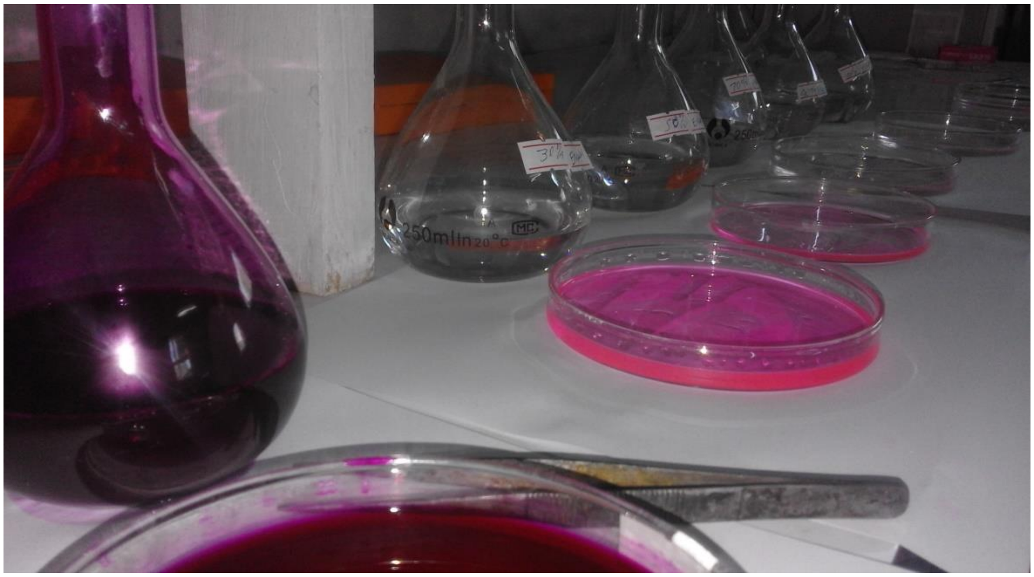


Figure 3.1: Safranin, ethanol and xylene treatment of teff straw slice

Finally, specimen was put on slide and one drop of Canada balsam was dropped and covered using cover slip and left the slide to dry. After making permanent slide, good quality images were taken with a total magnification of 400xs by using camera attached motic BA210 compound stereo microscope.

Derived values

Fiber indices were calculated from equations (3.1, 3.2, 3.3 and 3.4).

Runkle ratio = $\frac{2\times\mathrm{CWT}}{\mathrm{LW}}$ …………………………………………..……..……..… (3.1)

Filtering power (slenderness ratio) = $\frac{\mathrm{FL}}{\mathrm{FD}}$ …..……………………..……..……….. (3.2)

Rigidity coefficient = $\frac{\mathrm{CWT}}{\mathrm{FD}} \times 100$……………………..……… …………………... (3.3)

Flexibility coefficient = $\frac{\mathrm{LW}}{\mathrm{FD}} \times 10$……………………….................................... (3.4)

Where: CWT is average cell wall thickness, LW is average lumen width, FD is average fiber diameter and FL is average fiber length

3.1.2. Chemical characterization of Teff Straw

3.1.2.1. Materials and Chemicals

Materials: - Pre-treated teff straw, Laboratory electric mill, Vibratory sieving apparatus, Laboratory sieve mesh (100µm-1mm), Silica crucible, Desiccators, Drying oven, Electrical muffle furnace, Measuring cylinders (10-500mL), Stopwatch, Sox let extractor, Autoclave, Vacuum suction and Measuring balance.

Chemicals: - Nitric acid, Surphuric acid, Ethanol, Benzene, Acetic acid and Sodium chlorite

3.1.2.2. Methods

Teff straw pre-treatment: - Teff straw for proximate and chemical composition analysis was collected, washed, dried and milled with laboratory electric mill (DIETZ 7311) with output sieve size 1mm. The particle size distribution was determined by using a vibratory sieving apparatus (Retsch AS 200) for 10 minutes shaking time with different sieve sizes.

The chemical analysis was carried out using 40-60 mesh (0.250 to 0.450mm) particle size fractions (Berhanu *et al*., 2018).

Moisture content determination: - To obtain the percent moisture content of teff straw, sample was dried at 105 ± 2°C for 24 hours until a constant weight was measured. The moisture content was found on a percentage basis (TAPPI T 262 om-02) by following the formula.

$$\text{Moisture \%} = \frac{w1-w2}{w1} * 100\ \% \quad \text{……………………………………………………} 3.5$$

Where: w_1 is mass (g) of ground teff straw before drying and
w_2 is mass (g) of ground teff straw after drying

Determination of ash content (w_{ash}): - A sample was ignited in a muffle furnace at 525 ± 25°C and burnt for 3 hours (TAPPI T211 om-12). Ash content was calculated as follows:

$$W_{ash} = \frac{m1-m2}{mu} * 100 \quad \text{………………………………………………………} 3.6$$

Where: m_1 is weight (g) of moisture-free sample before ignition,
m_2 is weight (g) of sample after ignition,
m_u is oven-dried weight (g) of sample.

Extractives content determination (w_{Ex}):- A weight chopped sample was extracted with a mixture of benzene - ethanol (C_6H_6 - C_2H_50H) solvent in a ratio of 1:2 (v/v) for 8 hours in Soxhlet apparatus. The material, extracted in a round bottom flask, was dried in an oven at the temperature of 80°C to constant weight (TAPPI T204 cm-07). The extracted content was calculated as follows:

$$W_{Ex} = \frac{m2-m1}{mu} * 100 \quad \text{……………………………………………………....} 3.7$$

Where: m_1 is oven-dried weight (g) of flask,

m_2 is oven-dried weight (g) of extract in flask plus oven dried weight of flask (g),

m_u is oven-dried weight (g) of sample.

Lignin (w_{lignin}): -The Klason Lignin (defined as composition which is insoluble in 72% H_2SO_4) was determined by acid hydrolysis as TAPPI standard procedure (T 222 om-11). A 0.1 g of dried and extracted teff straw sample was hydrolyzed with 15mL of 72% sulfuric acid at room temperature for about two hours. The hydrolyzate was then diluted with deionized water (560mL) to 3% concentration of sulfuric acid and placed in an autoclave at 121°C for two hours for the second hydrolysis reaction. The solid residue lignin was obtained by filtration and drying in an oven at the temperature of 105°C to constant weight. The Klason lignin content is calculated as follows:

$$W_{lignin} = \frac{m2-m1}{mu} * 100 \quad \ldots\ldots 3.8$$

Where: m_1 is oven-dry weight (g) of filter paper,

m_2 is oven-dry weight (g) of filtrated lignin plus weight (g) of filter paper,

mu is oven-dry weight (g) of sample.

Cellulose ($W_{cellulose}$): - Küschner–Hoffer method was used for the determination of cellulose. The extracted sample was cooked in a mixture of nitric acid–ethanol (HNO_3 - C_2H_5OH with a ratio of 1:4) in a hot water bath at the temperature of 100°C with a Solid/liquid ratio of 1:25 (5g of extractives-free samples with 125mL of alcoholic nitric acid solutions under reflux during four cycles of 1 hour) (Browning, 1967). Cooking was done through four extraction cycles until the sludge became completely bleached. After each cycle, the alcoholic nitric acid solution was removed and a fresh volume was added. Its filtration and drying in an oven at the temperature of 105°C to constant weight provided Küschner–Hoffer cellulose, which was calculated as follows:

$$W_{cellulose} = \frac{m1-m2}{mu} * 100 \quad \ldots\ldots 3.9$$

Where: m_1 is oven-dry weight (g) of filter paper funnel,

m_2 is oven-dry weight of funnel + extracted cellulose (g)

m_u is oven-dry weight (g) of sample.

Hemicellulose ($W_{hemicellulose}$): - Two grams of extractives free sample was placed in an Erlenmeyer flask and 64mL of distilled water was added. While slowly shaking, 0.80g of

$NaClO_2$ and 0.5mL of acetic acid were added and the flask was covered with watch glass and boiled at 70℃ for three hours. After cooling, the sample was filtered using filtering crucible and washed with 100mL of 1% aqueous glacial acetic acid and then washed with 10mL acetone. Filtering crucible containing the holocellulose was oven dried at 105 ± 3℃ and placed in a desiccator to cooled to room temperature and weighed repeatedly until a constant weight was obtained (Rowell R.M., 2005) as follows,

$$\text{Holocellulose \%} = \frac{W2}{W1} * 100 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 3.10$$

Where, W1 is the oven dried extractive free sample and

W2 is the weight of oven dried holocellulose

Hemicellulose content was calculated by subtracting cellulose content from holocellulose content, because holocellulose contains both cellulose and hemicellulose.

Hemicellulose % = Holocellulose – cellulose

3.2. Teff straw pulping process and Product characterization

3.2.1. Materials and Chemicals

Materials: - Pre-treated teff straw**,** Fourier Transformed Infrared (FTIR) spectroscopy, Spectro UV-VIS double beam PC (UVD-3200), Autoclave, Sieve mesh (0.125 & 0.15mm), Polyethylene bag and Water bath.

Chemicals: - Sodium hydroxide, Anthraquinone, Sulfuric acid, Potassium permanganate, Hydrogen Peroxide, Magnesium hydroxide,

3.2.2. Methods

3.2.2.1 Experimental design

Experimental data analysis was done using DESIGN EXPERT® 7.0.0 software. The experimental design selected during this experiment was Response Surface Methodology of Central Composite Deign/CCD). Response surface methodology (RSM) is a mathematical and statistical method used for modeling purpose and problems analysis in which the variables used have direct effect on the response. This methodology was conducted to get optimum value not only for the response but also for the variables (Mesa *et al.*, 2011). A central composite design (CCD) is a very efficient design tool for fitting second-order models (Montgomery DC., 2001).

The RSM procedure was carried out by considering the process factors (independent variables) satisfy important assumptions that they are measurable, continuous/numeric, and controllable by experiments with negligible errors.

- A series of experiments were performed for adequate and reliable measurement of the response of interest.
- A mathematical model of the second-order response surface with the best fit was developed.
- The optimal set of experimental parameters producing the optimum response value was determined.
- The direct and interactive effects of the process parameters (factors) were represented through two and three-dimensional plots

Table 3.1: The Response Surface Design with 3-level CCD results 27 runs

Std	Run	Factor 1 A: Temp. (°C)	Factor 2 B: Time(min.)	Factor 2 C: Conc. NaOH, (%)	Response 1: Yield (%)	Response 2: Kappa num.
6	1	130.00	120.00	10.00		
4	2	150.00	60.00	10.00		
17	3	120.00	90.00	15.00		
24	4	140.00	90.00	15.00		
20	5	140.00	150.00	15.00		
25	6	140.00	90.00	15.00		
10	7	130.00	60.00	20.00		
8	8	150.00	120.00	10.00		
27	9	140.00	90.00	15.00		
19	10	140.00	30.00	15.00		
16	11	150.00	120.00	20.00		
1	12	130.00	60.00	10.00		
22	13	140.00	90.00	25.00		
11	14	150.00	60.00	20.00		
26	15	140.00	90.00	15.00		
3	16	150.00	60.00	10.00		
13	17	130.00	120.00	20.00		
15	18	150.00	120.00	20.00		
18	19	160.00	90.00	15.00		
9	20	130.00	60.00	20.00		
7	21	150.00	120.00	10.00		
21	22	140.00	90.00	5.00		
23	23	140.00	90.00	15.00		
14	24	130.00	120.00	20.00		
12	25	150.00	60.00	20.00		
5	26	130.00	120.00	10.00		
2	27	130.00	60.00	10.00		

The experiments were completely randomized design with three main factors (soda concentration, cooking temperature and cooking time at three levels with five center points (three to five center runs are recommended) and two response variables (pulp yield and kappa number).

Table 3.2: Level and code of variables used for Response Surface Design

Factors	Unit	Code	Levels		
			-1	0	+1
Temperature	°C	A	130	140	150
Time	min.	B	60	90	120
NaOH Concentration	%	C	10	15	20

In order to determine if a relationship existed between the factors and the responses investigated, the collected data was analyzed statistically using regression analyses. A regression design is employed to model a response as a mathematical function (either known or empirical) of a few continuous factors and 'good' model parameter estimates are desired (Montgomery DC., 2001). Each response of Y can be represented by a mathematical equation that correlates the response surface. The responses can be expressed as second-order polynomial equations, according to equation 3.11.

$$Y = \beta_0 + \sum_{i=1}^{k} \beta i x i + \sum_{i=1}^{k} \sum_{j=i+1}^{k} \beta ij\ x i x j + \sum_{i=0}^{k} \beta ii x i^2 \text{ ……………..3.11}$$

Where, Y is the predicted response (pulp yield and Kappa number) used as a dependent variable; k the number of independent variables (factors), xi (i = 1, 2, 3) the input predictors or controlling variables (factors); β_0 the constant coefficient, and βi, βij and βii the coefficients of linear, interaction and quadratic term, respectively. The coefficient parameters were estimated using a multiple linear regression analysis employing the software Design-Expert (version 7.0.0). Design-Expert was also used to find the 3-D surface and 2-D contour plots of the response models.

The values of experimental variables were normalized as:

$$\text{Xn} = 2\,\frac{X - Xm}{Xmax - Xmin} \text{ ……………………………………………3.12}$$

Where, n is the normalized value of temperature, time and NaOH concentration;

X is the absolute experimental value of the variable concerned;

Xm is the mean of the extreme values of X; and Xmax and Xmin are its maximum and minimum value, respectively.

Table 3.3: Design summary

Factors						Response	
Factors	Type	Low actual	High actual	Low coded	High coded	Name	Model
Temp. (°C)	Numeric	130	150	-1	+1	Pulp yield (%)	Quadratic
Time (min.)	Numeric	60	120	-1	+1	Kappa No.	Quadratic
NaOH Con. (%)	Numeric	10	20	-1	+1	Experiment No.	27

3.2.2.2. Teff straw pulping process

The teff straw used in this study was collected from Tullubollo, South West of Addis Ababa and was thoroughly washed with distilled water to remove unwanted impurities and sun dried for three days; the straw was manually chopped to 1-5mm length. The pulp was obtained by cooking sun dried teff straw together with soda and anthraquinone in autoclave heated by means of electrical resistances. The effects of (1) soda concentration: 10%, 15% and 20%; (2) cooking temperature: 130°C, 140°C and 150°C; (3) cooking time: 60min, 90min, and 120min; (4) anthraquinone amount of 0.2% (based on dried teff straw) on pulp and kappa number were studied by taking liquor to solid ratio (teff straw on dry basis) of 12:1. Afterwards, the cooked material was unloaded into 125µm mesh sieve size in order to remove the residual coking chemicals and black liquor. The pulp was washed and screened by using 0.15mm mesh sieve screen to separate yield and yield reject/uncooked material; and then analyzed for its kappa number and lignin (T222 om - 88) as per TAPPI Standard Test Methods (Anonymous 2007).

The ranges of operating variables were taken based on the results of other the researchers on different non-wood raw materials as it was discussed under section 2.8.

3.2.2.3 .Analysis and characterization of the product

Pulp characterization has special relevance in studies related to the use of alternative raw materials through less polluting processes in the pulp and paper industry. Pulp properties are closely linked to the quality of the final product. The products from each experiment were collected and measured for different parameters as follows.

Yield: - The pulp was dried in an oven at 105°C for 24 hours. The dried samples were weighed and the yield was determined as equation 3.13:

$$\text{Pulp yield} = \frac{\text{oven dry pulp after cooking}}{\text{Oven dry sample taken before pulping}} * 100\ \% \ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ 3.13$$

Kappa number:- In the pulp and paper industry, the determination of Kappa number is a parameter of special significance, since it is an indirect method to estimate the content of residual lignin and an indicator of bleachability (J. S. Shenk and M. O. Westerhaus, 1991). It aims to determine the degree of delignification of pulp. It is defined as the volume (in mL) of a 0.1N solution of potassium permanganate that is consumed per gram of dry pulp. Spectrophotometric method (Zhu and chai, 2014) was used to measure pulp's kappa number under strongly acidic reaction conditions; and it was derived from the ratio of the absorption spectral intensities at a specific wavelength measured at the beginning and end of the reaction of the pulp with permanganate. Strong acidification is used to prevent MnO_2 precipitation and interference with the permanganate absorption spectrum.

5mL of 0.1N concentration potassium permanganate solution was first measured for its spectral intensity at beginning Ao. Then 20mL of standardized sulfuric acid 2mol/L concentration was added to the permanganate solution in order to make strong acidic reaction solution. Then 100mg oven dried pulp was added to the prepared reaction solution and stirred by magnetic stirrer. After five (5) minutes reaction time, filtration was done and the filtrate reaction solution was measured for spectral intensity at the end, Ae. Then kappa number is calculated by equation (3.14).

$$K = \frac{a}{w}\left(1 - \frac{Ao}{Ae}\right) \ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ 3.14$$

Where, a is the initial volume of 0.02 mole/L permanganate in the blank solution in mL, w is the amount of pulp used in grams, Ao and Ae are the permanganate absorbance (or spectral intensity) in the beginning blank solution and at end of the oxidation reactions in the solution respectively.

3.2.2.4. Pulp bleaching

Alkaline peroxide bleaching is one of the most common processes for high yield pulp bleaching by preventing cellulose degradation and reduces the effect of bleaching chemicals on the environment. Produced pulp was bleached in three stages, using hydrogen peroxide and magnesium hydroxide during the first and the last stages, and only a sodium hydroxide solution in the second one. Bleaching experiments were conducted in polyethylene bags using the following conditions: 560g of teff straw pulp produced at optimum conditions stated in the table 4.9 (145.13℃, 71.50 minutes and 13.76% NaOH), 4% H_2O_2, 3% NaOH, 2.4% $Mg(OH)_2$, 70℃ and 90 minutes retention time. According to FARHAD ZEINALY *et al.*, (2014), in order to keep the pH of bleaching process to optimum (usually 9-11), the ratio of alkali to hydrogen peroxide should be from 0.6 to 0.8. For the bleaching process, prepared bleaching agents were added to the pulp, which had been heated to the reaction temperature, and good mixing was provided by kneading. The polyethylene bag was sealed and placed into a water bath for the desired retention time at the set temperature. After the completion of the bleaching time, the pulp sample was cooled down with cold running water to room temperature and washed with excess deionized water. The well-mixed pulp suspension was then filtered by 125μm laboratory mesh screen and dried at room temperature. Finally, the pulp yield of bleached pulp and its Kappa number was determined.

3.2.2.5. FTIR analysis of raw material and product

Powered by diffuse reflectance system (DRS), samples of dried raw matter of teff straw and pulp (unbleached and bleached) produced from it were taken to Fourier Transformed Infrared (FTIR) spectroscopy in order to analysis of functional group. A regular scanning range of 4000-400 cm^{-1} was used and all the spectra are recorded and processed using essential FTIR software.

3.3. Hand sheet preparation and testing

After optimization of the cooking conditions, hand sheets were prepared with the help of laboratory sheet former from teff straw pulp produced at optimized pulping condition and tested for different physical properties were tested.

3.3.1. Materials

Measuring balance, Drying oven, Drying plates, Beating machine**,** Disintegrator machine, Canadian Standard Freeness (CSF) tester, Measuring cylinders (100-2000mL), Wet pressing and laboratory sheet molder machine, Tensile strength tester, Tear strength tester, Burst strength tester and Porosity tester machine.

3.3.2. Methods

3.3.2.1. Pulp hand sheet preparation

Dried teff straw pulp produced from optimized pulping condition was used for sheet preparation; 400g of oven dry pulp was mixed with 23 liters water and pulp slurry was made (1.74% pulp consistency). The prepared pulp slurry was then added to the beating machine. Freeness of slurry was checked out at each ten-minute beating interval. When the freeness of pulp is 30 Canadian standard of freeness (CSF), 800mL sample was taken from beater and diluted to 2 liters of water and disintegrated at 1500rpm for five minutes.

3.3.2.2. Paper hand sheet test

Grammage: -The beated and disintegrated pulp suspension was taken from the disintegrator and diluted to 4 liters of water and agitated well by hand. 400mL from the diluted suspension was taken 60 gm/m^2 was prepared by sheet forming machine. Ones the sheets are prepared two stage pressing was followed by applying 0.47MPa pressure for four minutes by pressing machine. Then the stocks are removed from the press and attached to the drying plates in order to dry by oven at 150℃ for 20 minutes. Then Grammage of paper sheet was calculated as:

$$\text{Grammage} = \frac{\text{Weight (g)}}{\text{area } (m^2)} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots.... \; 3.15$$

Tear strength: - The tear strength measures the internal tearing resistance of paper sheets obtained by dividing the tearing resistance measured in units of millinewtons (mN) by the grammage of the paper in units of grams per square meter (g/m^2) (TAPPI T414 om-98).Tear factor and tear index was also determined.

Tensile strength: - It was tested by using tensile tester when 10mm width and 100mm length strip of paper was prepared. Tensile index was tensile strength divided by grammage (TAPPI T494 om-01).

$$y_1 = \frac{a}{w} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \; 3.16$$

Where; y_1 is tensile strength (kN/m); (a) is maximum tensile force in N (instrument reading in kg is changed to N by multiplying kg * 9.807) and (w) is initial width of the sample in (mm).

$y_2 = 1000 * \frac{y1}{b}$ ……………………………………………………....... 3.17

Where, (y_2) is tensile index (mN/g); (b) is mean Grammage in (g/m^2)

Breaking length

$y_3 = \frac{a*102,000}{b}$ ………………………………………………………….. 3.18

Where, (y_3) is breaking length in meter (m);

(a) is mean tensile strength in kN/m; and

(b) is Grammage in, g/m^2.

Burst strength: - It is a pressure measured at which a pulp sheet will burst, used as a measure of resistance to rupture. Burst strength depends largely on the tensile strength of extensibility of pulp sheet. The test specimens was first prepared as 10cm by 10cm sheet and clamped in the tester tightly with burst strength tester and the maximum reading pointer was set to zero position. The pump motor was then started 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 was in kg/cm^2 and to change kg/cm^2 in to kPa (Kilo Pascal), kPa = kg/cm^2 * 98.07.

Burst factor 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 = $\frac{\text{burst strenght}}{\text{basis weight}} * 1000$………………………………………….. 3.19

Burst index (kPa * m^2/kg) is obtained by dividing burst strength (kPa) to basis weight (g/m^2).

Porosity: - is the air resistance of paper defined as the number of seconds required for 100mL of air to pass through one inch of a piece of paper measured by porosity tester. The unit of which is sec/100mL air. TAPPI T-460 om-02 method was used to measures the amount of time required for a certain volume of air to pass through a test specimen.

4. RESULTS AND DISCUSSION

4.1. Morphological analysis and Chemical Compositions of Teff Straw

4.1.1. Morphological analysis of teff straw fibers

Fiber length greatly affects the strength of paper, the tearing resistance in particular and to a lesser extent the burst index, the tensile index and the folding endurance. Fiber width and wall thickness, on the other hand, affect the flexibility of the fibers and their tendency to collapse in the paper production process. Conformable fibers form better bond in a sheet structure and make denser, stronger and smoother sheets (R. P. Kibble white, R. Evans and M. J. C, 1995). Figure 4.1 and 4.2 shows the images of teff straw fibers obtained by optical microscope (BA210).

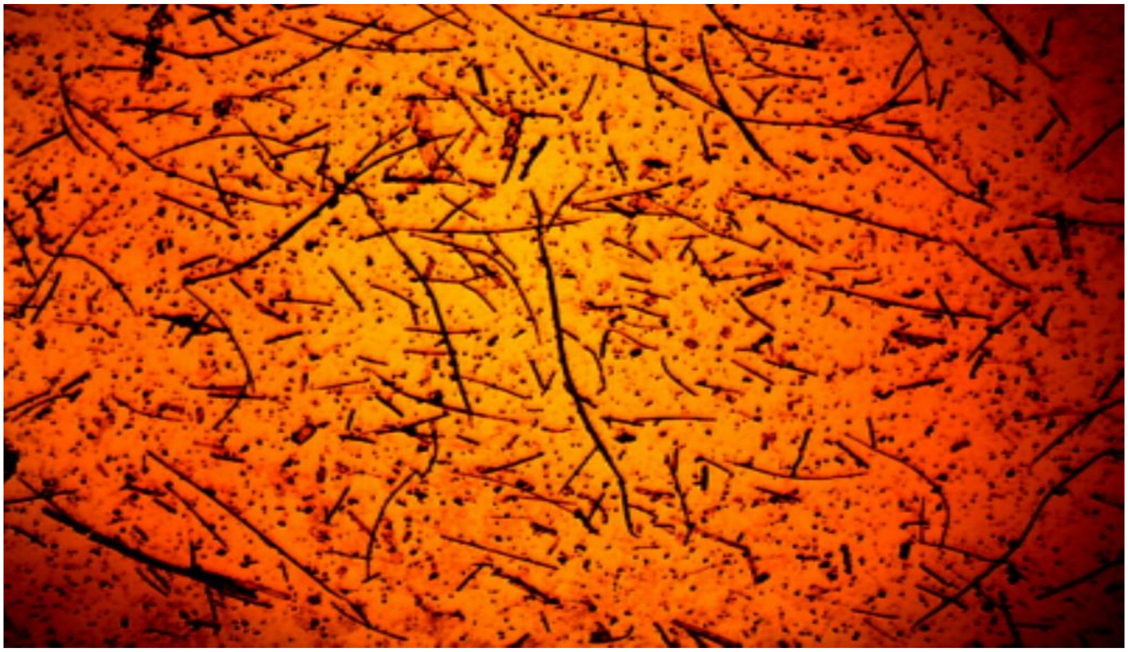


Figure 4.1: Fibers image of teff straw taken from Motic Microscope (BA210, 40X magnified).

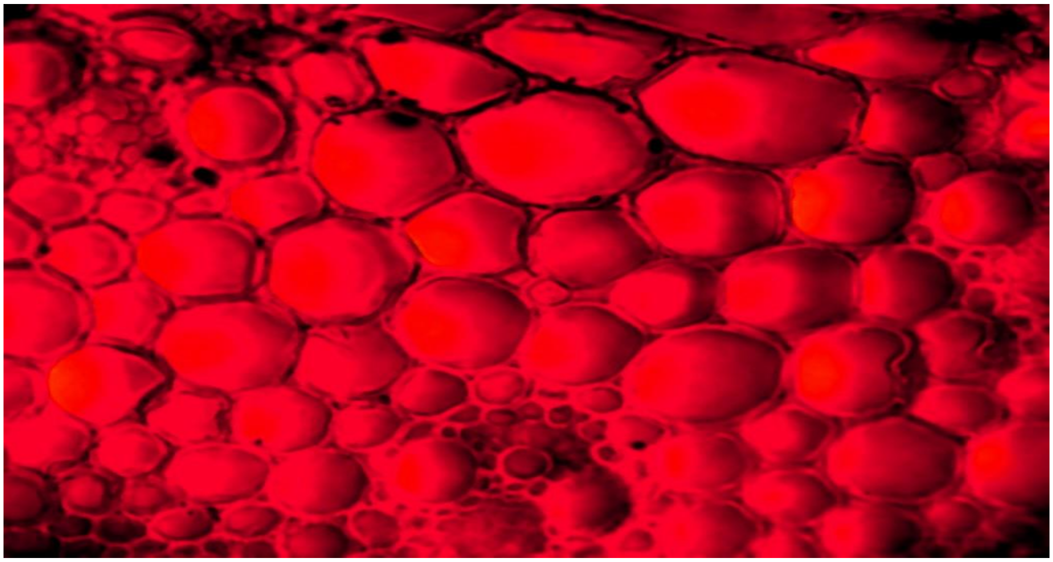


Figure 4.2 Fiber diameters, lumen diameter and cell wall thickness images by Motic Microscope (BA210, 100X magnified)

The average measured values of teff straw fiber dimension which were obtained from the experiments and their derived values computed by equation (3.1) to (3.4), were then computed to some non-wood and hardwood to access the acceptability of raw material for the pulp and paper production.

Table 4 .1: Fiber dimensions of teff straw

Fiber dimension	Symbol	Average value
Fiber length (mm)	L	1.235 ± 0.078
Fiber diameter (μm)	D	15.30 ± 5.18
Lumen width (μm)	LW	21.28 ± 5.77
Cell wall thickness (μm)	CWT	3.83 ± 0.64
	Derived values	
Derived indices	Formula	Average values
Slenderness ratio	L/D	80.78 ± 0.015
Runkel ratio	2CWT/LW	0.36 ± 0.22
Flexibility coefficient (%)	(LW/D) * 100	138.7 ± 1.11
Wall rigidity (%)	(CWT/D) * 100	25 ± 0.12

Table 4.2: Morphological characteristics of teff straw and other plants

Parameter	Wheat straw	Bagasse	Eucalyptus species	Enset ventricosum stem	Teff straw
Fiber length (mm)	1.18	1.7	0.6-1.2	1.66	1.235
Fiber diameter (µm)	13.6	23	13-27	28.48	15.30
Lumen width (µm)	5.68	19.55	5-15	25.87	21.28
Cell wall thickness (µm)	3.96	4.77	2.3-5.2	2.88	3.83
Slenderness Ratio	86.76	73.4	2.28-55.18	58.48	80.78
Runkle ratio	1.39	0.49	0.4-1.64	0.22	0.36
Flexibility coefficient	41.76	85	34-72	90.83	138.7
Wall rigidity coefficient	28.38	23.7	28-62	21.4	25
Source	Singh *et al.*, 2011	Singh, 2004 a	Gedefaw A., 2015	Hanna *et al.*, 2018	Current study

The fiber morphology and the values derived from teff straw fiber are presented in table 4.1 and teff straw has good derived values (especially slenderness ratio) compared to those of some non-wood plants and hard wood. Generally, it is stated that if the slenderness ratio of fibrous material should be greater than 70 to be valuable for quality pulp and paper production (Ververis *et al.*, 2004). Therefore, papers made from teff straw fibers are expected to have increased strength and suitable for writing, printing, wrapping and packaging purposes. The length of teff straw fibers (1.23mm) was found to be nearly within the same range as hardwood (Eucalyptus species) and other agricultural residues, such as rapeseed residue (1.19) (Enayati *et al.*, 2009) but, shorter than that of wheat straw, bagasse and Enset ventricosum stem.

The cell wall thickness of teff straw fiber (3.83µm) is longer than that Enset ventricosum stem; but, shorter than that of bagasse and wheat straw. The thickness of the fiber wall has an important bearing on most paper properties, with thick-walled fibers forming bulky sheets of low tensile, burst and folding endurance but with a moderate tearing strength (Haygreen and Bowyer, 1996). The teff straw fiber has also a good Runkel ratio which is greater than that of Enset ventricosum stem and smaller than that of wheat straw, bagasse and Eucalyptus species. Higher

Runkel ratio fibers are stiffer, less flexible and form bulkier paper of lower bonded areas than lower Runkel ratio fibers (Ververis *et al*., 2004). High average fiber length and low Runkel ratio result in good pulp properties (Shakhes *et al*., 2011).

4.1.2. Teff Straw Proximate and Chemical Compositions Analysis

Chemical composition of teff straw was determined by applying standard isolation methods for major plant chemical components (cellulose, hemicellulose, Klason lignin, extractives matter, ash content and moisture content).

4.1.2.1. Proximate analysis

The moisture content and ash content of teff straw were analyzed; and the results were reported on the basis of an oven-dried raw material and compared with some other plants' contents.

Table 4.3: Proximate analysis of tefff straw and some plants.

Agricultural residue	Ash content (%)	Moisture content (%)	Reference
Sun dried banana pseudo stem	11.4	12.4	Tesfaye K., 2018
Wheat straw	7.9	6.9	Gedefaw A., 2015
Teff straw	7.89	na	Andualem Tonamo *et al*., 2015
Teff straw	6.78	5.69	Current study
Bagasse	3.8	na	Dutt, 1994
Rice straw	16.6	na	Tutus *et al*., 2010.

na: not available

The mineral component of lignocellulosic material is generally indicated as ash content (Shakhes *et al*., 2011). The ash content is undesirable during refining and recovery of cooking liquors (Rodra-Gueza *et al*., 2008). It also causes operational problems in material handling and in the pulp washing process as the trace elements interfere with the bleaching agents such as H_2O_2 (Akpakpan *et al*., 2012). The ash content of teff straw (current study) was markedly higher than that of bagasse; but lower than that of wheat straw, banana pseudo stem and rice straw. The ash content of teff straw which was collected from Dawaro zone and studied by Andualem Tonamo *et al*., (2015) is obviously higher than that of current study which was collected from Tullubolo (South Western of Addis Ababa). According to the study by Han (1998), chemical composition of annual plants varies not only based on the type and cultivar of cereals but also in respect to the geographic location of cereals, climate and soil conditions.

Teff straw had less moisture content as analysis made by this study when compared to wheat straw and banana pseudo stem. The high moisture content can affect the mechanical and surface properties of the paper produced which indicates a less dimensional stability against the grain. The presence of extractives can influence the wettability of materials (Young, 1976; Hes and Kuo, 1988). The low wettability is related to the existence of non-polar extractives (Nguyen and Johns, 1979). Generally, there is waxy layer on crop material surface (Loxton and Hague, 1996; Sauter, 1996). Quality paper needs a very good dimensional stability against the grain because the structure and the strength of the paper depend on it. Cellulose fiber can swell from 15 to 20% from dry condition to saturation where it can cause the change in dimension stability. Such change in dimension will make the dimensional stability decrease cause the undesirable cockling and curling in the dimensional stability of the paper (Rafiu, 2015).

4.1.2.2. Chemical compositions

The chemical composition of the lignocellulosic material has a strong influence on the fiber properties. Cellulose is the main strength-giving component; as hemicelluloses are softeners in the wet state, and lignin gives wet stiffness and resistance to strength development through refining. Cellulose removal rate highly depends up on loss of physical protection from lignin and hemicelluloses (Hendricks and Zeeman, 2009).

Table 4.4: Chemical composition teff straw and other materials

Agro residue	Cellulose (%)	Hemicellulose (%)	Lignin (%)	Extractives (%)	Reference
Wheat straw	43.2	28.5	21.12	5.3	Singh *et al*., 2011
Rice straw	32	24	18	na	Goyal & Ray, 1989
Bagasse	42	28.45	20.3	1.73	Dutt, 1994
Teff straw	39.4	29.6	14	7.2	Current study
Hardwood	38-48	na	23-30	na	Ward *et al*., 2008
Softwood	40-45	na	26-34	na	Ward *et al*., 2008

na: not available

The percentage values of cellulose, hemicellulose lignin and extractives soluble in alcohol-benzene of teff straw and some other plants were compared and summarized in Table 4.4.

According to chemical composition analysis of current study, the cellulose content of teff straw is higher that rice straw, lower than that of bagasse and wheat straw; but in the range of hardwood. Chufo *et al*., (2015) investigated the composition of teff straw cellulose (36.7 ± 3.2) which was collected from Gamo Gofa. So, teff straw is one of the promising agricultural residues of pulp and paper production of Ethiopia. Cellulose is the component that makes the fiber inside non-wood materials stronger. These are important parameters in determining the suitability of a raw material for pulp and papermaking. According to rating system designated by Nieschlag *et al*., (1960) plant materials with 34% and over α-cellulose content were characterized as promising for pulp and paper manufacture from chemical composition point of view. The α-cellulose content of a raw material, which is directly correlated with pulp yield, the quality of fiber produced from non-wood materials depends on the contents of cellulose, hemicellulose, and holocellulose (Jahan *et al*,. 2010). Higher contents of cellulose can provide stronger fibers, thereby increasing the quality of the paper produced.

It has also higher amount of hemicellulose than the other agro residues as it can be seen from the above table. The higher the hemicellulose contents, the weaker will be the mechanical properties of the produced paper like tensile and burst index. The result also showed that teff straw contains lower lignin content than that of other plant materials. Low lignin content has been reported as one of the advantages inherent in the use of non-wood materials for pulp production as lignin functions as adhesive to bind the cellulose fiber together. Also, materials with low lignin contents require relatively small amount of chemical for pulping (Hurter, 1998). Lower lignin content is easier to discard from the pulp, and the paper that will be produced is of greater quality compared to that from other non-wood materials. The amount of lignin is directly related to the consumption of cooking liquor and the length of cooking cycle. The value of lignin content indicates that milder condition of pulping is required to obtain a satisfactory Kappa number in shorter cooking time.

The extractives content of the teff straw was 7.2% which is higher than wheat straw 5.3 (Vargas *et al*., 2012) and bagasse 1.73% (Jimenez *et al*., 2005); but, lower than barley straw 8.3% (Ferrer *et al*., 2015).The extractives fraction consist primary of resin and fatty acids and their esters;

along with waxes and unsaponifiable substances (Babtista *et al.*,2006). Higher extractives increase the chemical consumption during pulping and bleaching processes and may lead to pitch deposits in mill machinery. This may result in high maintenance costs and decrease the quality of the final product (Gellerstedt *et al.*, 1986).

4.2. Soda-Anthraquinone pulping of Teff Straw

In this study, the experimental data analysis was carried out using response surface methodology (RSM). Three factors (process variables) were chosen and central composite design (CCD) was used to determine the effect of each variable on the model of pulping process. Operational variables, experimental values of pulp yield and kappa number obtained by soda-anthraqiunone pulping of teff straw are given in table 4.4. These results were inputs to the DESIGN EXPERT® software version 7.0.0 for further analysis and the statistical analysis of the pulping conditions is discussed in the following section.

Table 4.5: CCD and results obtained

Std	Run	Process Factors						Response 1; Pulp yield (%)	Response 2; Kappa number
		Coded			Actual				
					Temp. (°C)	Time (min)	NaOH (%)		
6	1	-1.0	1.0	-1.0	130.00	120.00	10.00	26.7	30.3
4	2	1.0	-1.0	-1.0	150.00	60.00	10.00	23.9	34.4
17	3	-2.0	0.0	0.0	120.00	90.00	15.00	22.8	38.7
24	4	0.0	0.0	0.0	140.00	90.00	15.00	35.3	22.97
20	5	0.0	2.0	0.0	140.00	150.00	15.00	29.5	15.5
25	6	0.0	0.0	0.0	140.00	90.00	15.00	36.4	22.4
10	7	-1.0	-1.0	1.0	130.00	60.00	20.00	28.3	28
8	8	1.0	1.0	-1.0	150.00	120.00	10.00	26.5	23.5
27	9	0.0	0.0	0.0	140.00	90.00	15.00	35.9	22.05
19	10	0.0	-2.0	0.0	140.00	30.00	15.00	24.8	34.3
16	11	1.0	1.0	1.0	150.00	120.00	20.00	29.9	13.6
1	12	-1.0	-1.0	-1.0	130.00	60.00	10.00	20.2	39.79
22	13	0.0	0.0	2.0	140.00	90.00	25.00	28.3	18.7

11	14	1.0	-1.0	1.0	150.00	60.00	20.00	33.4	22.5
26	15	0.0	0.0	0.0	140.00	90.00	15.00	34.8	21.1
3	16	1.0	-1.0	-1.0	150.00	60.00	10.00	24.3	34.37
13	17	-1.0	1.0	1.0	130.00	120.00	20.00	29.5	23
15	18	1.0	1.0	1.0	150.00	120.00	20.00	32.3	13
18	19	2.0	0.0	0.0	160.00	90.00	15.00	28.8	23.3
9	20	-1.0	-1.0	1.0	130.00	60.00	20.00	28.9	28.78
7	21	1.0	1.0	-1.0	150.00	120.00	10.00	27.2	23.05
21	22	0.0	0.0	-2.0	140.00	90.00	5.00	17.2	40.2
23	23	0.0	0.0	0.0	140.00	90.00	15.00	35.4	23.8
14	24	-1.0	1.0	1.0	130.00	120.00	20.00	30.1	22.8
12	25	1.0	-1.0	1.0	150.00	60.00	20.00	32.5	22
5	26	-1.0	1.0	-1.0	130.00	120.00	10.00	27.8	31.14
2	27	-1.0	-1.0	-1.0	130.00	60.00	10.00	22.6	38.7
a)	28	_	_	_	145.1	71.5	13.76	29.2	32.8
b)	29	0	0	0	140	90	15	33.5	30.4

Soda pulping of teff straw at optimum operating conditions (a) and at center points of operating variables (b) without addition of AQ.

From the analysis indicated in table 4.4, soda pulping of teff straw with 0% AQ at optimum pulping conditions obtained from RSM/CCD (Table 4.10) and at center points of pulping parameters (140℃, 90 min. and 15% NaOH) was done. The effects of AQ on pulp yield and Kappa number were compared. The results showed that pulp yield was increased by 5.8% and Kappa number was decreased by 26.1% when 0.2% of AQ was added to the pulping process at optimum operating conditions. At center points of process variables, addition of 0.2% AQ to soda pulping of teff straw increased the pulp yield to 12.07% and reduced Kappa number by 20.94%. The increase in pulp yield and decrease in Kappa number can be explained on the basis of catalytic redox activity of AQ. AQ is the pulping additive that accelerates delignification and protects carbohydrate against degradation (Singh *et al.*, 2011). The difference in pulp yield with soda-AQ pulps, compared to the soda method can be attributed to the retention of hemicelluloses; once the absolute proportion of the cellulose remains constant with pulping

(Atik, 2002; Copur et al., 2007; Lowendahl & Samuelson, 1978; Nelson & Irvine, 1992). This shows the addition of AQ in soda pulp can be used to reach a certain Kappa number in shorter cooking time resulting in advantage of shorter process and reduced energy consumption.

4.2.1. Effects of pulping conditions on pulping process

4.2.1.1. The effect of Individual Process variables on Teff straw pulp yield and kappa number

Percent yield of teff straw pulp was calculated by equation (3.13) and the results are presented in table 4.4.

The maximum pulp yield obtained was 36.4 at the cooking temperature of 140℃, 90 minutes of holding time and 15% of NaOH concentration. The minimum pulp yield 17.2% was found at 5% NaOH concentration, 140℃ and 90 minutes cooking time.

Effects of temperature on pulp yield

As it can be observed from figure 4.4, temperature has a positive effect on pulp yield of teff straw for the temperature increment from 120℃ to 140℃ (the yield was increased from 21.5 to 30.24%) and decreased when temperature is increased from 140℃ to 160℃ (30.24 to 27.5%) by keeping other two factors at their central points. This shows temperature has a significant impact on reaction rate of soda-anthraquinone pulping of teff straw. As the temperature increases, the dissolving capacity of sodium hydroxide increases. Before 140°C, the amount of dissolved lignin increases; and this makes pulp yield increases. After 140°C, the pulp yield begins to drop; because of higher temperature, cooking of teff straw damage pulp yield as the rate of delignification is much higher and degree of de-polymerization increases which can affect and damage the fibers; hence contributes in decreasing the yield.

During pulping, both lignin and cellulose are dissolved at different rates. This rate is much accelerated by increasing the temperature (Iglesias *et al*., 1996). There was a general decrease in the pulp yield and Kappa number due to increases in the pulping temperature at constant time (Akpakpan *et al*., 2011).

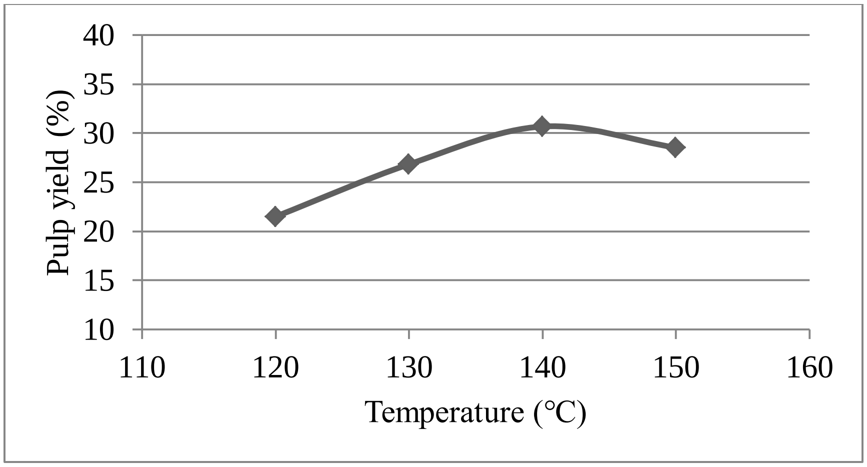


Figure 4.3 : The effect of temperature on pulp teff straw yield

The delignification reaction of the soda-anthraquinone pulping of teff straw was rapid and tended to increase with increasing cooking temperatures. The rapid reaction was probably because teff straw is a porous structure with pores much larger than those of the woody plants, thus, ensuring the penetration of the cooking liquor and a rapid delignification reaction due to higher content of hemicellulose which is branched and amorphous. Moreover, at the higher temperature, degradation of carbohydrate fractions increases; thereby resulting in a reduced pulp yields (Kleinert, 1965) due to peeling reactions (Hinrichs, 1967).

Effects of cooking time on pulp yield

Figure 4.5 shows the effect of cooking time on pulp yield of teff straw which is similar to that of temperature. Increasing cooking time from 30 mints to 90 minutes increases pulp yield averagely from 22.8 to 30.9% at center points of the other two factors. But further cooking the teff straw to the cooking time of 150 minutes was decreased the pulp yields because of severe cooking condition that could damage the cellulose.

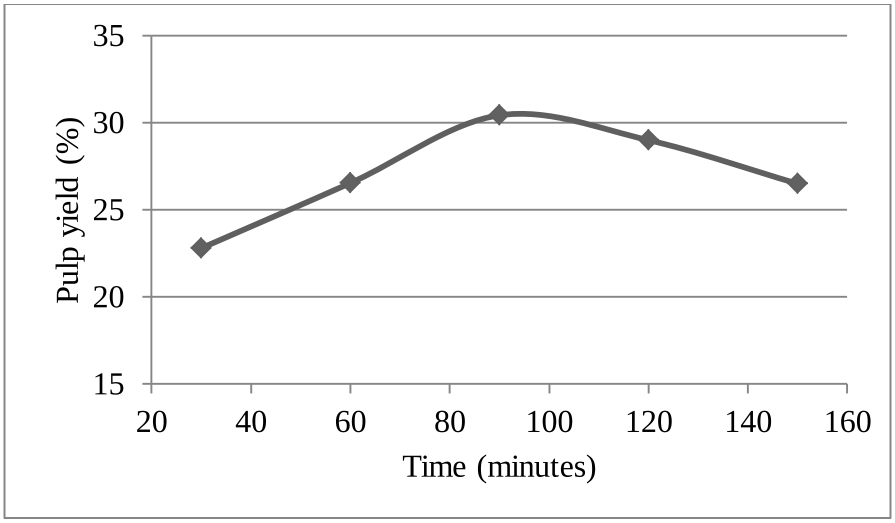


Figure 4.4: The effect of cooking time on teff straw pulp yield

Effects of sodium hydroxide charge on pulp yield

The increase in concentration of caustic soda (from 5 to 15%) highly improved the pulp yield of teff straw because of better delignification rate. But unfortunately pulp yield decreased as active alkali charges increased above 15%. The pulp yield decreases due to the cellulosic fibers degradation and solubilization of hemicelluloses in caustic soda.

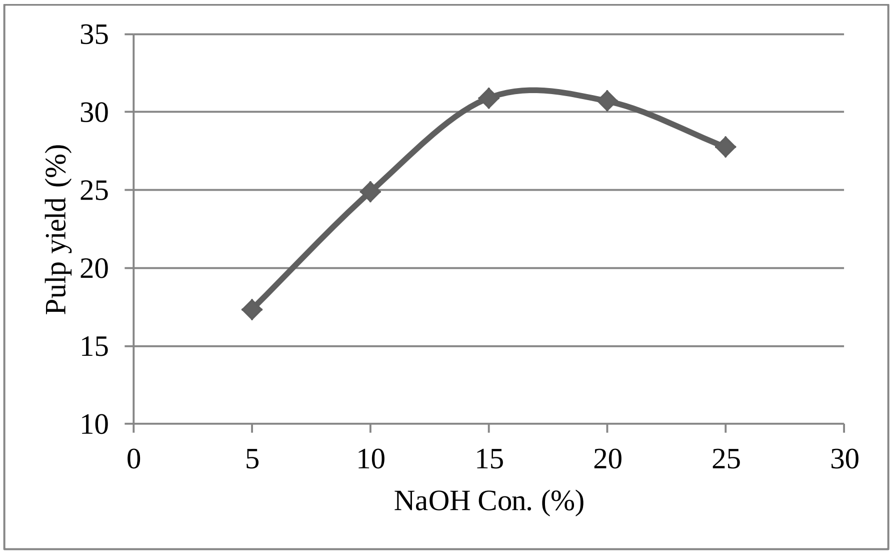


Figure 4.5: The effect of sodium hydroxide concentration on teff straw pulp

Effects of cooking temperature on Kappa number

As it can be seen from figure 4.6, when temperature is increased from 120℃ to 140℃, kappa number of teff straw pulp was decreased rapidly from 38.7 to 24.55 at 15% NaOH concentration and 90 minutes cooking time. Lower temperature makes the lignin remove insufficiently, which results in a high kappa number and as temperature increases the degree of delignification is high (bulk delignification) which can result in lower kappa number. When cooking temperature was varied from 140℃ to 160℃ the kappa number was decreased slightly since slow solubilization of residual lignin. Bulky delignification correspond to the removal of easily accessible lignin present in the middle lamella; and the residual lignin corresponds the removal of lignin present in primary and secondary cell walls and central inter connections cavity (Singh *et al.*, 2011).

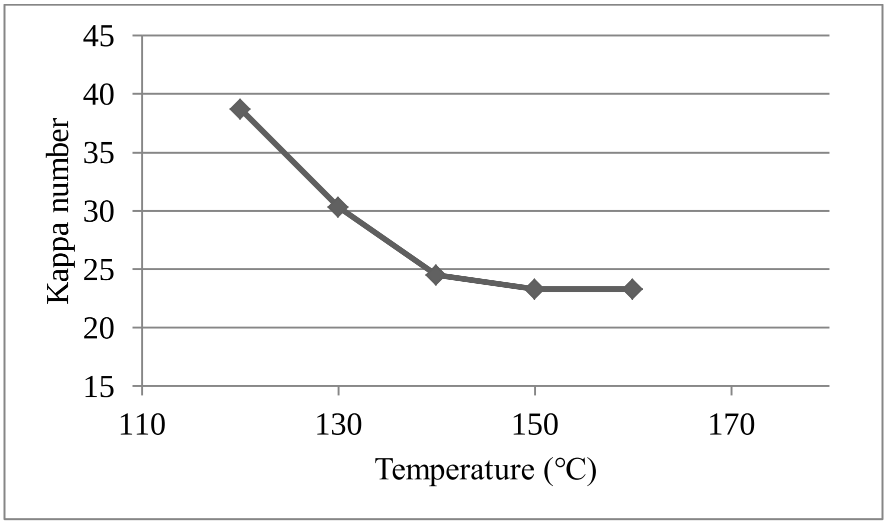


Figure 4.6: The effect of temperature on kappa number of teff straw pulp

Effect of cooking time on kappa number

Cooking time has higher effect on kappa number of teff straw pulp's as increasing the cooking time increases the rate of delignification and hence decreases the Kappa number.

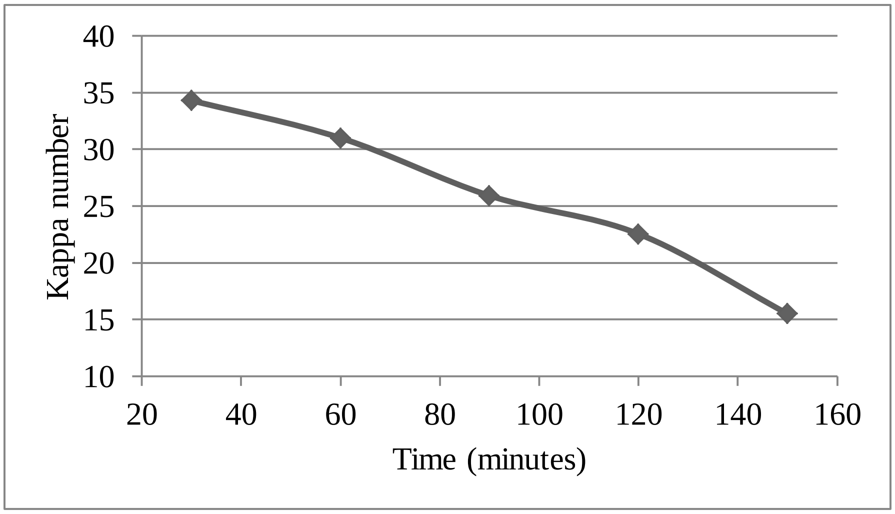


Figure 4.7: The effect of cooking time on kappa number of teff straw pulp

Effects of caustic soda on Kappa number

At lower amount of NaOH concentration (5%), small amount of pulp was obtained which has higher kappa number of 40.2. Increasing NaOH concentration from 5 to 25% by holding cooking temperature and time at their center point decreased Kappa number from 40.2 to 18.7. But, carbohydrates degradation is very fast than delignification rate at higher NaOH concentration which can lead the higher loss of pulp yield.

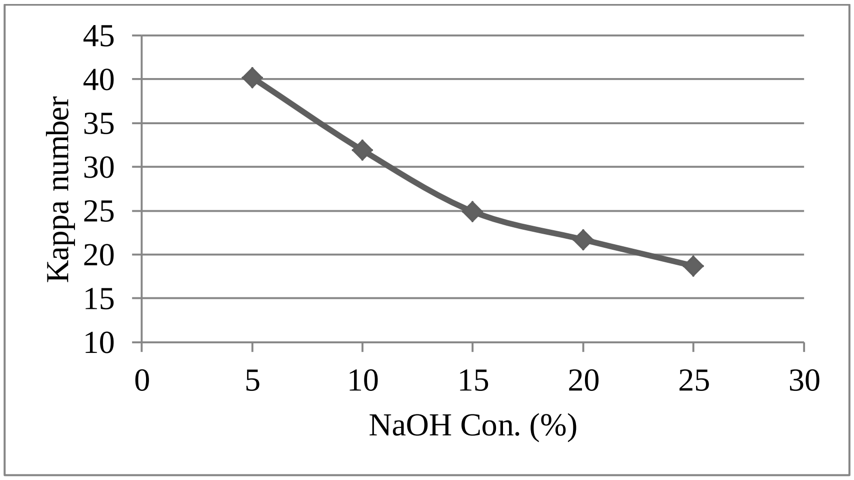


Figure 4.7 : The effect of sodium hydroxide concentation on kappa number of teff staw pulp

Generally, since teff straw has low lignin content, it requires moderate pulping conditions to get good pulp yield and satisfactory kappa number.

4.2.1.2. Interaction Effects of Process Variables on Pulp Yield and Kappa number

An interaction occurs when the response is different depending on the settings of two factors. Plots make it easy to interpret two factor interactions. They will appear with two non-parallel lines, indicating that the effect of one factor depends on the level of the other. The contour plots of each effect were given under Appendix C of this document.

Effects of temperature and cooking time at constant concentration of NaOH

A pulp yield 21.4% and kappa number 39.24 were obtained at a temperature of 130°C, cooking time of 60 minutes and 10% NaOH concentration. Having the same concentration of NaOH, when temperature and cooking time were increased to 150°C and 120 minutes respectively, the pulp yield was increased to 26.85% and Kappa number was decreased to 23.27. These showed that increasing temperature and time at same concentration of NaOH had greater influence to bring better delignification reaction. The others points that indicated the effects of temperature and time on pulping condition were seen at constant 15% of NaOH concentration when temperature and time were increased from 140°C at time of 30 minutes to 160°C at a time of 90 minutes. The pulp yield was increased from 24.8 to 28.8% and the Kappa number was decreased from 34.4 to 23.3. But, these conditions hold true if increment of temperature and time do not go beyond the above points; otherwise it is obvious that over cooking and extended time pulping can reduce pulp yield significantly.

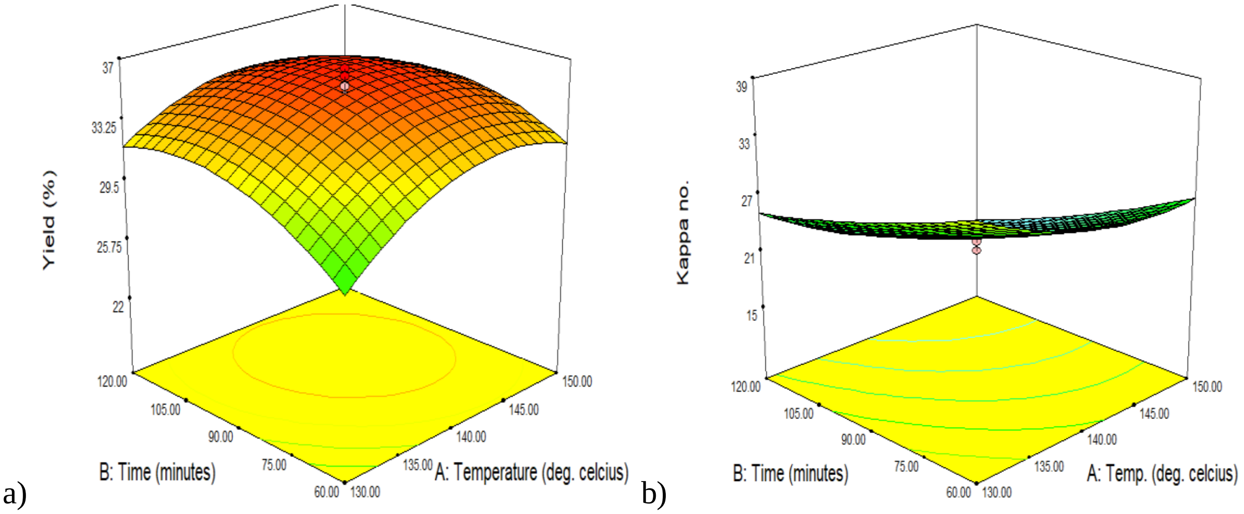


Figure 4.8: 3D plot of pulp yield (a) and Kappa number (b) showing the interaction effect of Temperature and cooking Time at constant 15% concentration of NaOH).

The effects of Temperature and NaOH concentration at constant cooking Time

Figure 6.9 represent the effect of temperature and NaOH concentration at constant cooking time of 90 minutes. The minimum pulp yield (17.2%) and a maximum Kappa number (40.2) were obtained at temperature of 140°C and 5% NaOH concentration when the cooking time was 90 minutes. This showed a low pulp yield of higher Kappa number; hence, weak delignification reaction and small amount of raw material (teff straw) was solubilized. The influences of temperature and NaOH concentration were see by increasing the temperature to 160°C and NaOH concentration to 15%; and the pulp yield was increased from 17.2% to 28.8 and Kappa number was decreased from 40.2 to 23.3. This shows greater interaction effects of temperature and NaOH concentration on pulp yield and kappa number of teff straw pulping process.

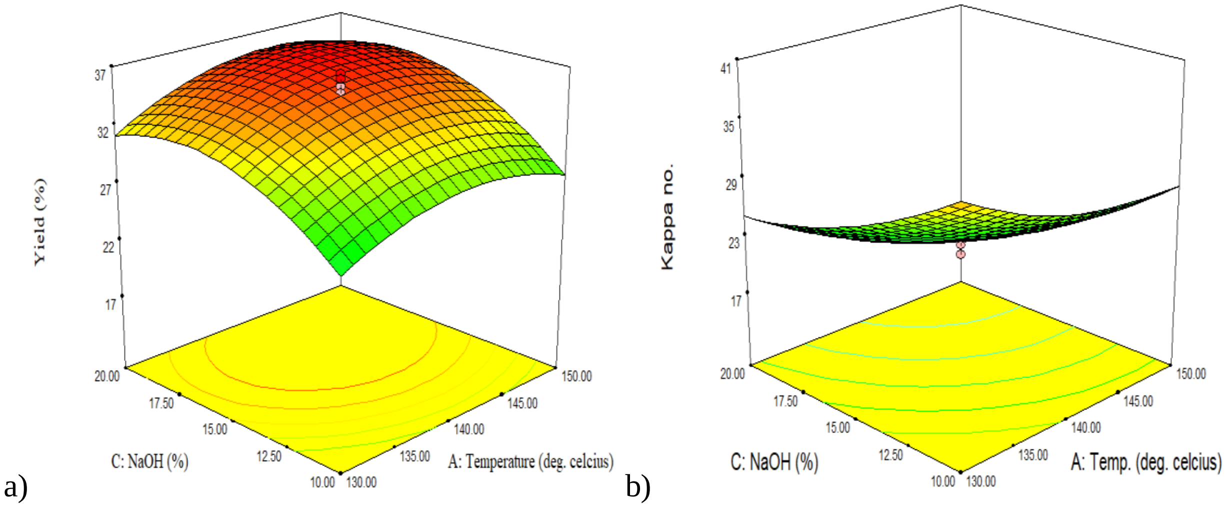


Figure 4.9: 3D plot of pulp yield (a) and Kappa number (b) showing the interaction effect of Temperature and NaOH concentration at 90 minutes constant cooking time.

Interaction effects of NaOH concentration and cooking time at constant cooking Temperature

As it can be seen from figure 4.10 below, increasing cooking time from 30 minutes to 150 minutes and NaOH concentration from 5 to 15% at constant temperature of 140°C had very significant effects on pulp yield and kappa number.

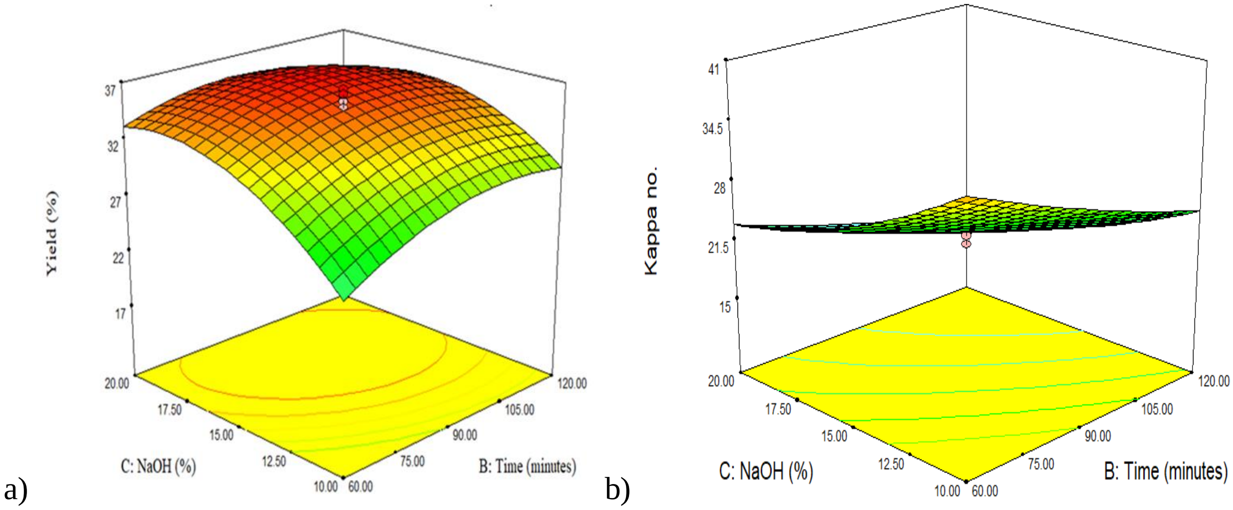


Figure 4.10: 3D plot of pulp yield (a) and Kappa number (b) showing the interaction effect of cooking Time and NaOH concentration 140°Cconstant cooking Temperature.

The pulp yield and kappa number were changed from 24.8 to 17.2% and 34.4 to 40.2 respectively when the cooking time was increased from 30 minutes to 90 minutes and the concentration of NaOH decreased from 15 to 5%. Here, the cooking time increment did nothing on pulping process when the concentration of NaOH was decreased to minim amount; but at the same condition of temperature (140°C) and time (90 minutes) and 15% of NaOH concentration, the maximum average of 35.56% pulp yield was obtained and the kappa number reduction to average of 22.46 was seen. The center points of the three factors were the best to get the maximum pulp yield of teff straw soda-anthraquinone pulping process.

4.2.2. Validation and Adequacy check for the developed quadratic models

It is usually necessary to check the fitted model to ensure it provides an adequate approximation to the real system. Unless the model shows an adequate fit, proceeding with investigation and optimization of the fitted response surface is likely to give misleading results. Graphical and numerical methods are the primary tools and give confirmation of the model fitting. The graphical method characterizes the nature of residuals of the models. A residual is defined as the difference between predicted and experimental value. The graphical residual analysis for both pulp yield and Kappa number indicated the residuals of the models were randomly distributed The data were plotted against a theoretical normal distribution in such a way that the points should form an approximate straight line, and a departure from this straight line would indicate a departure from a normal distribution, which was used to check the normality distribution of the residuals. As shown in (Appendix C; Figure C1 & C2), it is plausible that the assumptions of normality were satisfied for the data.

The models were then checked using a numerical method employing the analysis of variance. The regression model was found to be highly significant with the coefficient of determination (R^2), adjusted R^2 (R^2_{adj}) and predicted R-Squared. R^2 indicates how much of the observed variability in the data was accounted for by the model, while R^2_{adj} modifies R^2 by taking into account the number of covariates or predictors in the model. The quality of the model developed could be evaluated from their coefficients of correlation.

Based on ANOVA analysis in table 4.5, the regression model indicated that it was significant for both pulp yield and kappa number. The Model F-value of 112.26 for pulp yield and 368.9 for kappa number 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, AB,AC, BC, A^2, B^2, C^2 are significant model terms for pulp yield and A, B, C, AB,AC,BC, A^2, C^2 are significant model terms for kappa number. Values greater than 0.1000 indicate the model terms are not significant. If there are many insignificant model terms (not counting those required to support hierarchy), model reduction may improve your model. Model P value (Prob>F) is very low [<0.0001]. This reiterates that the model is significant. The P values are used as a tool to check the significance of each of the coefficients, which in turn are necessary to understand the pattern of the mutual interactions between the test variables.

Table 4.6: ANOVA for Response Surface Quadratic Model of pulp yield [Partial sum of squares]

Source	Sum of Squares	Df	Mean Square	F Value	p-value Prob > F	
Model	626.72	9	69.64	112.26	< 0.0001	significant
A-Temp.	32.43	1	32.43	52.29	< 0.0001	
B-Time	26.67	1	26.67	42.99	< 0.0001	
C-NaOH	192.10	1	192.10	309.68	< 0.0001	
AB	9.46	1	9.46	15.24	0.0011	
AC	2.81	1	2.81	4.52	0.0484	
BC	21.39	1	21.39	34.48	< 0.0001	
$A^{\wedge 2}$	143.65	1	143.65	231.58	< 0.0001	
$B^{\wedge 2}$	106.75	1	106.75	172.09	< 0.0001	
$C^{\wedge 2}$	247.15	1	247.15	398.42	< 0.0001	
Residual	10.55	17	0.62			
Lack of Fit	1.60	5	0.32	0.43	0.8201	not significant
Pure Error	8.95	12	0.75			
Cor Total	637.27	26				

The "Lack of Fit F-value" of 0.43 implies the Lack of Fit is not significant relative to the pure error. There is a 82.01% chance that a "Lack of Fit F-value" this large could occur due to noise. Non-significant lack of fit is good. This means that the model can be used for the experiment.

Table 4.7: ANOVA for Response Surface Quadratic Model of Kappa number [Partial sum of squares]

Source	Sum of Squares	Df	Mean Square	F – Value	P –value Prob > F	
Model	1591.34	9	176.82	368.90	< 0.0001	significant
A-Temp.	314.58	1	314.58	656.33	< 0.0001	
B-Time	465.96	1	465.96	972.17	< 0.0001	
C-NaOH	646.57	1	646.57	1348.98	< 0.0001	
AB	9.14	1	9.14	19.06	0.0004	
AC	2.95	1	2.95	6.15	0.0239	
BC	6.75	1	6.75	14.08	0.0016	
A^2	107.65	1	107.65	224.59	< 0.0001	
B^2	8.44	1	8.44	17.60	0.0006	
C^2	71.86	1	71.86	149.92	< 0.0001	
Residual	8.15	17	0.48			
Lack of Fit	2.39	5	0.48	1.00	0.4591	not significant
Pure Error	5.75	12	0.48			
Cor Total	1599.49	26				

The "Lack of Fit F-value" of 1.00 implies the Lack of Fit is not significant relative to the pure error. There is a 45.91% chance that a "Lack of Fit F-value" this large could occur due to noise. Non-significant lack of fit is good to show that the model to fit.

Table 4.8: Model adequacy measures for pulp yield and Kappa number

Pulp yield				Kappa number			
Std. Dev.	0.79	R-Squared	0.9835	Std. Dev.	0.69	R-Squared	0.9949
Mean	28.64	Adj R-Squared	0.9747	Mean	26.37	Adj R-Squared	0.9922
C.V. %	2.75	Pred R-Squared	0.9574	C.V. %	2.63	Pred R-Squared	0.9873
PRESS	27.13	Adeq Precision	38.585	PRESS	20.38	Adeq Precision	63.166

The "Pred R-Squared" of 0.9574 and 0.9873 is in reasonable agreement with the "Adj R Squared" of 0.9747 and 0.9922 for pulp yield and kappa number respetively.

"Adeq Precision" measures the signal to noise ratio or it is a measure of the range in predicted response relative to its associated error. A ratio greater than 4 is desirable. The ratio of 38.585 and 63.166 for pulp yield and kappa number respectively indicates an adequate signal. This model can be used to navigate the design space or decide whether the model can be used or not. The fit of the regression model to experimental samples data was also expressed by the coefficient of regression R^2, which was found to be 0.9835 and 0.9949 indicating that 98.35% and 99.49% the variability in the response could be explained by the model for pulp yield and kappa number respectively. The closer the value of R^2 (correlation coefficient) to 1, the better is the correlation between the experimental and predicted values. Since the values of R^2 (0.9835 and 0.9949) for both pulp yield and Kappa number close to 1, there is good indication of agreement between the experimental results and the theoretical values predicted by the model equation. In this model, 98.35% and 99.49% of the response variables (pulp yield and Kappa number respectively) is explained by the controllable variables (temperature, time and NaOH concentration) and 1.65% and 0.51% of pulp yield and kappa number respectively can be affected and explained by some external factors that did not appear in the model. This implies that the prediction of experimental data is quite satisfactory. R^2 value which is higher than 0.75 (>0.75) implies that the model can be used properly (Fibrillian Z. L. *et al.*, 2018). Furthermore, an R^2_{adj} close to the R^2 values insures a satisfactory adjustment of the quadratic models to the experimental data for both pulp yield and Kappa number.

Generally, the results indicated that it was successful in capturing the correlation between the three soda-anthraquinone pulping process variables to the pulp yield and Kappa number; and show how the data generated from developed model equation is close to the actual data obtained. The coefficient of variation (CV) is the error expressed as a percentage of the mean and computed as 100 x (Std Dev)/(Mean) and indicates the degree of precision with which the experiments are compared. Generally, the higher the value of the CV is, the lower the reliability of the experiment. Here a lower value of CV (2.75 for pulp yield and 2.63 for kappa number) indicates greater reliability of the experiments performed.

PRESS is the Predicted Residual Sum of Squares for the model which is a measure of how well a particular model fits each point in the design.

From the experimental data, quadratic regression models were obtained as shown in equations 4.1 to 4.4.

Final Model Equation of Pulp Yield in Terms of Coded Factors:

$$\begin{aligned}\text{Yield} = {} & +35.54 + 1.16*A + 1.05*B + 2.83*C - 0.77*A*B + 0.42*A*C - 1.16*B*C \\ & -2.45*A^2 - 2.11*B^2 - 3.21*C^2 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 4.1\end{aligned}$$

Where, A - Temperature (°C)

B - Time (min.)

C - NaOH Concentration (%)

Final Equation of Pulp Yield in Terms of Actual Factors:

$$\begin{aligned}\text{Yield} = {} & -544.87060 + 7.07153*\text{Temp.} + 0.93132*\text{Time} + 3.93792*\text{NaOH} \\ & -2.56250\text{E-}003*\text{Temp.}*\text{Time} + 8.37500\text{E-}003*\text{Temp.}*\text{NaOH} \\ & -7.70833\text{E-}003*\text{Time}*\text{NaOH} - 0.024465*\text{Temp.}^2 \\ & -2.34336\text{E-}003*\text{Time}^2 - 0.12836*\text{NaOH}^2 \ldots\ldots\ldots\ldots\ldots\ldots 4.2\end{aligned}$$

Final Equation of Kappa number in Terms of Coded Factors:

$$\begin{aligned}\text{Kappa no.} = {} & + 22.42 - 3.62*A - 4.41*B - 5.19*C - 0.76*A*B - 0.43*A*C + 0.65*B*C \\ & +2.12*A^2 + 0.59*B^2 + 1.73*C^2 \ldots\ldots\ldots\ldots\ldots\ldots 4.3\end{aligned}$$

Final Equation of Kappa number in Terms of Actual Factors:

$$\begin{aligned}\text{Kappa no.} = {} & +493.97794 - 5.93651*\text{Temp.} + 0.022243*\text{Time} - 2.30187*\text{NaOH} \\ & -2.51875\text{E-}003*\text{Temp.}*\text{Time} - 8.58750\text{E-}003*\text{Temp.}*\text{NaOH} \\ & +4.32917\text{E-}003*\text{Time}*\text{NaOH} + 0.021178*\text{Temp.}^2 \\ & +6.58719\text{E-}004*\text{Time}^2 + 0.069214*\text{NaOH}^2 \ldots\ldots\ldots\ldots\ldots\ldots 4.4\end{aligned}$$

Model equations of both coded and actual factors can be used to make predictions about the response for given levels of each factor. The coded model equation is useful for identifying the relative impact of the factors by comparing the factor coefficients. Whereas, equation in terms of actual factors should not be used to determine the relative impact of each factor because the coefficients are scaled to accommodate the units of each factor and the intercept is not at the center of the design space.

4.2.3. Process factors and response variables optimization

Optimization is the act of achieving the best possible result under given circumstances. One of the objectives of this study was to find the optimal process parameters for better pulp yield at minimum kappa number. Optimization allows generating predicted response(s) for any set of factors. The process variables such as cooking temperature, concentration of NaOH and pulping time have been optimized 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, 400g teff straw pulp was produced and paper sheets formed. The produced paper sheet was tested for several strength and optical properties.

Table 4.9: Summary of constraint responses and goals of optimization

Constraints Name	Goal	Lower limit	Upper limit	Lower weight	Upper weight	Importance
Temp.	is in range	130	150	1	1	3
Time	minimize	60	120	1	1	3
NaOH	minimize	10	20	1	1	3
Yield	maximize	17.2	36.4	1	1	3
Kappa no.	minimize	13	40.2	1	1	3

Optimization of pulp yield and Kappa number was carried out by a multiple response method called desirability (D) function to optimize different combinations of process parameters. The desirability lies between 0 and 1, which represents the closeness of a response to its ideal value. If a response falls within the unacceptable intervals, the desirability is 0 and if a response falls within the ideal intervals or the response reaches its ideal value, the desirability is 1. Meanwhile, when a response falls within the tolerance intervals but not the ideal interval, or when it fails to reach its ideal value, the desirability lies between 0 and 1. Based on desirability analysis 27 optimum points via numerical optimization generated (Appendix C, Table C3). As per the goals set in the criteria part the actual response out puts (pulp yield and kappa number) were almost the same since all the process variables in all possible solutions were very close to each other.

Table 4.10: Optimum operating point

Temp. (°C)	Time (min)	NaOH (%)	Yield (%)	Kappa no.	Desirability
145.13	71.5	13.76	33.1567	25.8512	0.686

The model validations have been determined as optimum levels of the process parameters to achieve the predicted optimum response variables. For the verification of this prediction, experiments were conducted and the result showed that 33.22% of pulp yield and 25.93 Kappa number. Therefore, the numerical optimization can be taken as optimal value because the predicted value is close enough with experimental.

Table 4.11: Model validation

Temperature (℃)	Time (min)	NaOH (%)	Yield (%)		Kappa no.	
145.13	71.5	13.76	Predicted	Experimental	Predicted	Experimental
			33.1567	33.2194	25.8512	25.93

4.2.4. Pulp Bleaching

As it was mentioned in the section 3.6, about 560g of un-bleached teff straw pulp that produced at optimum condition was bleached by alkali peroxide process in three stages before the formation of paper hand sheet. Evidently, the bleaching yield from the $Mg(OH)_2$ process was higher than that of the NaOH process because of bleaching condition was more severe for the NaOH process (FARHAD ZEINALY *et al.*, 2014). For example, at 4% peroxide charge, the bleaching yield was 94.85% averagely for the first and the third $Mg(OH)_2$ process, compared to 91.8% for the NaOH process. These results can be explained by the stronger reaction conditions of the NaOH-based process and accordingly, the higher production of hydrophilic functional groups and fiber swelling in this process which leads to degradation of soluble carbohydrates. The Kappa number of un-bleached pulp was 25.93; but, it was significantly reduced to 7.6 after three stages alkaline peroxide bleaching process. This showed that the removal of lignin present in un-bleached pulp after bleaching processes. The pulp yield and Kappa number at each stage were given in Table 4.11.

Table 4.12: The summary of bleaching result

Bleaching sequence	Pulp yield (%)	Kappa number
First stage	94.5	19.48
Second stage	91.8	12.2
Third stage	95.2	7.6

4.2.5. FTIR analysis of teff straw and pulp

FTIR analysis is an important technique for identifying functional groups. Each part of biomass has different types and amount of functional groups. For example, aromatic rings and hydroxyl functional groups are dominantly available in lignin component of the biomass. Peak strength increases in some functional groups due to the increment in surface area and loss of certain functional group due to removal of certain lignocellulosic part during chemical modification. Hence, to identify the types of functional groups in the un-treated and treated teff straw, an FTIR analysis was carried out from the powdered samples prepared in a KBr disk.

The spectra of the samples were measured within the range of 4,000–400 cm^{-1} and confirmed removal of certain functional groups after pulping and bleaching processes. A wide absorption (3420-3405 cm^{-1}) band focused at 3400 cm^{-1} is assigned to aromatic and aliphatic OH (hydroxyl) groups and bonded O-H stretching vibration present in carbohydrates (holocellulose). The peaks at 2,920 cm^{-1} can be assigned to the stretching vibration of the C–H groups (Alamri H and Low IM., 2012) present in cellulose. Compared to raw teff straw, the peak around 1740 cm^{-1} (due to carboxylic and carbonyl groups from aldehydes, ketones as well as aromatic rings mainly due to the C=O stretching of hemicelluloses (Suresh Kumar SM. *et al*., 2014) is highly reduced in NaOH-AQ treated teff straw and bleached pulp.

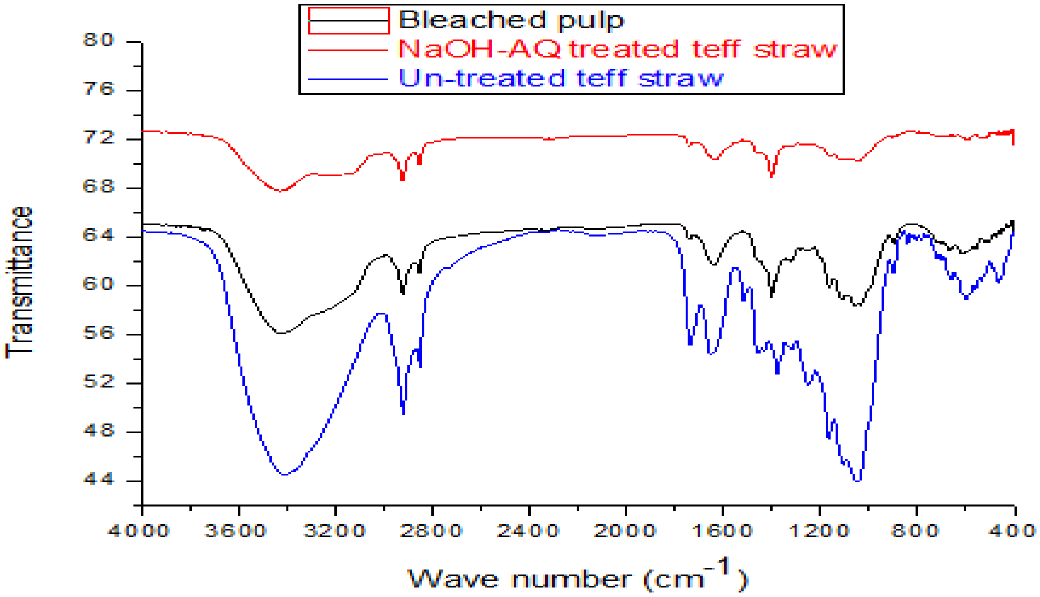


Figure 4.11: FTIR spectra analysis of teff straw and its pulp (unbleached and bleached)

The strong bands in 1700 - 1410 cm^{-1} region can be ascribed to aromatic skeletal vibrations (He *et al.*, 2008). The absence of the band in the NaOH-AQ treated teff straw and bleached pulp indicated the hydrolysis of ester functional groups (Lawther *et al.*, 1996). Furthermore, the absorption band at 1380 cm^{-1} is attributed to aliphatic C-H bending (Karthika *et al.*, 2012). The absence of this absorption band for NaOH-AQ treated teff straw showed a partial decomposition of aliphatic and release of $-CH_3$, and $-CH_2-$ groups. The decrease in the intensity of the absorption band at 1250 cm^{-1} (-C-O- stretching) for NaOH-AQ-treated teff straw and bleached pulp shows partial hydrolysis of ester functional groups (Xu et al., 2007).

The most noticeable effect of pulping of teff straw in FTIR spectra is the disappearance of the bands in un-treated teff straw found at 1515, 1270, 1115 and 855-810 cm^{-1} which represent aromatic ring stretch (C-C), (C-O) aromatic ring of lignin, in plane deformation vibration of aromatic ring in lignin (C-H) and out plane deformation vibration of aromatic C-H parts of lignin (A. Tejado *et al.*, 2007) respectively. The difference between absorption bands of NaOH-AQ treated teff straw (pulp) and bleached pulp can be seen from 850-765 cm^{-1} where most of in-plane and out-plane deformation vibration of lignin aromatic groups found in un-treated teff straw and highly removed in bleached teff straw pulp.

4.3. Paper hand sheet and some of mechanical properties test

By using combination of operating conditions corresponding to optimum results teff straw pulp were prepared; bleached, and hand sheets were made and different strength properties were tested as per the methods mentioned in section 3.8 and the result presented in following table and compared with the paper sheet made from that of hard wood pulp (short fiber) which is imported by Ethiopian Pulp and Paper Share Company and some non-wood plants.

As the results presented in the Table 4.13, the strength properties of paper sheet made from teff straw pulp were almost higher than that of wheat straw; lower than that of bagasse and it meets the minim standard specification set by ISO by its tensile index slightly except tear index and burst index. The reason for lower tear index was the fibers by being shorter in length and the degree of bond among fibers. The work done on pulling the short fibers out of a sheet is less than that required to break the fibers because of higher inter-fibers bond. As inter-fiber bonding increases, the proportion of the fiber that is fractured rather than pulled out rises (Singh *et al.*, 2011). The tear index is the function of fiber length (Akgül and Tozluo_lu, 2009; Azizi *et al.*, 2010; Shakes *et al.*, 2010). Therefore, teff straw paper can be used for the purpose printing and writing. The lower values of burst and tensile index came from the higher content of hemicellulose, which can make inter fibers bonding weaker.

Table 4.13: Strength properties of teff straw and some plants

Properties	Teff straw [a]	Bagasse [b]	Wheat straw [c]	Paper from imported pulp [d]	ISO requirement [e]
Gramme (g/m^2)	60	60	60	60	60
Breaking length (m)	4294.2	4850	na	4600	na
Tensile strength (kN/m)	7.578	na	na	na	na
Tensile index (Nm/g)	42.1	73.8	15.6-27.2	65-80	≥40
Tear index (mNm^2/g)	5.2	5.7	2.0-2.8	10-12	≥5.4
Burst index (kPam^2/g)	1.41	4.9	0.8-1.7	na	≥1.45
Porosity (se)	19.5	na	na	21	na

[a]: current study, [b]: INSAF GALAL ELDIN KARAR, [c]: MARIA T. GARCÍA *et al.*, 2015,
[d]: Ethiopian pulp and paper share company, [e]: International standard for Organizations, na: not available.

5. CONCLUSION AND RECOMMENDATION

5.1. Conclusions

This study was aimed at determining the morphological properties, the proximate and chemical composition of teff straw. Analysis of soda-anthraquinone teff straw pulping process and the influences of process variables (cooking temperature, cooking time and sodium hydroxide concentration) on response variables (pulp yield and Kappa number) were done. Some strength properties of the paper hand sheets made from teff straw pulp were also tested.

From the morphological characterization, the results indicated that the length of teff straw fibers (1.23mm) and its width (15.28μm) was found to be nearly within the same range as hardwood (Eucalyptus species) and other no-wood. This showed that teff straw had good slenderness ratio (80.78) that was comparable to that of bagasse and greater than the minimum requirement (70) to produce quality paper. Due to less fiber diameter and shorter fiber length, the sheets made from such types of fibers give more tear strength and higher porosity. The flexibility coefficient (138.7) and Runkle ratio (0.36) of teff straw resemble to those of bagasse fibers. Good flexibility coefficient indicates that the ability of fibers to collapse easily and to form inter fiber bonding important for paper strength.

The chemical composition of teff straw showed the cellulose content was 39.4%; hemicellulose (29.6%), lignin (14%), extractives (7.2%) and ash content (6.78%). It had acceptable content of the cellulose which was comparable to the reported cellulose content of hardwood (38-52%). Teff straw also had higher amount of hemicellulose than most of non-wood that made it to have a total carbohydrates fraction of (holocellulose) that was almost equal to that of hardwood. It also contains lower lignin content than most of non-wood plants; hence, it requires moderate pulping condition to reach satisfactory Kappa number. And it was also found that the teff straw contained moderate amounts of extractives and ash content.

For experimental design, Response Surface Methodology/Central Composite Design was used to compare the effects of cooking temperature (130, 140 and 150℃) cooking time (60, 90 and 120 minutes) and active alkali concentration (10, 15 and 20%) on pulp yield and Kappa number. The results indicated that the influence of NaOH concentration on both pulp yield and Kappa number was significantly higher than that of cooking time and cooking temperature. At the optimal pulping condition (13.76% active alkali, at 145.13°C for 71.5 minutes) pulp yield of 33.15% (on oven dried raw material) with kappa number 25.85 were obtained. Additionally, soda pulping of teff straw was done with 0% anthraquinone catalyst at optimum conditions to see its effect on pulp yield and Kappa number. The result showed that the pulp yield was increased by 5.8 % and Kappa number decreased by 26.1% when 0.2% anthraquinone was added to soda method.

By using combination of operating conditions corresponding to optimum results, the teff straw pulp was prepared; bleached and paper hand sheets of 60 g/m^2 were made and tested for strength properties. Breaking length (4294 m), tensile strength (11.6 kN/m), tensile index (42.1 Nm/g), tear index (5.2 $mN.m^2/g$) and burst index (1.41 $kPa.m^2/g$), and porosity of (19.5 se/100 air) were obtained. The tested strength properties were almost higher than that of wheat straw and lower than that of bagasse.

Teff straw is the most abundant agricultural residue in Ethiopia; hence, it has potential to be one of the significant sources of short fibers. So, this study offers a baseline for research focus on utilization of teff straw as an alternative material for pulp and paper application.

5.2. Recommendations

- Teff (Eragrostis tef) straw (obtained from brown teff) that has been used for the study was collected from specified part of farming area, but the mineral content the soil, geographical area and variety of the teff will have an impact on the pulp yield and physical properties of the sheet, therefore one can do investigate the effects by collecting teff straw from different parts of country and different species of teff and even by using them in combinations.
- Deep anatomical structures and analytical studies of teff straw chemical composition should be undertaken to identify the components of hemicelluloses (i.e. pentosans), extractives and lignin types.
- It is also possible to study the effects on pulp yield and paper sheet physical characteristics by using teff straw in combination with other widely available agricultural by products such as barley straw, wheat straw, etc. for industrial pulp and paper applications which might be feasible environmentally and economically.
- In industrial pulping of non-wood raw materials, higher content of silica and black liquor is the major by product released from the process containing both organic materials and

inorganic minerals which can be valuable inputs for petroleum industries and heat generation. Therefore investigations should be carried out on black liquor characterization and chemical recovery process.

- The method of chemical pulping of teff straw might be investigated if higher pulp yield and easily bleachable grade of pulp is obtained other than soda-anthraquinone pulping.
- Alkali-peroxide bleaching of teff straw pulp gave almost semi-bleached pulp; so, the other types of total chlorine free bleaching agents and oxygen such as chlorine oxide can be tested to get fully bleached paper sheet.
- Transportation and storage techniques of teff straw could be another research in the field work.

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APPENDICES

Appendix A: Supporting pictures during laboratory work

Figure A1: Raw material washing (a), Drying (b) and Size reduction (c)

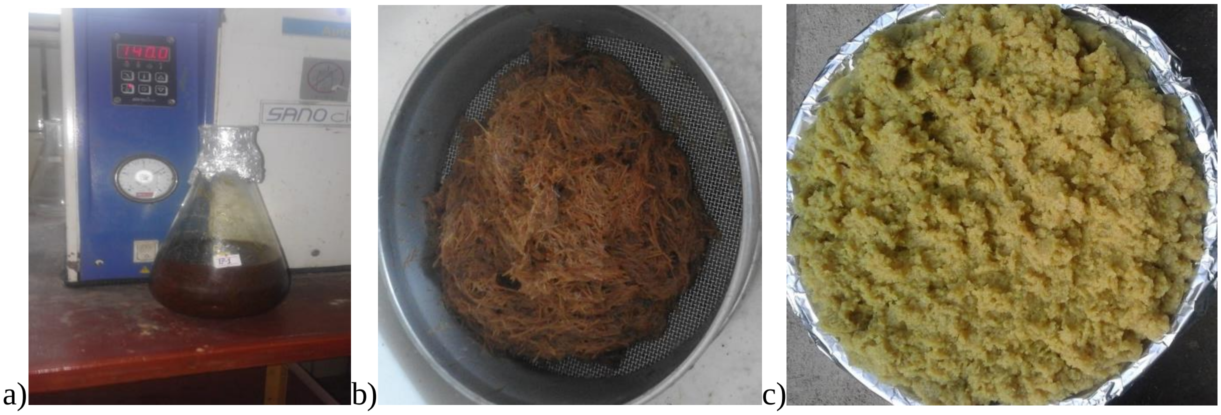


Figure A2: Cooked teff straw (a), Un-washed pulp (b) and Washed and un-dried pulp (c)

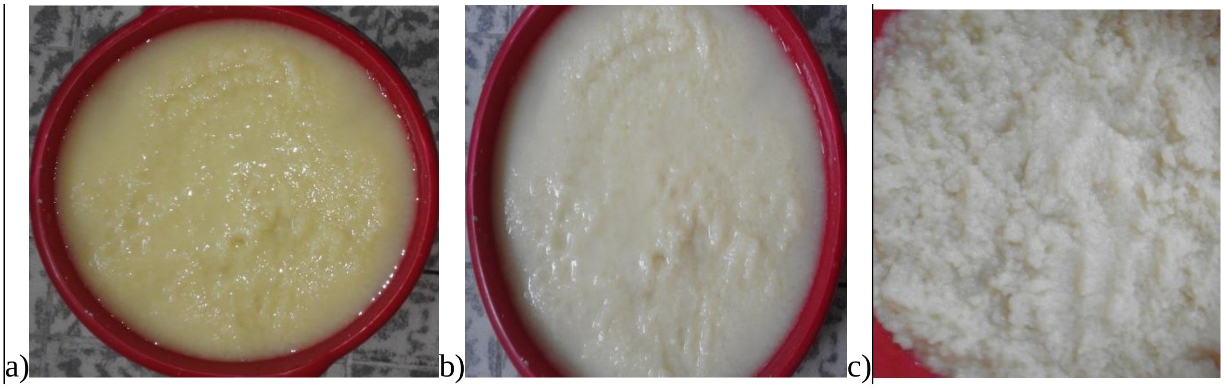


Figure A3: Bleached pulp after the first stage (a), second stage (b) and third stage (c).

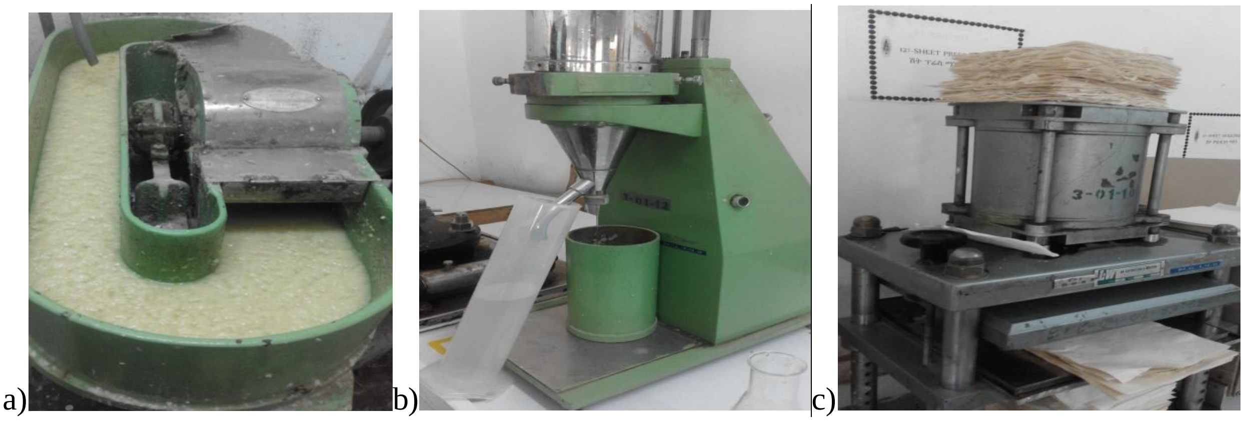


Figure A4: Beater machine (a), Freeness tester (b) and sheet molding (c)

Figure A5: Prepared pulp slurry for sheet forming (a) Un-dried sheet (b) Dried paper sheet (c)

Figure A6: Tensile strength tester (a) Tear strength tester (b) and Burst strength tester (c)

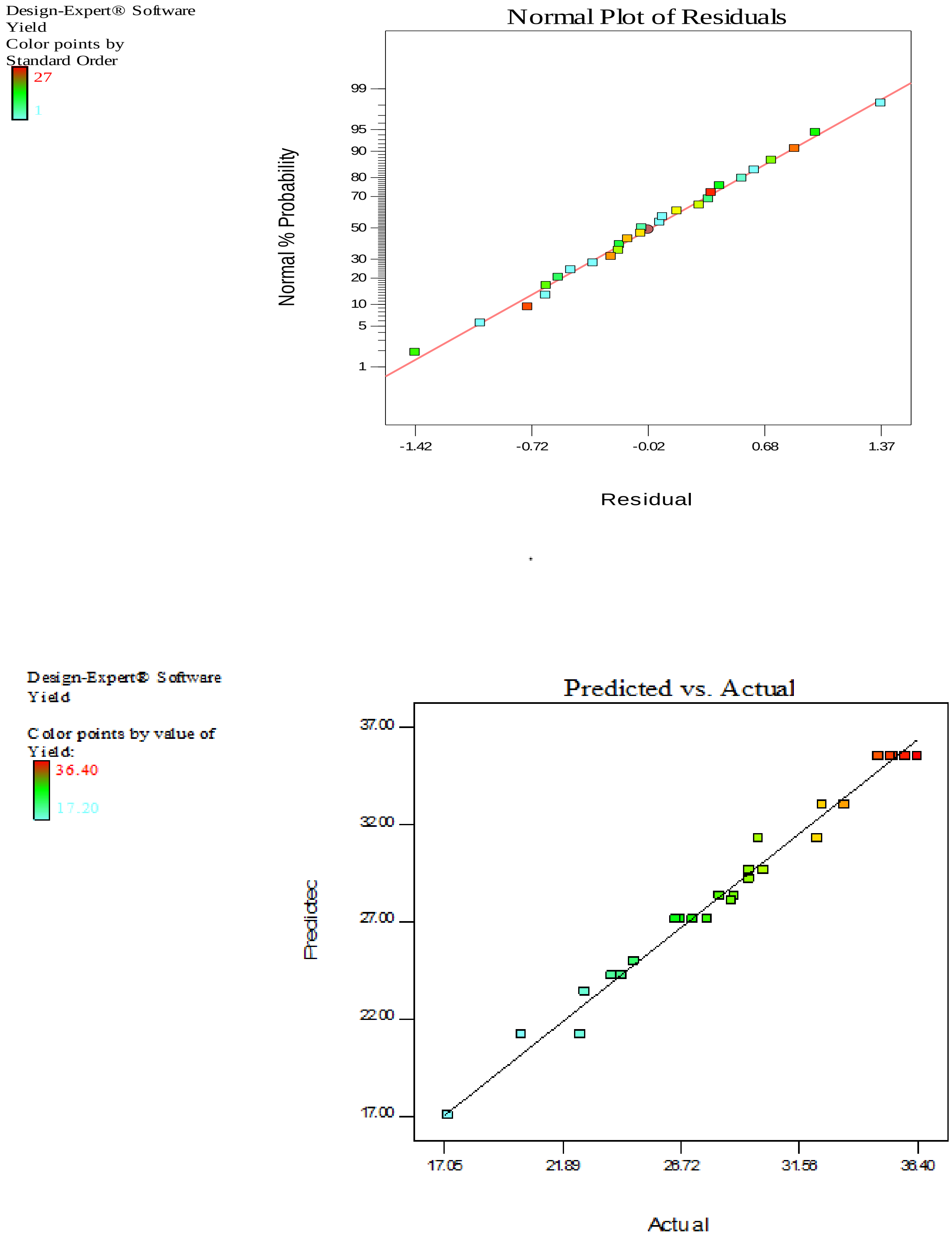
Appendix B: Fiber morphology data of teff (*Eragrostis tef*) straw

Table B1: Fiber length, width, lumen diameter and cell wall thickness of teff straw

No.	Fiber length (mm)	Fiber width (µm)	Lumen diameter(µm)	Cell wall thickness (µm)
1	1.2835	12.9	22.5	3.4
2	1.3423	20.3	16.67	3.6
3	1.2456	21.3	19.94	4.2
4	1.2195	18.4	25.9	4.5
5	1.2256	19.3	25.1	3.7
6	1.1931	22.9	12.41	4.3
7	1.16	21.4	22	4.7
8	1.1139	24	17.7	3.6
9	1.2112	20.4	16.5	2.9
10	1.1756	13.3	16.3	2.67
11	1.2111	17	15.6	3.5
12	1.1904	8	21	4.4
13	1.1928	10.3	17.4	3.9
14	1.2804	21.8	23	4.53
15	1.3206	5.1	16.8	3.82
16	1.1248	15.8	15.9	3.34
17	1.1946	16.5	14.5	3.53
18	1.2084	21.8	33	4.22
19	1.432	13.7	15.5	4.3
20	1.3145	5.8	16.8	3.7
21	1.3382	19.3	17.8	2.8
22	1.2216	9.3	33.6	4.72
23	1.3297	20.5	16.8	3.7
24	1.1835	17.5	26.9	3.53
25	1.2472	8.2	29.6	4.58
26	1.3576	25	24.5	3.98

27	1.1636	14.5	13.6	2.82
28	1.225	12.9	30.6	3.49
29	1.1735	12.9	26.7	3.53
30	1.1742	9.3	19.6	2.66
31	1.1357	11.5	25.78	4.79
32	1.13	16.3	27.5	4.63
33	1.4346	10.1	10.13	2.61
34	1.3179	8.2	21.98	3.8
35	1.2546	16.1	23.7	3.72
36	1.2902	13.2	27.9	3.8
37	1.1469	15.8	16.9	2.34
38	1.2135	17.7	14.89	4.45
39	1.1653	20.9	15.13	3.73
40	1.2591	8	16.19	3.98
41	1.289	8.2	13.4	3.9
42	1.1974	16	21.9	4.43
43	1.193	16	25.4	4.55
44	1.1979	23.1	26.89	3.6
45	1.2166	11.5	23.6	4.8
46	1.1973	12.2	28.67	4.53
47	1.3193	9.1	22.5	4.78
48	1.3981	19.8	28.54	3.45
49	1.1631	15.2	27.67	3.71
50	1.1849	16.1	21.5	3.45
Average	1.235168	15.288	21.2878	3.83

Appendix C: Design Expert data



a)

b)

Figure C1: Normal probability plots versus Residual (a) and Predicted versus actual experimental value (b) for pulp yield

Table C1: Difference between the actual (experimental) value and predicted value of pulp yield

Standard order	Actual value	Predicted value	Residual	Run order
1	20.20	21.23	-1.03	12
2	22.60	21.23	1.37	27
3	24.30	24.25	0.049	16
4	23.90	24.25	-0.35	2
5	27.80	27.18	0.62	26
6	26.70	27.18	-0.48	1
7	27.20	27.13	0.066	21
8	26.50	27.13	-0.63	8
9	28.90	28.36	0.54	20
10	28.30	28.36	-0.059	7
11	33.40	33.06	0.34	14
12	32.50	33.06	-0.56	25
13	29.50	29.69	-0.19	17
14	30.10	29.69	0.41	24
15	32.30	31.32	0.98	18
16	29.90	31.32	-1.42	11
17	22.80	23.43	-0.63	3
18	28.80	28.08	0.72	19
19	24.80	25.00	-0.20	10
20	29.50	29.21	0.29	5
21	17.20	17.05	0.15	22
22	28.30	28.36	-0.065	13
23	35.40	35.54	-0.14	23
24	35.30	35.54	-0.24	4
25	36.40	35.54	0.86	6
26	34.80	35.54	-0.74	15
27	39.9	35.54	0.36	9

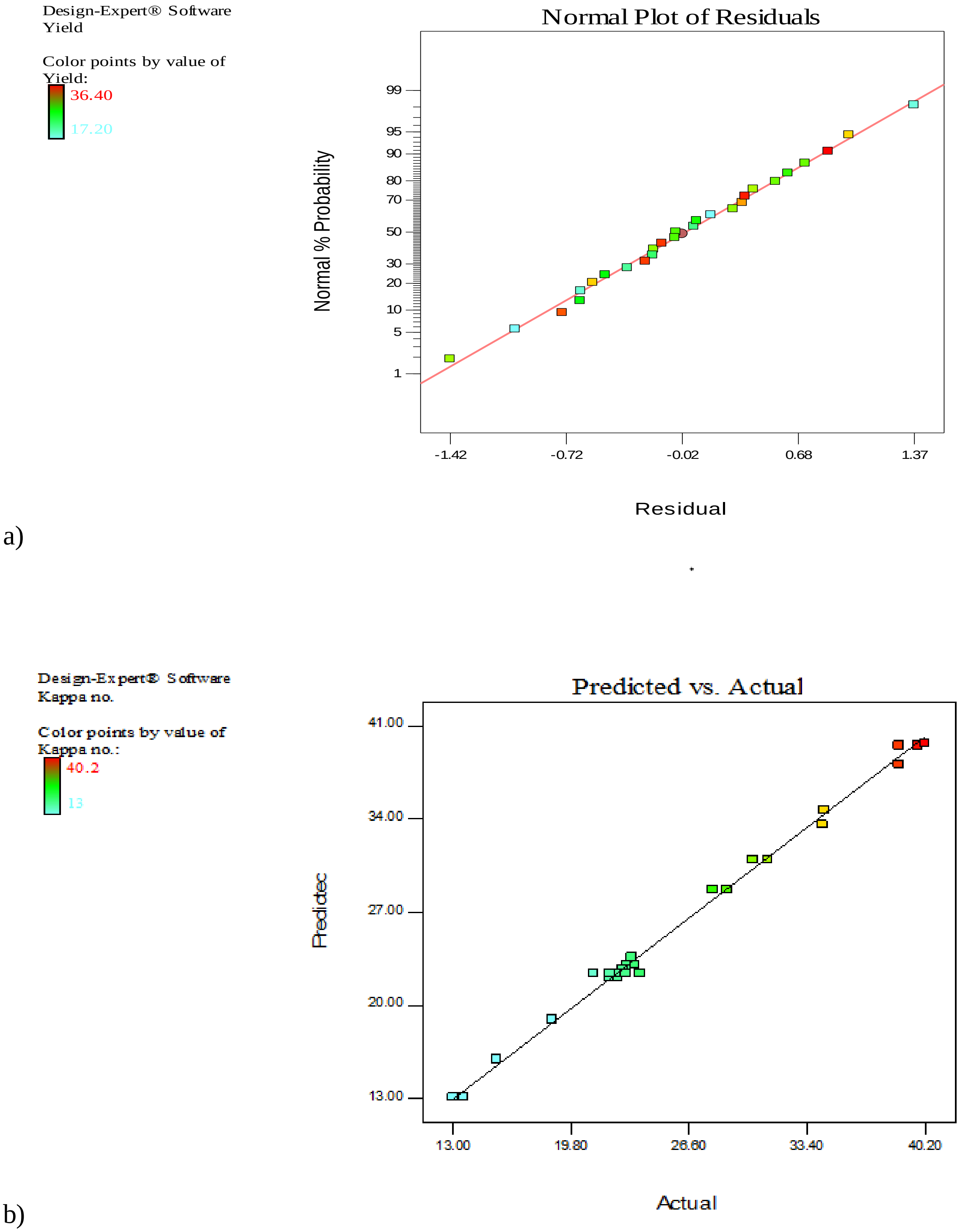


Figure C2: Normal probability plots versus Residual (a) and Predicted versus actual experimental value (b) for Kappa number

Table C2: Difference between the actual (experimental) value and predicted value of Kappa number

Standard order	Actual value	Predicted value	Residual	Run order
1	39.79	39.54	0.25	12
2	38.70	39.54	0.25	27
3	34.37	34.67	-0.84	16
4	34.40	34.67	-0.30	2
5	31.14	30.94	-0.27	26
6	30.30	30.94	0.20	1
7	23.05	23.05	-0.64	21
8	23.50	23.05	-9.259E-005	8
9	28.78	28.72	0.45	20
10	28.00	28.72	0.057	7
11	22.50	22.13	-0.72	14
12	22.00	22.13	0.37	25
13	23.00	22.72	-0.13	17
14	22.80	22.72	0.28	24
15	13.00	13.11	0.080	18
16	13.60	13.11	-0.11	11
17	38.70	38.13	0.49	3
18	23.30	23.65	0.57	19
19	34.30	33.60	-0.35	10
20	15.50	15.98	0.70	5
21	40.20	39.72	-0.48	22
22	18.70	18.96	0.48	13
23	23.80	22.42	-0.26	23
24	22.97	22.42	1.38	4
25	22.40	22.42	0.55	6
26	21.10	22.42	-0.021	15
27	22.05	22.42	-1.32	9

Table C3: Solutions for numerical optimization

Number	Temp. (℃)	Time (min)	NaOH (%)	Yield (%)	Kappa no.	Desirability	
1	145.11	71.48	13.76	33.1523	25.8609	0.686	Selected
2	145.13	71.55	13.76	33.1609	25.8438	0.686	
3	145.12	71.50	13.75	33.1467	25.8641	0.686	
4	145.12	71.53	13.76	33.1619	25.8443	0.686	
5	145.15	71.51	13.76	33.154	25.8506	0.686	
6	145.12	71.49	13.76	33.1592	25.85	0.686	
7	145.10	71.54	13.75	33.1571	25.8541	0.686	
8	145.11	71.52	13.75	33.1524	25.8605	0.686	
9	145.10	71.51	13.76	33.1592	25.8536	0.686	
10	145.14	71.58	13.75	33.1585	25.844	0.686	
11	145.15	71.49	13.76	33.1542	25.8496	0.686	
12	145.15	71.57	13.76	33.1581	25.8426	0.686	
13	145.16	71.51	13.76	33.1501	25.8531	0.686	
14	145.11	71.54	13.75	33.1491	25.8636	0.686	
15	145.12	71.45	13.75	33.1429	25.8728	0.686	
16	145.16	71.51	13.76	33.1538	25.8483	0.686	
17	145.14	71.46	13.76	33.154	25.8529	0.686	
18	145.10	71.44	13.76	33.1533	25.8629	0.686	
19	145.12	71.51	13.74	33.142	25.8711	0.686	
20	145.13	71.58	13.76	33.1671	25.8347	0.686	
21	145.12	71.61	13.75	33.1595	25.8454	0.686	
22	145.10	71.58	13.76	33.1665	25.8419	0.686	
23	145.15	71.59	13.75	33.1596	25.8388	0.686	
24	145.15	71.54	13.74	33.1438	25.8608	0.686	
25	145.10	71.43	13.76	33.156	25.8601	0.686	
26	145.12	71.51	13.77	33.1688	25.8382	0.686	
27	145.15	71.60	13.74	33.1499	25.8514	0.686	

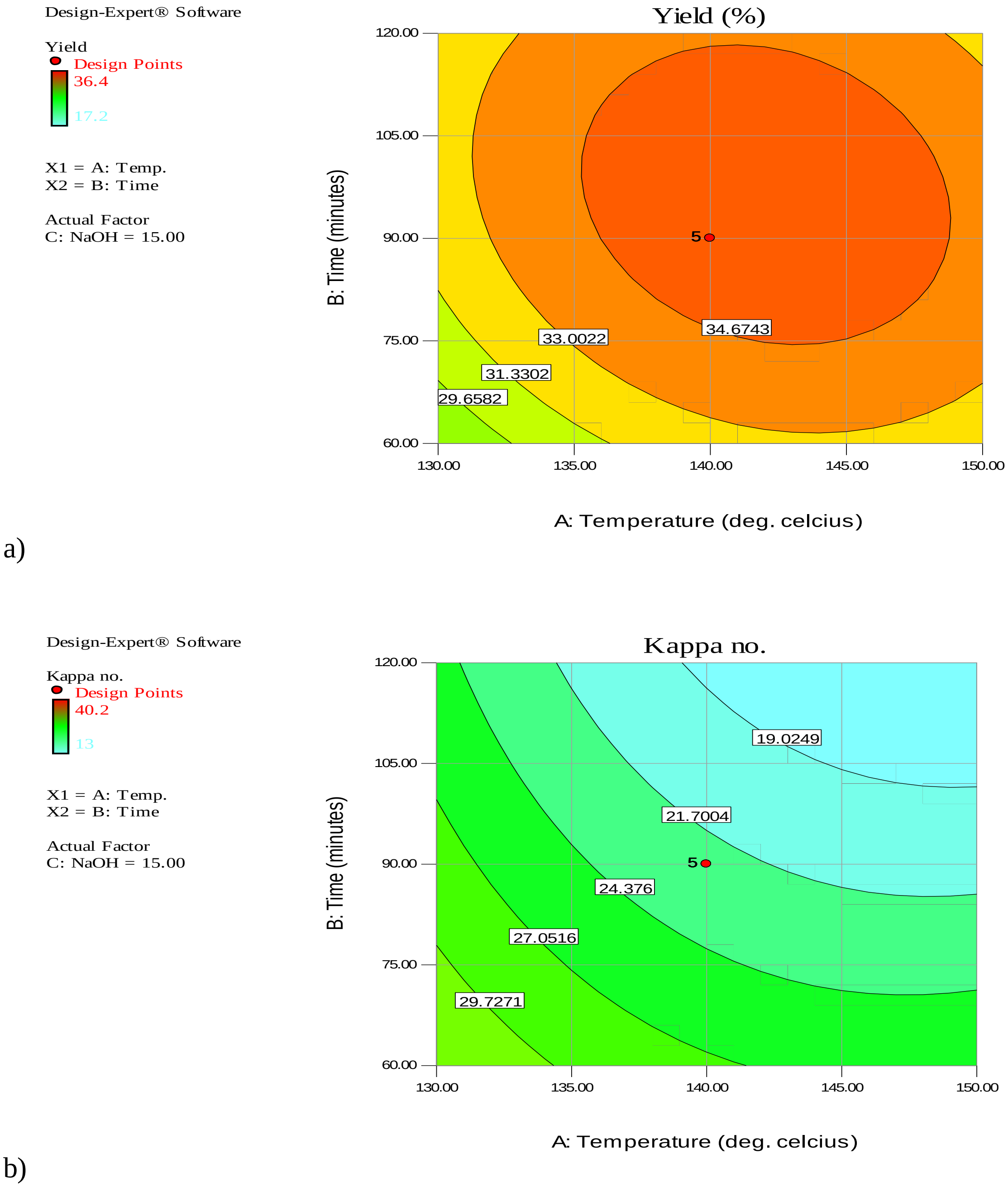
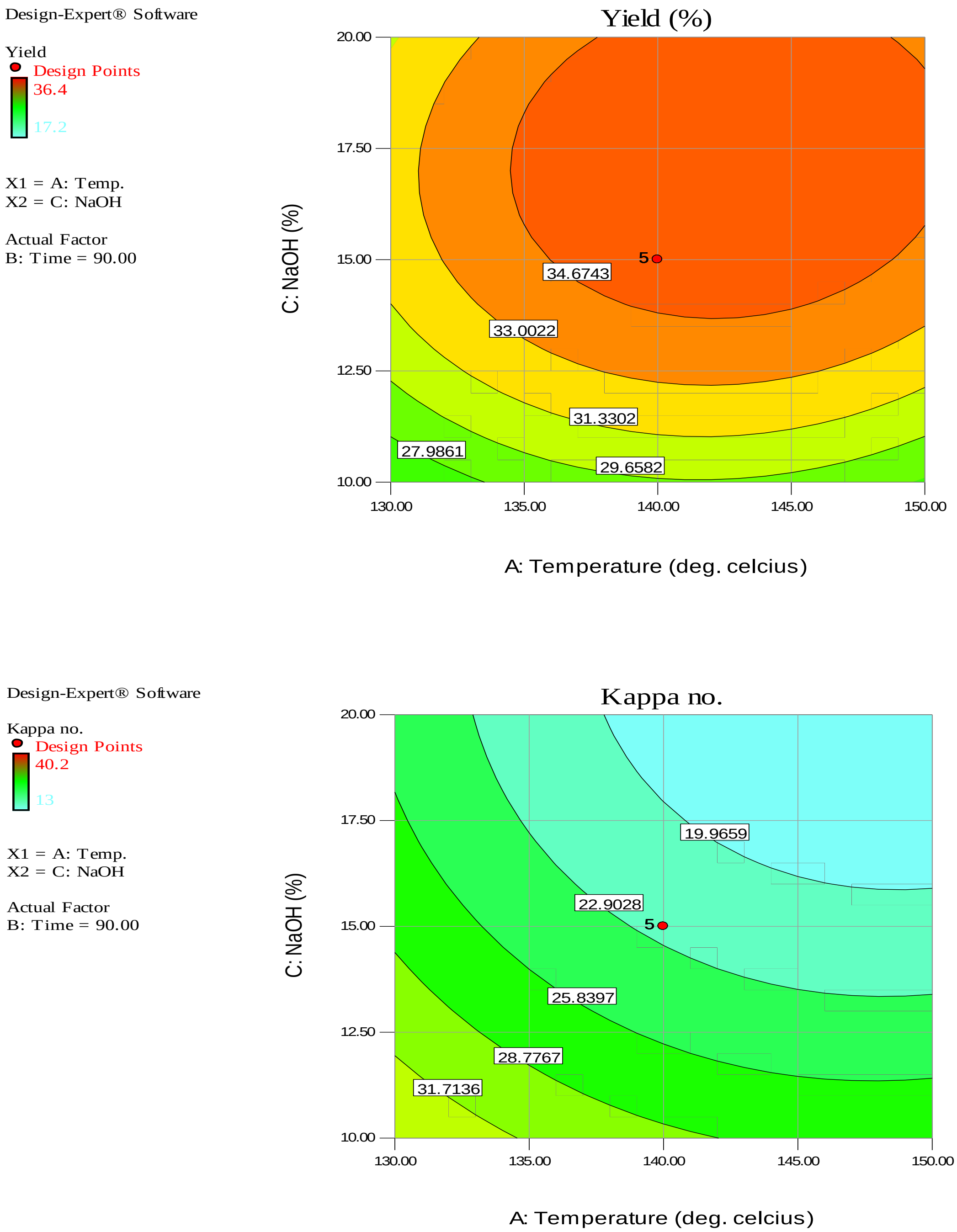


Figure C3: Contour plots that show interaction effects of temperature and time on pulp yield and Kappa number at constant NaOH concentration of 15%.



a)

b)

Figure C4: Contour plots showing interactions effect of temperature and NaOH concentration on pulp yield and Kappa number at constant cooking time of 90 minutes

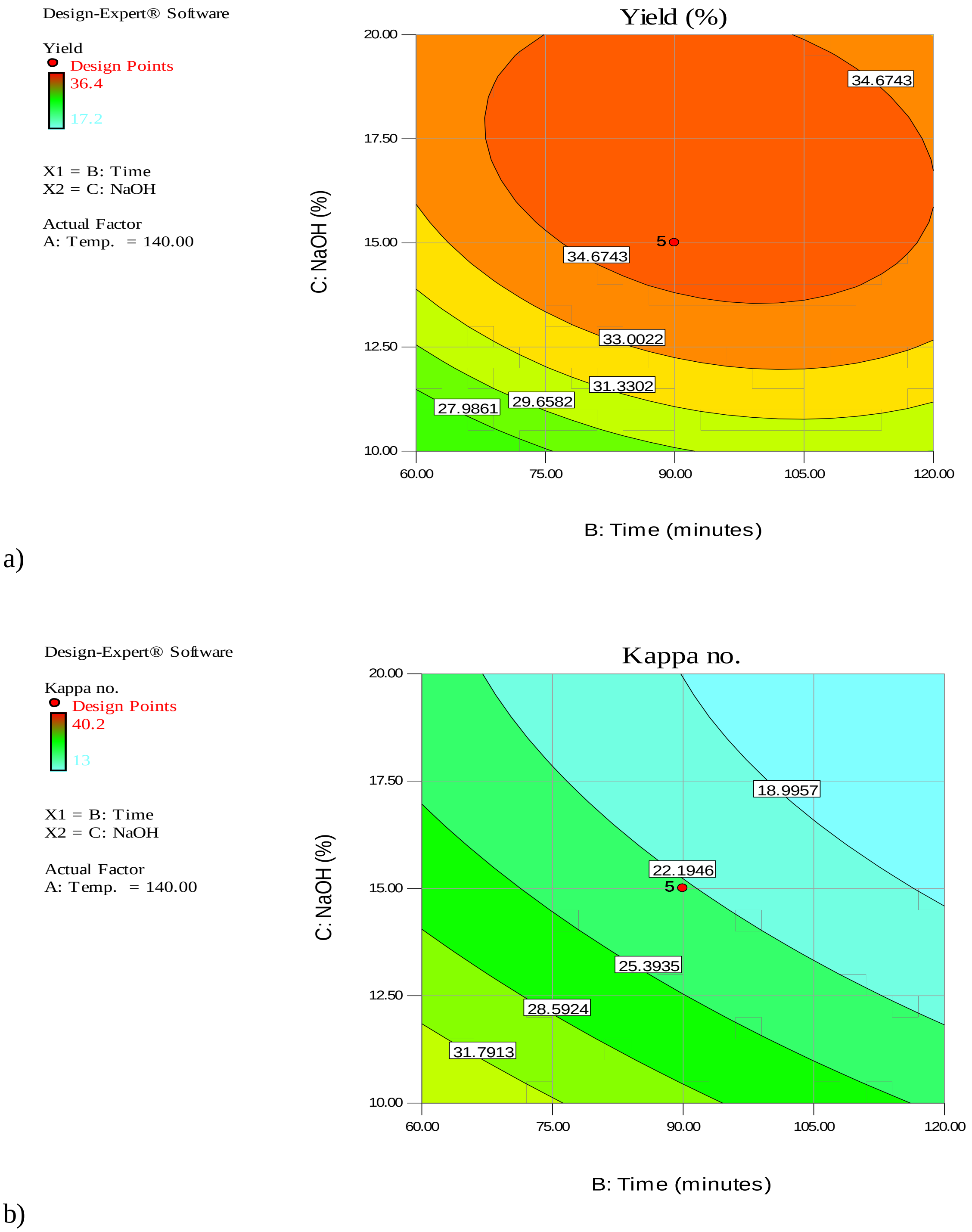


Figure C5: Contour plots showing the interaction effect of time and NaOH concentration on pulp yield and Kappa number at constant temperature of 150°C.