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CHEMICAL PULPING OF *OXYTENANTHERA ABYSSINICA* BAMBOO

BY

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Process Engineering Stream

Chemical Pulping of Oxytenanthera abyssinica Bamboo

A Thesis Submitted to the School Graduate Studies of Addis Ababa University, Addis Ababa Institute of Technology, School of Chemical and Bio Engineering in Partial Fulfillment of the Requirements for the Attainment of the Degree of Masters of Science in Chemical Engineering Under Process Engineering Stream.

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ACRONYMS

$(C_6H_{10}O_5)_n$	Cellulose
µm	micrometer
2FI	Two Factor Interaction
3-D	Three Dimensional
A.D	After Death
A.D	Air Dry
AAIT	Addis Ababa institute of Technology
AAU	Addis Ababa University
ANOVA	Analysis of variance
AQ-	Anthraquinone
ASTM	American Society for Testing and Materials
C.V	Coefficient of Variations
CI	Confidence Interval
Df	Degree Freedom
O.D	Oven Dry
FAO	Food and Agricultural Organization of the United Nations
FPURC	Forest Product Utilization Research Center

ha	Hectares
hr	Hours
Kpa	Kilopascal
Min.	Minute
mN	millinewtons
MPa	Mega Pascal
MS	Mean Square
NaOH	caustic soda
O. abyssinica	Oxytenanthera abyssinica
SS	Sum of Square
Std. Dev.	Standard Deviation
USD	United States Dollar

ABSTRACT

Bamboo is a fast growing non-wood plant with long and thin fibers. Therefore, it has potential as a raw material for pulping and papermaking. Oxytenanthera abyssinica bamboo samples were harvested, sorted, dried and milled using Wiley Mill and sieved with 250µm mesh for chemical analysis. In this work, the chemical composition of Oxytenanthera abyssinica bamboo, the effect of soda-AQ pulping conditions on pulp yield and kappa number and also the mechanical properties of paper made from lowland bamboo (Oxytenanthera abyssinica) was evaluated. Oxytenanthera abyssinica bamboo chemical composition contains higher cellulose content (52.06%) and pulp yield which make bamboo a preferred raw material for pulping. The bamboo chips were pulped using digester pulping unit with 15, 20 and 25% varying alkali charge; 60, 120 and 180 min cooking times and 150, 175 and 200^{o}C cooking temperature. The maximum pulp yield and minimum kappa number obtained was 52.24% and 12.16 respectively were achieved under the optimum conditions; at the active alkali of (20%), cooking temperature of 150^{o}C and the cooking time of 180 min with high value of combined desirability, i.e. 0.98. *The bamboo pulp was then made into 60 g/m^2 laboratory scale papers and their mechanical properties were assessed. The results revealed that tensile index, bursting index, and tearing index were 33.58 Nm/g, 1.303kPa.m^2/g, and 11.5mN.m^2/g respectively. This study indicates that comparable moderate strength mechanical properties of paper can be produced from Oxytenanthera abyssinica bamboo pulp with more environmentally friendly pulping process. Finally, it can be concluded that Oxytenanthera abyssinica bamboo has a great potential for substitution of imported pulp in paper and paper products processing industry.*

CHAPTER ONE

1. INTRODUCTION

1.1 Background

Bamboo is a naturally occurring composite biological plant material which grows abundantly in most of the tropical countries. It is considered a composite material because it consists of cellulose fibers agglomerated in hemicelluloses matrix and lignin as an encrusting substances. Cellulose fibers are aligned along the length of the plant (bamboo) providing maximum tensile flexural strength and rigidity in that direction [Lakkad and Patel 1980]. More than 1,500 species and 90 genera of bamboos are found in the world, covering 36 million hectare (ha) of land which is distributed in the tropical and sub-tropical belt between 46^0 north and 47^0 south latitude at elevations as high as 4000m above sea level (FAO, 2007). Bamboo has a very long history and the oldest building materials used by human kind (Abd.Latif1990). Bamboo chips were used to record history in ancient China. It has been used widely for household products and extended to industrial applications due to advances in processing technology and increased market demand. It is fast growing species and with a daily increment of 15 to 18 cm attains its maximum height in 4 to 6 months maturing to harvesting cycle of normal 3 years.

There are about 43 species of bamboo under 11 genera in Africa, covering over 1.5 millions of hectares (Kigomo 1988). About 93% of Africa bamboo species are found only in Madagascar (FAO, 2007; Seyoum, 2008). Bamboo forest in Ethiopia is the largest in Africa and it has two indigenous bamboo species: the highland bamboo *Arundinaria alpina* (synonym *Yushania alpina*) and the lowland bamboo *Oxytenanthera abyssinica*. Out of which the high land bamboo comprises about 130,000 ha and low land bamboo covers over 850,000 ha (Ensermu et al., 2000; Kassahun, 2003).In Ethiopia, the potential of bamboo resources have been used for bamboo-based panel and some hand woven products only. Currently, there are some works on the physical and mechanical properties of these species are coming to surface (Seyuom et al., 2008). However, the selection of bamboo species for various applications is not only related to the physical and the mechanical properties but knowledge on the chemical composition is the determinant one particularly for the pulp production. Pulp is the most important product of chemical conversion of ligno-cellulosic materials. In bamboo growing countries, like India,

bamboo is the main raw material for the production of pulp for paper and rayon. Pulping can be done chemically, semichemically, mechanically, thermo-chemi-mechanically and thermo-mechanical (Reydholm 1967, Fengel et al 1983). The pulp yield is affected by the method of pulping and the selection of pulping methods itself also depends on the end use of the producing pulp, the type of raw material and the recovery economics. From fiber length and strength point of bamboo, its fiber is almost similar to softwood. As reported by Seyoum et al (2008) and Liese (1980) the fiber length of bamboo species varies from 1.3 mm to 4.3 mm.

Chemical pulping method resulted in low yield 50-65% by removing the lignin, hemicelluloses and extractive components, and reduces the energy consumption. Chemical pulping besides the low yield is a high quality product and become an expensive pulp for other uses than paper (Reydholm 1967). The major chemical pulping are kraft and sulfite methods used to liberate the fiber from the wood by delignification from the cell wall components.

Information on the chemical composition of bamboo is important as far as its utilization for pulping is concerned. Holocellulose (is a technical term used for combined cellulose and hemicelluloses components) is the main component contributing to the strength of paper made from bamboo. Paper is mainly made of cellulose fiber used in manufacturing of different products. The products made from cellulose as a raw material have specific property demand from the material from which it is produced (Rydholm 1967, Obolenskaya 1991).

Bamboo is preferred because it has an important role to play in the balance of oxygen and carbon dioxide in the atmosphere, a viable replacement for wood as an enduring natural resource.

Therefore, to utilize the vast *Oxytenanthera abyssinica* resource in Ethiopia in fiber based products, the chemical composition (cellulose, lignin and hemicelluloses) of the raw material and pulp properties of the fiber have to be investigated.

1.2 Statement of the problem

The ever growing demand for pulp and paper products has forced countries of the world to look for potential and sustainable raw material for industries. Ethiopia as a developing country with very low paper and paper board consumption per capita (1kg/ person/ year) is expected to grow significantly. The ongoing economic development and livelihood improvement in Ethiopia inevitably would create huge demand and consumption of pulp and paper products due to increasing economic welfare household consumption, expansions of schools and universities, and increasing of manufacturing sectors that needs packaging and wrapping.

In Ethiopia one of the problems in pulp and paper industry is almost absence of pulp mill but there are over 22 companies involved in paper making and trading businesses, of which only 'Ethiopia pulp and paper share company' and 'Barguba' plc uses imported pulp for their paper mills while others import, produced paper rolls for further processing. Ethiopian paper mills were designed to utilize mixture of short and long fiber pulp. The paper mills uses 10,000 tones/yr pulps imported at a cost of 8 million USD and only some 30% of the country's paper demand is produced in the country which implies every year the country spend 72 million USD per year (Dagim 2010).

Furthermore, the ever increase in price of raw material (pulp) for the production of paper and the absence of pulp mill in the country compared with the foreign exchange burden is a major motive to develop the pulp industry in the country. The growing demand for paper products has made the issue of paramount importance. Ethiopia is endowed with good agro-ecology to develop its natural resources that enable it produce pulp from both wood and non-wood inputs. Among the non-wood resources, the existence of bamboo forests creates a good opportunity for developing the pulp and paper industry sub-sector.

Bamboo forest in Ethiopia is the largest in Africa and the country can sustainably produce three million cubic meters of dry weight biomass annually from its two indigenous bamboo species: *Yushania alpina* and *Oxytenanthera abyssinica*. Despite this potential , current uses are primarily limited to construction of traditional houses, low-grade furniture, household utensils, beehives, fences, and handicrafts and laminated bamboo floor boards.

Therefore, the rationale of this research work is to investigate the potential of *Oxytenanthera abyssinica* bamboo pulp for paper production which could be a good source of raw material to help meet the Growth and Transformation Plan of the country.

1.3 Objectives of the Research

1.3.1 General objective

The general objective of this study is to evaluate the pulp yield and quality of lowland bamboo *Oxytenanthera abyssinica* in Ethiopia.

1.3.2 Specific objectives

The specific objectives of the study will be:-

- ✓ Characterization of chemical composition of *Oxytenanthera abyssinica* bamboo Culms.
- ✓ To identify the effect and interaction of the pulping parameters on the pulp yield and kappa number of the lowland bamboo culms.
- ✓ To determine the optimum operating parameters and generate the model equation for the independent variables which will maximize the pulp yield.
- ✓ Characterization and comparisons of *Oxytenanthera abyssinica* bamboo paper properties with other imported raw materials for the possibilities of pulp manufacturing in Ethiopia.

1.4 Significance of the Study

The contribution of forests to the society and country clearly viewed when it is used as a raw material in one or another way in the manufacturing system. Forest industries expand when the consuming or using industries able to convert the raw material to other form of products. Pulp is a product generated from plant either chemically, mechanically, thermo mechanically or in combination of these processes. Ethiopia has over 1 million ha of bamboo, corresponding to approximately 7% of the global bamboo resource. The country can sustainably produce three million cubic meters of dry weight biomass annually from its two commercially important bamboo species: *Yushania alpina* and *Oxytenanthera abyssinica*. Despite this potential , current uses are primarily limited to construction of traditional houses, low-grade furniture, household utensils, beehives, fences, and handicrafts.

However, several attributes of bamboo such as the abundant availability, their fast growth, adaptability on marginal lands, promising material properties, and potential to support rural development give high priority to the commercialization of bamboo species in Ethiopia.

Bamboo as a grass family with fast growing nature attaining its maximum height within short period of time can contribute a lot to the climate change, carbon sequestration. Frequent and continuously consuming of this raw material in the pulp production in turn contribute to the strategy of mitigating climate change and being climate resilient production system

Pulp production from bamboo species is well developed in China and India. The bamboo species used by these countries are different from the species Ethiopia has. The knowledge on the pulp characteristics, pulp yield and total chemical composition of the bamboo culms, which is a very good source of cellulose, enables the country to develop strategy on the resource development and utilization. Besides, the knowledge serves as a clue for further research studies on the application of lowland bamboo for fiber based products.

In addition to this it will create an opportunity to develop pulp technology locally, which will play a major role to substitute the imported pulp which saves hard currency and creates job opportunity for the society.

CHAPTER TWO

2 LITERATURE REVIEW

2.1 Introduction

Worldwide cellulose pulp is produced from hardwood, softwood and agro residues. Hard wood and soft wood pulping accounts to ~95% of the total worldwide pulp production. The rest 5% pulp comes from non wood raw materials, mainly agro residues and grasses (Jimenez et al., 2005). India and China are the major non-wood pulp producers and meet out 45-50% of their pulp requirement from these raw materials. Forest resources are experiencing increasing pressure due to the growing world population and improving living standards. Wood is a natural resource and a major raw material for the manufacture of pulp, paper and other similar products. Although wood is renewable, the rate at which wood is been used is not commensurate with the rate it is being replaced. The rate at which forests are declining has been estimated to be 13.0 million hectares per year in developing countries (FAO, 2005).In many developing countries of the world today, wood is becoming scarce and expensive because of the heavy dependence on wood for construction and building purposes, grazing, and conversion of forests to agricultural land to grow crops and felling of tree for firewood.

The ecological damage caused by the continual use of wood includes deforestation leading to soil erosion, desertification, extinction of certain species, flooding, drought, climatic change and the disruptions of water and carbon cycle (West and Marland 2002).

The obvious solution to this is to use wood sparingly while embarking on the massive plantation and development of non-wood species. Non-woods fibers are abundantly available and have become one of the important alternative and supplementary sources of fibrous material for pulp and paper making in some developing countries like China, India, Thailand and Indonesia (Ashori 2006).

Bamboo, “the green gold of the forest”, around 10 million tonnes of which are produced annually in the world, is fast growing, inexpensive, long-fibered, easy to load and unload, therefore, it is an important raw material for the pulp and paper industry. Sumg (1967) described

the pulp characteristics and technology for the manufacture of bamboo paper in the 17th century China.

Even though Ethiopia's forest cover estimated around 10% these lignocellulosic material with other agricultural residues never exploited the resource for pulp production. Bamboo is the most important non-wood forest product and in Ethiopia is known as the 'poor man's timber'. Bamboo is a rapid growing fibrous plant available in abundance in the tropical and subtropical regions. It mainly consists of the rhizomes (false roots), Culm and leaves and has tremendous economic potential. The culms are the most distinguishable part in a bamboo plant species. They are usually hollow and vary in sizes, diameters, colors and textures. Countless tiny black spots can be seen at the cross-section of the Culm (hollow stem). These are the fibers which run the length of the Culm carrying nutrients between roots and leaves. Individually, cellulose is stronger of the two components. The cellulose fibers can be compared with the reinforcing fibers in an advanced carbon/epoxy composite whereas the surrounding lignin can be compared with the epoxy matrix. (http://www.linanwindow.com/).

2.2 Raw materials for pulp and paper production

2.2.1 Raw materials

Pulp is one of the most important industries in paper and paper board manufacturing in the world. Pulp is manufactured from raw materials containing cellulose fibers, generally wood, recycled paper, and agricultural residues. Historically the first paper was made from non-wood material by Tsai Lun in China around 100 A.D. In 20th century, wood has been dominant to be the main source for pulp and paper material, due to its availability, low cost and good paper properties.

The demand and use of pulp and paper have marked the levels of civilization and development of many societies. Ethiopia as a developing country has significantly very low paper and paper board consumption per capita of 0.43 kilogram /person /year when compared with the world average of 54.48 kilogram/person/year in 2005 (WRI, 2005). The demand for pulp and paper fiber resources is largely determined by the society's dependence on paper, paper boards and other related products for human welfare. The pulp in society is used in education,

information storage, advertising, communication, in protection, packaging of food and non food goods, transportation and security of goods in transit; protection of human health and sanitation in form of tissues and sanitary paper products. Paper making process for long has mainly used wood from tree stems that are cut, debarked, chipped and pulped.

It is interesting to note that some environment advocates have proposed the use of non-wood fibers in paper making as a way to preserve natural forests. Both wood and non-wood resources are currently exploited for the manufacturing of pulp, paper and soft boards. But still the major source of pulp which meets more than 80% demand is still wood from forests. However scientists all over the world in the last two decade have been involved in intensive research for the alternative sources of pulp for paper industry (McClosekey 1995).

Recently, due to the shortage of wood supplies and the environmental concern related to deforestation, alternative raw material is needed to supplement or replace wood source to maintain the pulp industry. Many research and development have been done towards this issue. In developing countries, about 60% of lignocellulose fibers originate from non-wood raw materials such as bagasse (sugar cane fibers), cereal straw, bamboo, reeds, esparto grass, jute, flax, and sisal. Most of the countries still depend on the imported raw material for their pulp and paper production, including Ethiopia.

The pulp and allied products industry comprises two types of facilities: pulp and paper mills that process raw wood fiber or recycled fiber to make pulp and/or paper, and converting these primary materials to manufacture more specialized products such as paperboard boxes, writing paper, and sanitary paper.

Paper mills primarily are engaged in manufacturing paper from wood pulp and other fiber pulp, and may also manufacture converted paper products. The pulp and paper industry converts wood (harvested by logging firms) or recycled fiber into pulp and primary forms of paper. Raw material for pulping purpose chipped in sizes which are suitable for penetration of chemicals into the chips and maintaining the fiber length at the same time. The fiber length is the number of bonding sites that is available on an individual fiber to form an interwoven network of fibers. It is measured from one end to another end. Long fiber lengths are preferable for manufacture of

paper. Long fibers give a more open and less uniform sheet structure. Fiber length influences the tearing strength of paper. The higher of the fiber length had effect on the resistance of the paper to tearing (Oluwadare and Ashimiyu 2007, Wimmer *et al*. 2002). Fiber diameter is the diameter of fibre measured from side to side end and it is usually measured across the fiber length. Thick wall fibers adversely affect the bursting strength, tensile strength and folding endurance of paper. Relative fiber length is the ratio of the fiber length to its diameter; it gives the tearing resistance of a paper (Varghese *et al*. 1995). And also their average length, average diameter and length/diameter ratio of varies pulp fibers are shown Table (2.1) below.

Table 2.1: Average length, average diameter and length/diameter ratio of varies pulp fibers

	Length (mm)	Diameter (μm)	Ratio
Woods			
Coniferous(Soft wood)	4.0	40	100
Deciduous(Hard wood)	2.0	22	90
Straw & Grasses			
Rice	0.5	9	60
Misc (Wheat, Rye, Sabai)	1.5	13	120
ACanes & Reeds			
Bagasse (Sugar cane)	1.7	20	80
Miscellaneous	1.2	12	100
Bamboos			
Several varieties	2.8	15	180
Woody stuck with bast fibers (jute, flax, kenaf, cannabis)			
Woody stems	0.25	10	25
Baste fibers	20	20	1000
Baste fiber			
Linen	55	20	2600
Ramie	130	40	3500
Leaf fiber			
Abaca(Manila hemp)	6	24	250
Sisal	2.8	21	130
Seed fibers			
Cotton	30	20	1500
Cotton linters	20	20	1000

2.3 Chemical pulping

Chemical pulping employs chemical reagents to effect a separation of the cellulose fibres from other wood components. Wood chips are cooked with suitable chemicals in aqueous solution, usually at elevated temperatures and pressures with the objective of dissolving the lignin and other extraneous compounds, leaving the cellulose intact and in fibrous form. However, during pulping the chemicals employed for delignification purpose not only degrade and dissolve the lignin components but also the liable hemicelluloses and the cellulose components yielding about 50 per cent of the wood weight. Because the chemical processes consume relatively large quantities of inorganic chemicals such as alkalis and environmental pollution, paper makers devised methods for reagent chemical recovery from the spent cooking liquor; recovery has remained an integral part of chemical pulping. Environmental and economical concerns necessitated chemical recovery as a very important part of chemical pulping. Chemical pulping broadly categorized in to sulfite method and sulfate (Kraft) method.

2.3.1 Sulfite method of pulping

The 'sulfite process' was invented during 1857 by an American chemist, B.C. Tilaghman who observed the effect of sulphurous acid in softening wood. He obtained cellulose fibers by treating wood with bisulphate-sulphurous acid solutions under high temperature and pressure. The base used was calcium and later magnesium. Sodium and ammonium are also used as base, which are having advantages in liquor-recover operations. Sulphite pulps are relatively light in color, are easily bleached to a high-white colour, have moderately good strength properties. Sulfite pulp is almost pure cellulose and is used in fine papers.

2.3.2 Alkaline pulping processes

The soda process and the sulphate (or kraft) process are the two principal alkaline pulping techniques and the basis for several modified alkaline processes, including kraft pulping after a prehydrolysis step for the production of dissolving pulp. Sodium hydroxide is the principal cooking chemical in both processes, while in sulphate pulping sodium sulphide is an additional pulping component. Both processes received their names from the regeneration chemicals used

to compensate for the loss of sodium hydroxide, namely sodium carbonate (soda) and sodium sulphate, respectively.

2.3.2.1 Soda process

Soda process, the first process to manufacture chemical pulp, was invented by Hugh Burgess in 1851, employed caustic soda (sodium hydroxide) solution for cooking. For papermaking soda-AQ pulping, compared to kraft pulping is more environmentally friendly pulping process. A higher pulp yield with soda-AQ pulps, compared to soda method, was attributed to higher hemicellulose retention (Atik 2002).Previous studies have shown that the modified pulping process by AQ addition in laboratory and industrial scales resulted in more uniform pulps with lower rejects, higher pulp yield at constant kappa number, and lower consumption of alkali (Akgul and Tozluo 2009). Similar results by Kamthai (2007) and Miller and Gounder (1986), reported that the addition of AQ to soda pulping can raise the delignification rate and protect cellulose degradation, which was demonstrated by the quantity of screened pulp yield.

2.3.2.2 Kraft (Sulphate) process

At the pulping stage, the processed furnish (wood or other fiber source) is digested into its fibrous constituents. The choice of pulping technique is dependent on the type of furnish and the desired qualities of the finished product, but chemical pulping is the most prevalent. Table 2.2 presents an overview of the wood pulping types by the method of fiber separation and resultant fiber quality. Many mills perform multiple pulping processes at the same site, most frequently non-deink secondary fiber pulping and paper grade Kraft pulping. The three basic types of wood pulping processes 1) chemical pulping, 2) semi-chemical pulping, and 3) mechanical pulping are detailed below.

Table 2.2: General Classification of Wood Pulping Processes

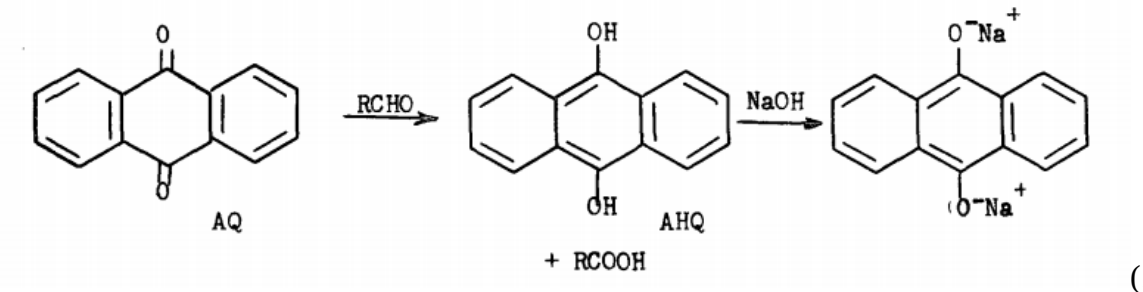
Process Category	Fiber Separation Method	Fiber Quality	Example
Mechanical	Mechanical energy	Short, weak, unstable, impure fibers	Stone ground wood, refiner mechanical pulp
Semi-chemical	Combination of chemical and mechanical treatments	"Intermediate" pulp properties (some unique properties)	High-yield kraft, high-yield sulfite
Chemical	Chemicals and heat	Long, strong, stable fibers	Kraft, sulfite, soda

2.3.2.3 Anthraquinone as an additive in alkaline pulping

The use of anthraquinone (AQ) as an additive in the alkaline pulping processes is found to have the benefits of increased delignification rates as well as reduced alkali charges and improved pulp properties and yields through its use with both softwoods and hardwoods. AQ acts as a redox catalyst in the liquor system. It makes the soda process useful for pulping softwoods as well as hardwoods.

By addition of 0.05 per cent AQ, the cooking time is reduced by 25-35 per cent and the alkali charge by 5 per cent while yields increase by 1.5-3 per cent at the same residual lignin level and comparable strength properties are obtained as in conventional kraft pulping (Goel et al. 1980).

In the presence of reducing sugars and alkali, AQ is rapidly reduced to the hydroquinone (AHQ), as shown in equation (1) below. The hydroquinone is acidic, and forms a water-soluble disodium salt in alkali. These reactions occur readily at room temperature if soluble carbohydrate are used, and can be seen by the deep red color of the disodium salt.



(1)

In this way, a substantial amount of AQ can be kept in solution in the reduced form. This soluble material is readily available if a catalytic cycle is involved.

Mechanism of anthraquinone pulping was reasonable to assume that carbohydrate end-groups are oxidized by AQ. Lignin can then complete the catalytic cycle by oxidizing AHQ back to AQ, being reduced in the process. This is shown in figure 2.1 below.

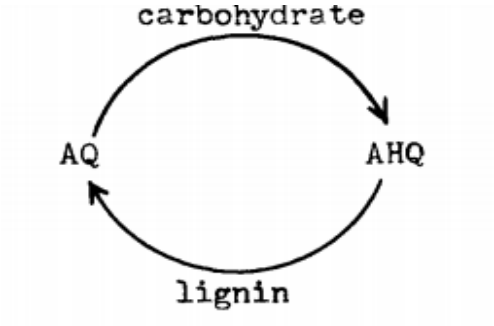


Figure 2.1: Mechanism of anthraquinone pulping

2.3.3 Chemical properties

The selection of bamboo species for various applications is not only related to physical and mechanical properties but also to the chemical composition (Tomalang *et al*., 2005).The main constituents of bamboo culms are cellulose, hemicellulose and lignin, which amount to over 90% of the total mass. The minor constituents of bamboo are resins, tannins, waxes and inorganic salts. Compared with wood, however, bamboo has higher alkaline extractives, ash and silica contents (Malanit *et al.,* 2009; Amu and Babajide, 2011). The chemical properties influence the growth and the mechanical properties of bamboos. Through the Chemical analysis more information on the taxonomical identification and propagation can be obtained. The chemical composition of bamboos also has an influence on deciding what kinds of bamboos with which kind of material in combination is suitable for the utilizations. Bamboo consists mainly of cellulose, lignin and hemicellulose which are not different to that of trees. The difference lies in the percentages of each component and their micro structures. Some minor chemical components are resins, tannins, waxes and inorganic salts. This chemical composition changes according to

the species, geographical location, the age and the parts of bamboo. The variation of bamboo's chemical composition has a big influence on the physical and mechanical properties of bamboos and therefore the treatment and utilization of bamboos (Liese 1985).

The bamboo cell walls consist of between 90 to 98% hemicelluloses, cellulose and lignin, while the other 2 to 10% are mainly of extractives, resins, tannins, waxes and inorganic salts (Razak *et al*., 2009; Liese, 1985, 1992; Tomalong *et al*., 1980). Some variation, however do occurred in the main chemical constituent as the bamboo culms matured and it also depend on the type of bamboo species. Ligno-cellulose is a loose compound of lignin, hemicellulose and cellulose. The name lignin represents a class of closely resembling chemical compound. Lignin is the binding material for the fibrous cellulose material in plants.

The hemicelluloses and cellulose are actually made of the carbohydrate polymers which made up of simple sugars monomer to form the linear structure of cellulose and the short and branched forms of hemicellulose (Browning, 1975 and Fengel 1983). Bamboo has been known difficult to work with as they blunt the cutting tools and deteriorate easily (Razak, 1998). Information on the chemical constituents of the bamboo culms will help the industry in overcoming this problem. Comprehensive knowledge of the chemical components in the bamboo species will facilitate the use of the materials in the forest industry sector and help to enhance their utilization in the chemical and biochemical related industry. The chemical composition of some non-wood raw materials for pulp manufacturing is shown in Table (2.3) below.

Table 2.3: The Composition of non-wood raw materials for pulp manufacturing

Characteristics	Bamboo	Bagasse	Rice straw	Wheat straw
Cellulose	50	40-45	30-35	30-35
Lignin	22-30	18-20	12-14	12
Ash content	1-3	2	15-20	15-20
Pentogens	15-20	30-32	23-25	23-25
Fiber length, mm	3-4	1.7	1.5	1.5
Fiber diameter, μ	15	20	8.5	8.5

2.3.4 Chemical constituents

2.3.4.1 Cellulose

Cellulose ($C_6H_{10}O_5)_n$: is the most abundant form of the naturally occurring compounds of carbon. This forms the principal component of the cell wall of all woods, straws and grasses (bamboo). As it is most frequently found in fibrous form, it has got good tensile strength, and as it is insoluble in cold and hot water, it forms an important component of pulp and paper. Cellulose is a polymeric carbohydrate, a polysaccharide with repeating units of glucose or it is a linear polymer of D-glucose units linked by β-1, 4-linked glucose that could be seen in figure 2.2. The neighboring glucose units are joined through carbon atoms 1 and 4 and all glucose unit in cellulose chain rotated 180^0 to each other which make to form a straight chain. Cellulose molecules are relatively linear and have strong tendency to form intra and intermolecular hydrogen bonds. Bundles of cellulose molecules are thus aggregated together in the form of micro-fibrils, in which highly ordered (crystalline) regions alternate with less ordered (amorphous) regions. The crystalline regions in which the linear molecules of cellulose are bounded laterally by hydrogen bonds characterized by the cellulose lattice which extends over the entire cross-section of the micro-fibrils. This crystalline region is bounded by a layer of cellulose molecules that exhibit various degrees of parallelism. The less ordered region is called the paracrystalline or amorphous region. The disordered region allows disintegration of the cellulose by hydrolysis into rod-like particles with aqueous, non-swelling, strong acid. Micro-fibrils build up fibrils and finally cellulose fiber bundles. As a consequence of its fibrous structure and strong hydrogen bonds cellulose has a high tensile strength and is insoluble in most solvents. Orientation of the linkages and additional hydrogen bonding makes the polymer rigid and difficult to break (Hamelinck et al, 2005; Sjostrom 1981).

The molecular arrangement of this fibrillar bundle is sufficiently regular that cellulose exhibits a crystalline X-ray diffraction pattern. Typically, cellulose chains in primary plant cell walls have degree of polymerization in the range of 5,000 to 7,500 glucose monomer units, with the degree of polymerization of cellulose from wood being around 10,000 and around 15,000 from cellulose cotton. The basic repeating unit of cellulose is cellobiose. The fibrils are embedded in hemicelluloses and lignin. Under normal conditions, cellulose is extremely insoluble in water,

which is of course necessary for it to function properly as the structural framework in plant cell walls (O'Sullivan, 1997).

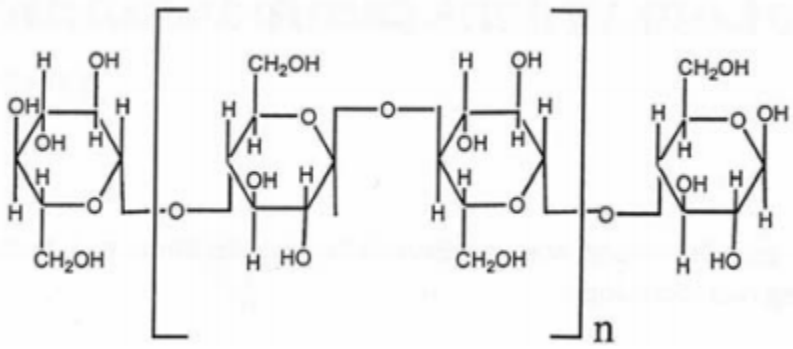


Figure 2.2 Cellulose molecules (from Theliander et al, 2002).

Cellulose being relatively resistant to oxidation, lignin and other coloring matters can be removed with bleaching agents without appreciable damage to the strength of pulp. The alpha or true cellulose content of a fibrous material does not affect directly its pulpability, but the higher the alpha-cellulose content of a material, the higher the yield of fully delignified, bleached chemical and semichemical pulps.

2.3.4.2 Hemicelluloses

Hemicelluloses: were originally believed to be intermediates in the biosynthesis of cellulose. Today it is known, however, that hemicelluloses belong to a group of heterogeneous polysaccharides which are formed through biosynthetic routes different from that of cellulose. In contrast to cellulose which is a homopolysaccharids, hemicelluloses are heteropolysaccharids. Hemicelluloses are heterogeneous polymers of pentoses (Xylose, Arabinose), hexoses (mannose, glucose, and galactose) along with acetyl groups (CH_3CO) figure (2.3), and sugar acids (uronic acids). They are generally cataloged according to the main sugar residue in the backbone, e.g., xylans, mannans, and glucans, with xylans and mannans being the most common. Hemicelluloses, because of its branched, amorphous nature, are relatively easy to hydrolyze. Among softwood hemicelluloses there are galactoglucomannans, arabinoglucuronoxylan, and arabinogalactan, meanwhile hardwood hemicellulose comprises mainly glucronoxylans and glucomannan (Saha and Bothast 1997) shown in figure 2.4.

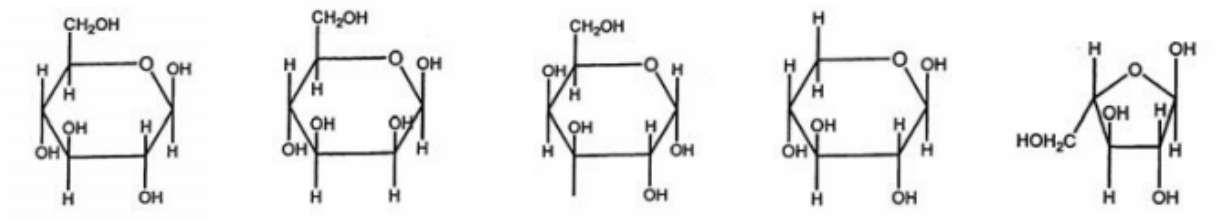


Figure 2.3 Sugar units in hemicelluloses. From left: β-D-Mannose, α-D-Galactose,β-D-Xylose and α-L-Arabinose (from Theliander et al., 2002).

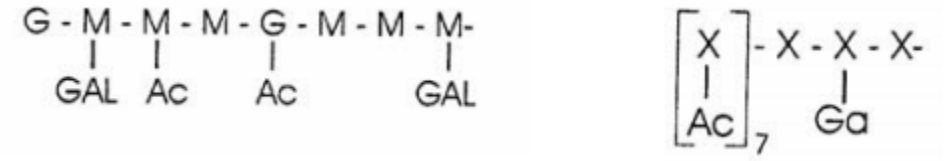


Figure 2.4 The two hemicelluloses glucomannan to the left and xylan to the right (from Theliander et at, 2002.)

When wood is freed from extractives (compounds which are soluble in cold water or in neutral organic solvents) and is then carefully freed from lignin, it yields a fibrous product termed holocellulose, which represents the sum total of cellulose and other polysaccharides; the latter are usually termed hemicelluloses (or polyoses). Pulping processes remove not only lignin (imperfectly) but also some of the less resistant hemicelluloses; so, holocellulose cannot be obtained by ordinary pulping operation.

The hemicelluloses contain mainly sugar units other than glucose (such as Xylose, mannose, Arabinose, rhamnose, galactose, etc.). Usually the dominant unit in the hemicelluloses is Xylose, but frequently mannose units are present in appreciable amounts, especially in the case of the hemicelluloses of coniferous woods. The hemicellulose fractions which contain Xylose (and uronic acid) units are often termed ‘xylans’ or more loosely ‘pentosans’. Those contain mannose units linked to each other and to glucose units have been referred as ‘mannans’.

The hemicelluloses (when freed from lignin) swell more than does cellulose and are in part dispersible in water. They have adhesive properties not shared by cellulose. Whereas cellulose is fibrous, hemicelluloses are non-fibrous. Whereas cellulose is quite insoluble in cold alkali, hemicelluloses are quite soluble in dilute caustic soda. In any chemical pulping operations, some

of the initial hemicelluloses are retained in the pulp. A portion of the less resistant hemicelluloses is removed during digestion, and their degradation products are then found in the spent liquors.

In the case of pulps freed from lignin by adequate and controlled bleaching, the hemicelluloses have been shown repeatedly to contribute greatly to tensile and bursting strength and to folding endurance of the pulp sheet. Both the quantity and the type of hemicelluloses in a pulp influence the pulp properties and the type of paper that can be made from such a pulp. There are certain disadvantages also about their presence. These are undesirable for dissolving grade pulp. In the case of certain bleached pulps, these are responsible for a loss in brightness of the bleached pulp on storage or aging.

2.3.4.3 Lignin

Lignin: is a complex, hydrophobic, cross-linked, three-dimensional aromatic polymer of phenyl propane building blocks. The mechanical; strength properties of plants are mainly due to incorporation of lignin into cell walls, whereby huge plants such as trees can remain upright. P-coumaryl alcohol (I), coniferyl alcohol (II) and sinapyl alcohol (III) are the primary precursors in the biosynthesis of lignin as shown in figure (2.5). Lignin is one of the most complicated natural

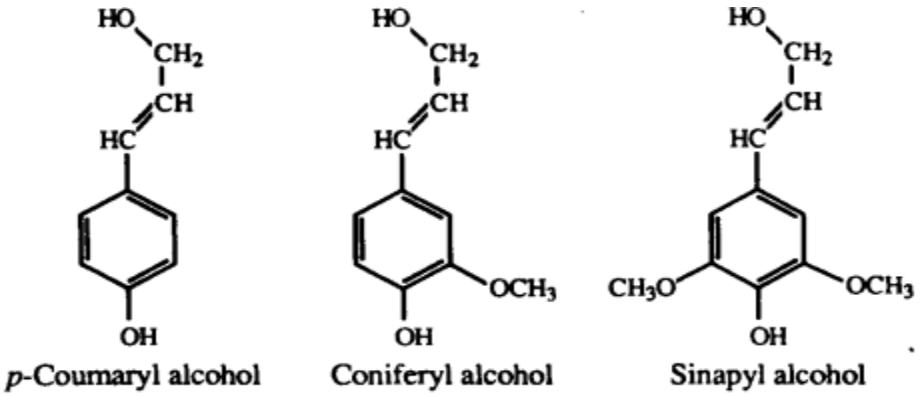


Figure 2.5 Lignin building blocks

polymers with respect to its structure and heterogeneity, which make it extremely resistant to chemical and biological degradation (Lee, 1997).

Lignin is the cementing substance between fibres and tissues and is concentrated mainly in the region of the middle lamella and imparts rigidity to wood tissue. Lignin exists in plant as

branched chain polymer molecules. Hardwood lignin consists of coniferyl and sinapyl structures whereas coniferyl structure is the dominating softwood lignin component (Sjodahl, 2004).

The lignin may be separated from an associated wood component either by preferentially dissolving lignin or by preferentially dissolving non-lignin components. The aim of soda cooking is to reduce the lignin content in the wood matrix so the fibres easily can be liberated. Isolated lignin, in general, are amorphous and non-crystalline, and show definite softening points at elevated temperatures. The average molecular weight is in the range of 11,000. An important property of lignin is its capacity to absorb ultra violet light. The chemical skeleton of lignin is phenyl propane or a "C6– C3" or a "C9" type.

Pulping is basically and mainly a delignification process employing inorganic acids or alkalis and other compounds or organic solvents (organosolv method) and compounds or by employing biological agents such as certain fungi which will selectively attack on lignin, causing its degradation and consequent dissolution. The amount and reactivity of lignin have a marked effect on the pulpability of the material which depends upon the type of raw material (softwoods, hardwoods, bamboos, etc.). During most pulping reactions, components other than lignin are simultaneously removed. The character of pulp depends upon the form and amount of energy supplied for accomplishing the separation. Chemical, mechanical or a combination of the two forms of energy is utilized. In general, when chemical energy alone is supplied, completely separated fibers are obtained; whereas in mechanical and semichemically pulping (combination of mechanical and chemical processing) whole fibers, fiber bundles, damaged fibers, and fiber fragments are produced. Bleaching of pulp is also a process mainly employed for further purification of the pulp by removing the remaining portions of lignin and other colour bodies in the pulp.

2.3.4.4 Extractives and ash

Extractive in wood are of low molecular organic compounds such as fatty acids, resin and sterols. Extractive along with cellulose, hemicelluloses and lignin solid material of bamboo includes less than 3%-5% which contribute to properties such as colour, smell, decay resistance, density and flammability. Extractives can be classified as lipophilic or hydrophilic organic compounds, which can be extracted from the samples by using neutral (non-polar),

organic solvents (methyl-tert-butyl ether, acetone, benzene, tetrahydrofuran) or water, respectively. Water soluble extractives are, among others, some carbohydrate of non-cell wall structural components and tannins. In contrast lipophilic extractives are classified into aliphatic hydrocarbons, fatty alcohols, fatty acids, resin acids and sterols as well as fats and waxes (Harinen, 2004). High amount of extrtractive substance in the raw material may result in poor quality of pulp and resulting in higher operating costs and an increased incidence of quality defects.

Ash is a term generally used to refer to inorganic substances such as silicates, sulfates, carbonates, or metal ions (Rydholm 1965). The fraction of inorganic compounds also called ash

constitutes of Ca, K, Mg, P, Mn, Fe, Si, Al and Na salts and the actual composition varies between wood species and is also influenced by the local compositions of the soil (Theliander et.al., 2002). The distribution range of different cellulosic feedstock composition is presented in the table (2.4) below.

Table 2.4: The distribution range of different cellulosic feedstock composition

Lignocellulosic materials	Cellulose (%)	Hemicellulose (%)	Lignin (%)
Hardwood stem	40-45	24-40	18-25
Softwood stem	45-50	25-35	25-35
Bamboo	41-49	28-32	20-22
Corn cobs	45	35	15
Wheat straw	50	30	15
Sorted refuse	60	20	20
Leaves	15-20	80-85	0
Cotton seed hairs	80-95	5-20	0
Coastal Bermuda grass	25	35.7	6.4
Switch grass	45	31.4	12

Source: Sun and Cheng (2003)

2.3.5 Soda-Anthraquinone pulping technology for bamboo

Nowadays interest has been given on sulfur free pulping. Therefore, studies on different pulping processes have been done (Sarwar, 2000). Among these processes used to get improved quality pulp and higher yield; soda-anthraquinone (AQ) process has given encouraging result. It is believed that AQ is still the most cost-effective sulfur free accelerator for alkaline pulping. The soda- anthraquinone process also offers a direct advantage of elimination the air pollution associated with the kraft process.

2.3.5.1 Processes descriptions of pulping of bamboo

i. Chippers of Bamboo

The bamboo from the stock is conveyed to the chippers (figure 2.6) below in trolleys which are weighted to the amount presented in each. It is charged in bundles of 15-20 bamboos in chipper feeder.

The outputs of chippers are varied from 2-4 tones per hour but it is around 3 tons on an average including the time for changing the knives. The life the knives are around 1500-2000 tons per set and the loose on chipping from 3-8 percent. The chips are screened in a vibrating screen, provided with screens having 3mm, 4030 round holes. Due to vibrating motion chips from 8cm to 12cm in length and 1.5cm to 2cm width pass through the screens and are pneumatically conveyed to the storage bins. The over size is charged to the chippers and the under sized contained about 50% from 2-30mm in size is separately digested. The dust is usually burnt in the boiler.

ii. Digesters of bamboo

The digesters in most of mills are of batch type although one or two mills have adapted continuous digestion. The digesters are situated just below the bins and are fed by gravity by opening a damper gate at the bottom of the bin. The chips fall in the mouth of the digester and are pushed manually. The digester a steel pressure vessel having at the top, opening for falling it with chips and at the bottom which is inclined at 60^0, a four way outlet .The middle portion of the digester contains a jacket made perforated steel plates, 8mm in diameter. The jacket has an outlet and the screen before the opening is unperforated. Near the top opening there are two

perforated pipes known as vomiting pipe and the vent pipe. The former is used to introduce the cooking liquor and the re circulating liquor while the later is used to release the gas and pressure after the cooking is over. The cover is secured by eye bolts. Bamboo can be digested by two methods namely: 1) fractional method 2) overhead method.

The chips are blown to the blow tank from where they pass to the coarse vibrating screens where jets of water make the pulp travel over the screen thus making the pulp separate from the knots. The undersize follows to the dilution cheats from where it follows to the thickener. The thickener or brown stock washer consists of a wire screen drum revolves in the suspension, the water pass through the screen living a layer the pulp on the other surface.

iii. Bleaching of bamboo pulp

The process of bleaching consists of solublizing & removal of coloring material namely lignin. While some of it removed in one process, in others is simply decolorized. Bleaching can be done either in single stage or in a multiple stage where the pulp is not easily bleachable. Bamboo pulp needs multi stage bleaching. The following stages of bleaching are generally used for bamboo pulp. Stage1 Chlorination, Stage2 Washing, Stage3 Alkali extraction, Stage4. Washing, Stage5.Hydro chlorite

iv. Soda recovery (chemical recovery)

No paper mills can expect to run economically without recovering the chemicals in the spent cooking liquor so called black liquor. It is a common practice, therefore, in all mills to treat the black liquor for the manufacture of white liquor. In brief the recovery operations consists of evaporating the black liquor to the desired concentration, burning the concentration with the makeup alkali to remove organic matter, caustisizing the product with milk of lime & setting & clarifying the liquor to yield white liquor. Recovering the alkali in most of the paper Mill is 80-90%.

2.3.5.2 Processes flow diagram of pulping of bamboo

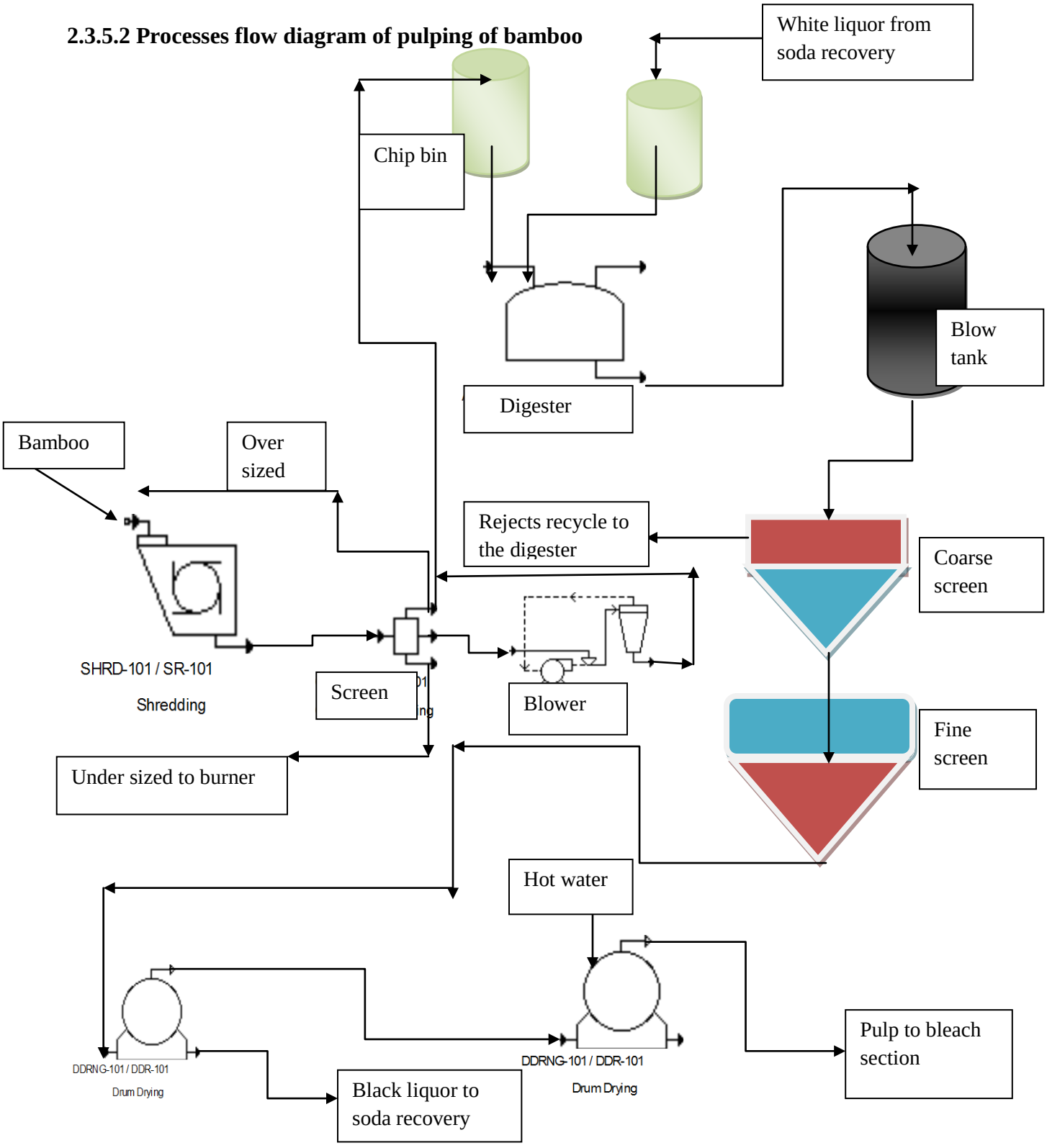


Figure 2.6 Process flow diagram of pulping of bamboo

2.4 Bamboos in Ethiopia

About 4.2% of Ethiopia's land area is forested with an area of 4.6 million hectares. Africa has about 43 species of bamboo covering about 1.5 million hectares (Kigomo 1988). Forty of these species are primarily distributed in Madagascar while the remaining three species are found in mainland Africa. Of the countries in Eastern Africa, Ethiopia possesses considerable bamboo resources, and there are two indigenous species of bamboo in Ethiopia. Ethiopia has over one million hectares of highland and lowland bamboo resources of which highland bamboo coverage is estimated to be 300,000 hectares (Kelbessa *et al*. 2000). This means that 86% of the African bamboo resource is found in Ethiopia. Ethiopia has over 1 million ha of bamboo (FAO,2013), corresponding to approximately 7% of the global bamboo resource. The country can sustainably produce three million cubic meters of dry weight annually from its two commercially important bamboo species: *Arundinaria alpine (Yushania alpina)* and *Oxytenanthera abyssinica* (FAO, 2005).

In Ethiopia, bamboo is a subsistence material for rural communities. Rural people are largely dependent on raw bamboo for construction, fencing, household furniture, household utensils like cups, local pipes, and vessels for carrying and storing, firewood for energy and food (bamboo shoot).

There is an an exercise in cultivating highland bamboos where an increasing number of households are realizing the economic potential of bamboo cultivation and these households have started to cultivate bamboo around their homesteads. The resource distribution in natural and plantation of lowland bamboo species is presented in table 2.5. Ethiopia does not have enough a modern bamboo based processing industry, and the handicraft sector is not well developed.

Table 2.5: Major Lowland Bamboo Distribution in Ethiopia

No	Bamboo Area	Region	Natural stand (Ha)	Plantation (Ha)	Total area (Ha)
1	Hinde/North of Nekemte	Amhara	8,670	-	8,670
2	Asossa	Benshangul Gumuz	77,947	-	77,947
3	Bambasi	"	64,245	-	64,245
4	Begi	"	21,509	-	21,509
5	Nejo	Oromiya	27,612	-	27,612
6	Dibate	Benshangul Gumuz	14,200	-	14,200
7	Guba	"	7,757	-	7,757
8	Kemashi	"	33,723	-	33,723
9	Pawe	"	53,830	-	52,830
10	Gimbi	Oromiya	29,125	-	29,125
11	Guten	"	6,044	-	6,044
12	Metema/Dansha/Humera	Tigray/Amhara	425,000	-	425,000
13	Didessa valley	Oromiya	135,000	-	135,000
14	Dangur	Benshangul Gumuz	27,350	-	27,350
15	Bulen	"	16,780	-	16,780
16	Galesa	"	10,870	-	10,870
	Total		**959,662**		**959,662**

In Ethiopia there are vast amount of cellulose containing materials and agricultural residues majority of whose pulp and paper potentials have not been exploited. Bamboo is the most important non-wood forest product and in Ethiopia is known as the 'poor man's timber'.

2.5 Effect of variables - Factors affecting pulp yield

The end results of pulping, as measured by pulp yield and quality, are affected by the variables controlling the chemical as well as mechanical stages of the process. The physical and chemical characteristics of the fibrous material, the composition of the pulping liquor, the amount of chemical applied, and the time and temperature of pulping are some of the variables affecting the chemical processing stage. An increase in temperature results in an increase in the rate of pulping and a decrease in pulping time for a given degree of delignification. The penetration of the cooking liquor into the fibrous material is an important dependent variable. The mechanical stage is affected by the properties of the materials from the chemical stage and its subdivision, the slurry consistency, the temperature, the number of passes, and the design of the machine and its elements.

Since small chips are more easily penetrated with the pulping chemical than large ones, the former are particularly favoured. It is recommended to use chips having a dimension of 20-30mm in the grain direction in full chemical pulping as against 10-13mm for semichemical pulping. Chips reduced laterally to matchstick dimensions by hammer or disk mills are used to some extent.

2.6 kappa number

The kappa number is an index used by the pulp and paper industry to express the residual lignin content in unbleached pulp after cooking. Lignin is responsible for the brown coloration of paper on service and residual lignin is removed at the subsequent bleaching stage to obtain desired brightness. Lower residual lignin in pulp content required less amount of bleaching chemicals to obtain the same brightness of bleached pulp. Therefore, the lignin content must be well known, so that only a minimum amount of bleach chemicals are used. The higher the lignin content in the pulp the more is the kappa number. The pulp having high lignin content is termed as hard cooked pulp and the pulp with low lignin content as soft cooked pulp. The hard cooked pulp requires more bleaching chemicals to attain particular brightness compared to soft cooked pulp.

CHAPTER THREE

3 MATERIALS AND METHODS

3.1 Characterization of chemical composition of *Oxytenanthera abyssinica* bamboo Culms

3.1.1 Materials

i) Sample Preparation of bamboo Culm

Oxytenanthera abyssinica bamboo, the main raw material for pulp production is available in Ethiopia grows in the western part along major river valleys and in the lowlands bordering Sudan. The *Oxytenanthera abyssinica* bamboo samples used for this study were collected on Dec, 2014 from Gembeshere, Afasezim and Abrhamo kebeles around Assosa town of Benishangul Gumuz region.

Bamboo stems from 3 and above 3 years old of lowland bamboo samples were harvested from Assosa areas. Then the harvested bamboo culms were air dried for two weeks. The bamboo culms for chemical analysis were cut into small strips with knife (surgical). The strips were small enough to be placed in a Wiley Mill. All of this material was ground in the Wiley Mill. The material was then placed in a shaker with sieves to pass through a No. 40 mesh sieve (1mm) yet retained on a No. 60 mesh sieve (250-µm). The resulting material was placed in plastic bags labeled with appropriate code for chemical analysis. These are shown in figure (3.1) below

(a) (b) (c)

Figure 3.1 Sample preparation stages (a) air dry, (b) milling and (c) ready for chemical analysis

After Sample preparation was done for lowland bamboo, Laboratory work and test were carried at Forest Products Utilization Research Center and School of Chemical and Bio Engineering (AAIT) of AAU.

ii. **Apparatus**

The equipments used during the experimentations includes razor blade, Wiley mill, sieve, strip road, Silica crucible, muffled furnace, desiccators, digital weighing balance, weight bottle, stopper, oven, tong, Bunsen burner, Erlenmeyer flask, water bath, heating mantle, vacuum suction, weighed sintered glass crucible, what-man filter paper, measuring cylinder, round bottom flask, soxh-let apparatus, cellulose extraction thimble, cotton, beaker, jar, scissor, dryer, glove, mask, goggles.

iii. **Reagent**

Chemicals/reagents used in this study are: - sodium chloride, ethyl alcohol, toluene, nitric acid, caustic soda (NaOH),acetic acid, distilled Water, anhydrous ethanol, phosphorus pent oxide, sulfuric acid.

3.1.2 Methods

Following standards of American Society for Testing and Materials (ASTM) shown in the below table, ash content, hot-water extractive content, alcohol-benzene soluble extractive, and lignin content were determined. While cellulose content was determined according to Kurchner-Hoffer method (Brown 1975) and there was a minor modification for alcohol-toluene solubility of bamboo extractive content test. Instead of benzene solutions, toluene solution was used. The exact standard that was followed for each chemical property performed is presented in Table 3.1.

Table 3.1: Standards followed for chemical analysis

Property	**Standard**
Alcohol-toluene solubility *	ASTM D 1107-56
Hot-water solubility	ASTM 1110-56
Klason lignin	ASTM D 1106-56
Hemicellulose	Direct extraction with aqueous alkali
Cellulose	Kurchner-Hoffer
Ash Content	ASTM D 1102-84

Each test was conducted using 3 replications. It was necessary to conduct additional experimentation when analyzing for alcohol-toluene extractive content. Both the lignin and Hemicellulose content test are performed with extractive-free bamboo that is derived from the alcohol-toluene extractive test.

The specific procedure is as follows.

i. Hot-water Solubility of Bamboo

Two-gram sample was oven-dried and placed into a 250 mL Erlenmeyer flask with 100 mL of distilled water. A reflux condenser was attached to the flask and the apparatus was placed in a heating mantel where the heat energy was regulated at water boiling temperature as shown in figure (3.2). Samples were then removed from the mantel, cooled to room temperature and filtered by vacuum suction into a fritted glass crucible of known weight. The residue was washed with hot tap water before the crucibles were oven-dried at 103±2^{o}C. Crucibles were repeatedly heated, cooled in a desiccator and weighed until a constant weight was obtained.

The following formula was used to obtain the hot-water solubility of bamboo:

$$Hot\ water\ soluble\ (\%) = \frac{w1-w2}{w1}100 \qquad (2)$$

Where, w1= weight of oven-dry test specimen (grams).

w2 = weight of oven-dry specimen after extraction with hot water (grams).

Figure 3.2 Hot-water determinations

ii. Extractive substances of Bamboo

Two-gram oven-dried sample was placed into a cellulose extraction thimble. The thimble was plugged with a small amount of cotton and placed in a soxhlet extraction tube. The boiling flasks containing 2:1 solvent mixture of 95 percent ethyl alcohol and distilled toluene respectively were placed on a heating mantle. The extraction was conducted for eight hours at the rate of approximately six siphoning per hour as shown in figure (3.3) below.

When the extraction was completed, all of the remaining solvents in the soxhlet were transferred to the boiling flask evaporated in a rotary evaporator. The flasks were oven-dried at 103±2 ^{o}C, cooled in desiccators, and weighed until a constant weight was obtained.

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

$$Extractives(\%) = \frac{W1-W2}{W1}100 \qquad (3)$$

Where, w1=weight of oven-dry test specimen (grams).

w2=weight of oven-dry extraction residue (grams).

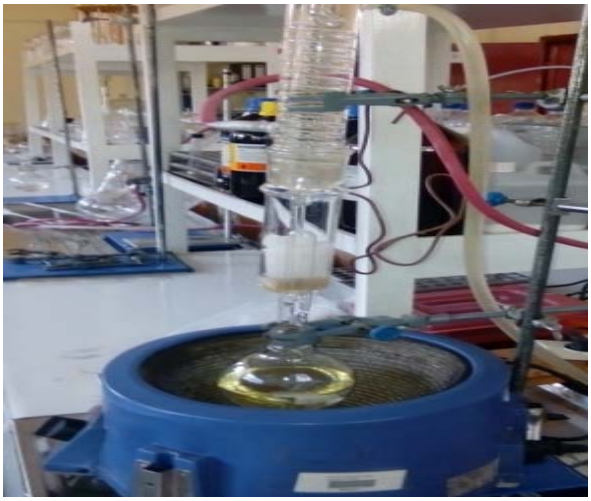


Figure 3.3 Extractive substance determinations

iii. Cellulose nitric acid method

A gram of the sample was refluxed with three successive portions of a mixture of concentrated nitric acid (20 percent volume by volume) in ethyl alcohol for 1 hr each, filtered, washed, dried, and weighed the white fiber residue as cellulose as shown in figure (3.4) below.

$$Cellulose\ (\%) = \frac{w2}{w1}100 \quad (4)$$

Where, $w1$ is the amount of extract free samples taken for analysis and $w2$ is the residual mass of cellulose

Figure 3.4 The cellulose sample after drying

iv. Hemicelluloses in bamboo by direct extraction with aqueous alkali

The defatted bamboo meal (200g) was extracted directly with 5% aqueous sodium hydroxide (2.5 liters) without prior delignification as shown in figure (3.5). The extract was filtered and acidified with acetic acid, and then the hemicelluloses fraction was precipitated by addition of three or four volumes of ethanol. The precipitate was collected by centrifugation and washed successively with 50% ethanol, anhydrous ethanol and ethyl ether. The product was dried over phosphorus pent oxide under a vacuum to give a pale brownish powder.

$$Hemicellulose\ (\%) = \frac{W2}{W1}100 \quad (5)$$

Where, w1 is the amount of dry sample for analysis and w2 is the dried residue after analysis

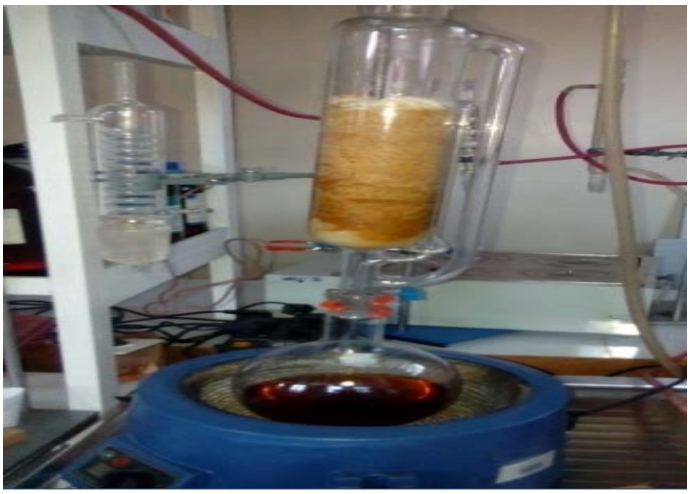


Figure 3.5 Defatting bamboos for Hemicellulose determination

v. Klason Lignin in Bamboo

One-gram, oven-dried sample of extractive-free bamboo was placed in a 150 mL beaker and 15 ml of cold sulphuric acid (72 percent) was added slowly while stirring and mixing well. The reaction proceeded for two hours with frequent stirring in a water bath maintained at 20 ^{o}C as shown in figure (3.6). At the end of 2nd hr the specimen were transferred by washing it with 560 mL of distilled water into a 1,000 mL flask, diluting the concentration of the sulfuric acid to three percent. Allihn condenser was attached to the flask and refluxed in a boiling water bath for four hours. The flasks were then removed from the water bath and the insoluble material was allowed for overnight to settle. The contents of the flasks were filtered by vacuum suction into a fritted-glass crucible of known weight. The residue was washed free of acid with 500 mL of hot tap water and then oven-dried at 103±2^{o}C. Crucibles were then cooled in desiccators and weighed until a constant weight will be obtained. The following formula was used to obtain the lignin content of bamboo:

$$Klason\ lignin\ (\%) = \frac{w2-w3}{w1}100 \quad (6)$$

Where,

w1=weight of oven-dried extractive-free sample (grams).

w2=weight of oven-dried residue and crucible (grams).

w3=weight of oven-dried crucible (grams).

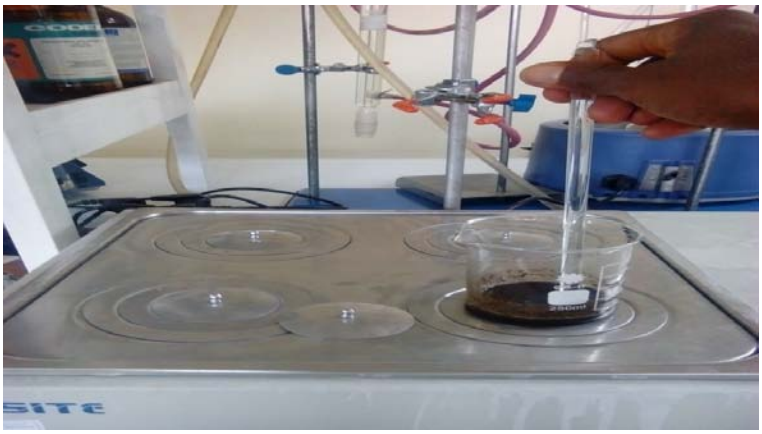


Figure 3.6 Klason lignin determinations

vi. Ash content

Silica crucible is dried over a burner for 10 min, cooled in a desiccator containing silica gel up to room temperature. About 2 gm of sample was taken (A') and crucible with sample was kept in a muffle furnace at 600 $\pm 50^0$C for 2 hrs as shown in figure (3.7). Ascertain all the carbon particles are removed by blocking air from the formation of black char particles Then Cooled the crucible in desiccators with silica gel to room temperature and weighed (B').

$$Ash\ content\ (\%) = \frac{w2}{w1}100 \quad (7)$$

Where, w1 is the amount of sample used for analysis and w2 is the mass of ash in gram

Figure 3.7 Muffle furnace

3.2 Effects of cooking conditions on *Oxytenanthera abyssinica* bamboo pulp yields and kappa number

3.2.1 Materials

i) Apparatus

The equipments used to conduct this study were:- oven, weighing bottle, desiccators, digital weighing balance, stopper, tong, plastic bags, autoclave, 500ml Erlenmeyer flask, alumiuium foil, 250-µm -1mm mesh sieve size, measuring cylinder, volumetric flask, stopwatch, sprayer Agitator, Constant temperature bath, Reaction beaker, 2000-mL, glass or porcelain, Pipettes, Burette, 50-mL, graduated to 0.1 mL, a Buchner funnel and filter flask to dewater three to four grams of pulp; stopwatch or clock; 1000-mL and a 25- or 50-mL graduated cylinder; 250-mL beaker, glove.

ii) Reagent

Reagents used in this study were: - caustic soda (NaOH), anthraquinone (AQ), distilled water, Potassium permanganate solution standardized 0.1000 $\pm$0.0005N $KMnO_4$, Sodium thiosulfate solution, approximately 0.2N $Na_2S_2O_3$, Potassium iodide solution 1.0N KI, Sulfuric acid 4.0N H_2SO_4 and Starch indicator solution 0.2%.

3.2.2 Pulping of bamboo

The bamboo *Oxytenanthera abyssinica* culms were chipped with hammer mill and chips of greater than 5mm in length was selected. Soda cooking liquor was prepared from a standard concentrated solution of sodium hydroxide by serial dilution with distilled water. Using alkaline pulping method (Soda – anthraquinone –Soda-AQ) the bamboo chips from the *Oxytenanthera abyssinica* were weighed and charged into a reactor with the required amount of chemical solution at liquor to solid ratio of 4:1. The reactor was heated to the operating temperatures, active alkali concentration and cooking time, which was then maintained throughout the experiment. The resulting pulp was thoroughly washed with tap water as shown in figure (3.8) and the pulp yield was determined gravimetrically after drying at 103 ±3 ^oC to constant weight in

the oven. In each batch of bamboo pulping were added 0.1% AQ in 1:4 bamboo chips to liquor ratio. The pulp was screened through a 250-µm -1mm mesh sieve size and separated for screened yield and yield reject.

Figure 3.8 Pulp washing and screening

Table 3.2: Pulping conditions used to cook bamboo chips

Cooking conditions	**Soda-(AQ)**
Active alkaline percent as oven dry	15%, 20%, 25%
Liquor to wood ratio	4:1
Anthraquinone (AQ) percent	0.1
Time to max. temperature (min)	30, 60, 90
Time at max. temperature (min)	60, 120, 180
Max. temperature (°C)	150, 175, 200

Pulp Yield Determination

The pulp yield was determined by weighing the wet pulps (W) and taking two representative samples each of 50 g for determining the dryness. The samples were weighed and dried in an oven at 105°C for overnight. The dried samples were weighed and the yield was determined as follow:-

$$Dryness\ \% = \frac{A}{B}100 \quad (8)$$

$$Total\ pulp\ yield\ \% = \frac{WA}{OD\ sample}100 \quad (9)$$

Where, A = O.D. weight of pulp taken for dryness

B = A.D. weight of the pulp taken for dryness (50 g)

W = Total A.D. weight of the pulp.

(a) (b)

Figure 3.9 Pulp after drying (a) unbleached (b) bleached

3.2.3 Determination of the kappa number of pulp

The kappa number is the volume (in milliliters) of 0.1N potassium permanganate solution consumed by one gram of moisture-free pulp. The results are corrected to 50% consumption of the permanganate added. It shows the degree of delignification of pulp and is proportional to the lignin content of pulp.

10 g of pulp (dry weight) was mixed and made into a pad by filtering on a Buchner funnel, avoiding any loss of fibers. Prior to weighing the test samples, conditioned for at least 20 min in the atmosphere near the balance. The test specimen was disintegrated in 500 ml distilled water until free of fiber bundles. The disintegrated test specimen was transferred to a

2000 ml reaction beaker with properly rinsed by adding enough distilled water to bring the total volume to 795 ml. 100 ml potassium permanganate solution (0.1N) and 100 ml of the sulfuric acid solution (4N) was pipetted in a 250 ml beaker. The mixture was brought to 25°C quickly and was added immediately to the disintegrated test specimen, simultaneously started a stopwatch. The beaker was rinsed with 5 ml of distilled water and the total volume was made to 1000±5mL.

At the end of exactly 10 min., the reaction was stopped by adding 20 ml of the potassium iodide solution (1.0N) from a graduated cylinder and immediately after mixing, the free iodine was titrated with the sodium thiosulfate solution (0.2N), adding a few drops of the starch indicator towards the end of reaction. A blank determination was carried out using exactly the same method as above without taking any pulp sample. This is shown in figure (3.10) below.

Kappa number is calculated as follows:

$$K = \frac{P*f}{w} \tag{10}$$

And

$$P = \frac{(b-a)N}{0.1} \tag{11}$$

Where:-

K = kappa number

f = factor for correction to a 50% permanganate consumption, dependent on the value of p.

w = weight of moisture-free pulp in the specimen, g

p = amount of 0.1N permanganate actually consumed by the test specimen, mL

b = amount of the thiosulfate consumed in the blank determination (without adding pulp),mL

a = amount of the thiosulfate consumed by the test specimen, mL

N = normality of the thiosulfate solution.

Figure 3.10 Titration for determination of kappa number

3.2.4 Design of Experiments

The first task before conducting the experiments was selection of potential parameters to be varied. The three main factors selected in this study were cooking temperature, concentration of active alkali, and pulping time. The level of the selected factors is determined from the literature research and is presented in table 3.3. The experiment performed as a completely randomized design with three main factors at three levels and two response variables. The two response variables were the pulping parameters; pulp yield and kappa number.

Table 3.3: Level and code of variables used for Full Factorial Design

Factors	**Unit**	**Coded symbol**	**Levels 1**	**Level 2**	**Level 3**
			-1	**0**	**+1**
Cooking temperature	^{0}C	A	150	175	200
Active alkali concentration	%	B	15	20	25
pulping time	Min	C	60	120	180

Data analysis has performed by DESIGN EXPERT® 7.0.0 software using general factorial design method and randomize the runs. Randomization ensures that the conditions in one run neither depend on the conditions of the previous runs nor predict the conditions in the subsequent runs. Randomization is essential for drawing conclusions from the experiment, in correct, unambiguous and defensible manner.

This design of the experiment helps us to differentiate the significance of the main and the interaction factors. This program software also used to develop the mathematical model that will describe the effects of the main and interaction factors on the response.

The proposed general factorial design required 27 runs. Detail of the experimental runs with the set of input parameters that were conducted are given in Table 3.4.

Table 3.4: Experimental design using design expert software (General Factorial Design)

Run order	A:temperature	B:active alkali	C: Time
1	200	15	180
2	175	25	60
3	175	15	120
4	200	25	180
5	150	25	120
6	200	15	120
7	150	20	180
8	200	20	180
9	200	25	60
10	150	15	120
11	175	25	120
12	150	15	60
13	175	15	60
14	175	15	180
15	150	20	120
16	200	20	60
17	150	25	60
18	175	20	180
19	200	15	60
20	175	20	60
21	150	20	60
22	150	25	180
23	200	25	120
24	175	25	180
25	200	20	120
26	175	20	120
27	150	15	180

3.3 Characterization and comparisons of *Oxytenanthera abyssinica* bamboo paper properties with other imported raw materials

3.3.1 Materials

i) Apparatus

The equipments used to conduct this study were:- Standard disintegrator, Standard 6 1/2 in diameter sheet machine with stirrer, Standard couch roll, Couch plate, Pump and press with pressure gage, suction template of sheet former, Disks,(mirror polished), Drying rings, Blotting paper, Cup. tea cup, Bucket.

3.3.2 Laboratory Hand Sheet Preparation and testing

3.3.2.1 Beating and Disintegrating

400gm oven dry pulp sample was transferred into the beater containing 23 lit of water and circulate pulp for 5 minutes without pressure between the roll and the bed plate. The motors were switched off and the roll and beater were stopped. By taking 130ml of sample from the beating machine diluted to 1000ml in measuring cylinder. The pulps suspensions were homogenized by disintegrating it at 8000 rpm in the disintegrator for 5 min and consistency of the stock after dilution (final) was calculated to work a sheet of desired weight. A hand sheet papers was made from the pulp slurry with a diameter of 25cm on a paper sheet former.

3.3.2.2 Sheet Preparation

Laboratory hand sheets were prepared of bamboo pulp in a laboratory sheet former, where pulp suspension of 5% consistency was drained through a wire. The sheet former was connected to a vacuum system to provide better water removal. After formation the sheets were separated from the wire and pressed with dry blotter on one side of a sheet and smooth metal plate on the other with pressure of 0.48 MPa for totally 5 minutes in two stages. First stage pressing was completed in 3 minutes and second stage pressing was completed in 2 minutes after pressing the sheets were dried on the metal plates at room temperature for a day.

Then they were cut accordingly for specific sheet testing. The hand sheets were measured for strength properties such as basis weight or grammage, tensile index, tear index, and burst index.

3.3.2.3 Sheet Testing

Tear Strength: The tear strength of the sheets was determined using L &W Tear tester to measures the internal tearing resistance of paper sheets. The results were reported as tear index 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/m2).

Apparatus: - L & W tearing tester ELMENDORF

Procedure:-

- The pendulum was raised to its initial position; clamp 4 pieces of specimens (65*7.5cm).
- A Silt in the specimens was made by completely pressing down the knife rocker arm.
- The pendulum was stop by quickly pressing down the releaser. Then softly break the pendulum after oscilation to the right. Read the scare valve and note it.
- The average of the reading was Calculated and multiplied with the factor of the pendulum. The product is equal to the tearing strength in millnewton (mN)

CALCULATION:-

The average reading was calculate and multiplied it with the factor of the pendulum and the product is equal to the tearing strength in mN.

$$a = P * S \quad (12)$$

Where a = tearing strength in mN.

S= the average strength reading from the instrument

P = 4, the factor of the pendulum i.e. the factor which is used for transferring the reading on the scale to the tearing strength in mN.

N.B:- 1sheet (specimen) = multiply 16(P=16)

2sheet (specimen) = multiply 8(P=8)

4sheet (specimen) = multiply 4(P=4)

$$Tear\ factor = \frac{Tear\ strength}{Basis\ weight\ (gm/m2)}\ (\text{MN})\ *100 \quad (13)$$

$$Tear\ index = \frac{Tear\ factor}{10.2} \quad (14)$$

Tensile Strength: Tensile strength was done using instrument L &W Tensile tester where 10mm width with 100mm length strip papers were prepared. The strip was gripped vertically and the tester started to operate at 2000 (unit of speed for the machine) and the reading where the strip break apart was taken as strength in kg. Tensile index is tensile strength divided by grammage.

Apparatus: - Schopper type tensile strength tester.

Procedure:-The sheet specimens were cut into 15mm± 0.1 wide by 230mm long test pieces.

- The test piece was placed in the clamps making sure that any slacks are eliminated.
- Avoid touching the test area between the clamps with the fingers. All readings were recorded except for test pieces that break with in 2mm of claming line.

Calculation

1) $Tensile\ strength\ X1 = a/b$ (15)

Where, X1 = tensile strength (kN/m)

a = maximum tensile force in (N)

= instrument reading = kg

= to change in to (N) = kg * 9.807

b = initial width of the sample in (mm)

2) $Tensile\ index\ X2 = 1000 * X1/W$ (16)

Where, X2 = tensile index (NM/gm)

X1 = tensile strength (KN/m)

W = mean grammage in gm/m^2

3) $Breaking\ length\ X3 = a * \frac{200{,}000}{3*b}$ (17)

Where, a = mean tensile strength in kg

b = grammage in gm/m^2

X3 = breaking length in metric (m)

Bursting Strength: The bursting strength of the sheets was determined using Bursting strength tester. As it is more meaningful to compare bursting strength of papers of differing grammages in terms of burst index, therefore burst index was obtained by dividing the bursting strength in kPa by the grammage of the paper in g/m^2.

Apparatus: - Motor driven Mullen (burst) testers.

Test specimen: - The test specimen was 2.5 by 2.5 inches sheet.

Procedure:-

- The test piece was clamped in the tester tightly.
- The maximum reading pointer was set to zero position.
- The pump motor was started; engage the pumping system and the test piece were waited to burst.
- The maximum read pointer was recorded and it was rested gently to zero position remove the broken sample.

Calculation: - Instrument reading = Kg/cm^2

To change Kg/cm^2 in to Kpa (Kilo pascal)

$Kpa = Kg/cm^2 * 98.07$

Where, Kpa = SI unit of bursting strength

Kg/cm^2 = instrument reading.

$$Burst\ factor = \frac{bursting\ strength\ (\frac{kg}{cm2})}{basis\ weight\ (gm/m2)} * 1000 \quad (18)$$

Burst index is bursting strength divided by basis weight, $X = \frac{a}{W}$ (19)

Where: - X = burst index kpa m^2/kg

a = burst strength in kpa

w = basis weight gm/m^2.

CHAPTER FOUR

4 RESULTS AND DISCUSSION

In this section, the results of the experiment carried out on *Oxytenanthera abyssinica* bamboo culms such as chemical composition, the effect of pulping parameters such as active alkali, cooking temperature and pulping time on the amount of pulp yield and kappa number for pulp potential through soda-anthraquinone pulping method, and its relationship with imported pulp was investigated and discussed here under.

4.1 Characterization of chemical composition of *Oxytenanthera abyssinica* bamboo Culms

Information on the chemical composition of bamboo is important as far as its utilization for pulping is concerned. Similar to other lignocellulosic materials, the primary components of *Oxytenanthera abyssinica* bamboo are cellulose, hemicelulose, and liginin. Holocellulose is the main component contributing to the strength of paper. The high cellulose content and a yield of 40-50 per cent pulp make bamboo an ideal raw material for manufacture of paper.

The average values for the chemical composition of bamboo (*Oxytenanthera abyssinica*) from Assosa, Benishangul gumuz region are given in Table 4.1. (Based on average values of three replicates, errors lower than 1% in all components, weight percent on dry basis). The amount of these chemical components affect pulp qualities, hence they were used to estimate the suitable pulping and bleaching conditions for appropriate pulp application (Kamthai, et al., 2005). Apart from the high cellulose content, the other factors like lignin, and silica contents as well as higher solubility are not in favour of ideal pulping conditions. But, since it contains higher cellulose content, bamboo is a preferred raw material for pulping.

Table 4.1: The chemical composition of Oxytenanthera abyssinica bamboo compared to Africa.

Species	Extractives %		Ash %	Cellulose %	Hemicelluloses %	Lignin %
	Hot-water	Alcohol-toluene				
O. abyssinica	6.80	5.60	5.30	52.06	16.90	22.47
Africa*	6.5	2.7	1-4	n.a	12-33	15-27

n.a not available *Source: Louppe, et al., (2008)

In general, non-woods differ somewhat from woods in their chemical composition and properties, which in turn have a direct influence on pulping and bleaching processes.

i. Hot-water solubility in bamboo

The hot-water extraction removes a part of extraneous components, such as inorganic compounds, tannins, gums, sugars and starches, present in bamboo. The results of hot water soluble extractive of *Oxytenanthera abyssinica* bamboo (6.8%) is in good agreement compared to that from Africa (6.5%). The results of *Oxytenanthera abyssinica* bamboo agreed with that reported by Dhamodarn et al., (2003) 3.1 – 7 % but higher than bamboo 5.8% Karar (2004). Soluble hot water extractive of *Oxytenanthera abyssinica* bamboo from Ethiopia is higher than from Africa. Such variations in plants exist with geographical location and plant portion.

ii. Alcohol-toluene extractives in bamboo

The alcohol-toluene extractives of bamboo consist of the soluble materials, not generally considered part of cell structural components bamboo substance. These are primarily the waxes, fats, resins and some gums as well as some water soluble substances. No single organic solvent is capable of removing all these substances, and different solvents remove only soluble components in their solubility range of polar to non-polar. The mixture, ethanol-toluene, appears to provide the most complete removal of residual solvent-extractable substances in bamboo.

The result of alcohol-toluene soluble in *Oxytenanthera abyssinica* bamboo (5.6%) are higher than those in wood, such as poplar with the benzene-alcohol extractive content of 2.14% (Gong 2007) and Africa (2.7%), but lower than that in grasses, such as rice straw with the benzene-alcohol extractive content of 7.45% (Liu *et al.* 2003). This results agreed with that reported by Dhamodarn et al (2003) 0.3 – 7.8 %, but higher than Karar (2004) 3.2 %. This indicated that *Oxytenanthera abyssinica* bamboo contained more substances like waxes, fats, resins, phytosterols, non-volatile hydrocarbons, low-molecular weight carbohydrates, salts, and other water-soluble substances. Wax material attached to the inner layer also contributed to the higher alcohol-toluene extractive content relative to the middle and outer layers. Higher alcohol toluene extractive in bamboo may be advantage for anti-decay and it will provide good strength in fiber processing because of its higher specific gravity. Generally the higher soluble extractive content (tannins, gums, sugars, starches and coloring matter) present in bamboo and indicated easy access and penetration of chemicals to the cell wall materials. It therefore means that the alkali charge must be kept low in order to preserve the cellulose content and enhance good pulp yield. But a higher extractive content is quite challenging for dissolving pulp production. Extractives may be converted into pitch, which can adversely affect the runnability of process equipment by choking the wire. Therefore, more attention should be given to the extractives in *Oxytenanthera abyssinica* bamboo during the manufacturing of dissolving pulp.

iii. Cellulose

Understanding the cellulose characteristics of bamboo is fundamental to its use as a feedstock. Cellulose is the main constituent of bamboo. Approximately 40-55% of the dry substance in bamboo is cellulose. Cellulose is a homopolysaccharide composed of β-D-glucopyranose units which are linked together by (1→4) -glycosidic bonds. Cellulose molecules are completely linear and have a strong tendency to form intra- and intermolecular hydrogen bonds. Bundles of cellulose molecules are thus aggregated together in the form of microfibrils, in which crystalline regions alternate with amorphous regions. Many cellulosic materials consist of crystalline and amorphous regions in different proportions, and these crystalline and amorphous regions affect the accessibility and chemical reactivity in pulp production (Ciolacu *et al.* 2011). Moreover, the crystallinity of cellulosic materials is affected by cooking and bleaching conditions, such as

chemical agents, temperature, and pressure (Gumuskaya *et al.* 2003; Carrasco *et al.* 1994).

The results of cellulose of *Oxytenanthera abyssinica* bamboo was high (52.06%) which indicate that bamboo species can be acceptable raw material for alkaline methods, since high pulp yield is expected. The result of cellulose content of *Oxytenanthera abyssinica* bamboo agreed with the results of Schott (2006) 50-70 %, but higer than that reported by Robert (1996) 50% and lower than by Judt (1993) 57-66%, Hurter (2001) 57 - 66%, Okubo et al., (2004) 60.8% and Yang et al,.(2008) 57– 66%. The thick cell wall cause for the increase of holocellulose content which is one of the major components of cell wall.

In general, the cellulose content in bamboo which is comparable to the reported cellulose content of softwoods (40-52%) and hardwoods (38- 56%). Therefore, cellulose contents in this range make bamboo a suitable raw material for the paper and pulp industry.

iv. Hemicelluloses

Hemicelluloses are heterogeneous polysaccharides, unlike cellulose, most hemicelluloses function as supporting materials in the cell walls and their effect on pulping characteristics is important. The hemicelluloses are reported to be retained in the pulping even after a final stage of cold-alkali purification with 17.5 percent NaOH. This suggests that there are 'alkali resistant' hemicelluloses components in close association with the cellulose property (Negi 1970). The result of hemicellulose of *O. abyssinica* was (16.9 %). This result shows that it is in the range (12-33) of *O. abyssinica* of Africa. The result of hemicellulose of *Oxytenanthera abyssinica* agreed with Judt (1993) 15-26 %, Hurter (2001) 15 - 26% and Dhamodarn et al., (2003) 16 – 21%, but disagreed with Schott (2006) 20-30% and Yang et al., (2008) 20–25%.

v. Klason Lignin Content

Lignin is one of the structural components of cell wall and is polymer of phenylpropane units. Many aspects in the chemistry of lignin still remain unclear. Klason lignin is obtained after removing the polysaccharides from extracted (resin free) wood by hydrolysis with 72% sulfuric acid. The Lignin in *O. abyssinica* isolated from extractive free sample as an insoluble residue

after hydrolytic removal of the polysaccharides. Bamboo lignin is built up from three phenyl-propane units, p-coumaryl, coniferyl and sinapyl alcohols interconnected through biosynthetic pathways [Liese 1987].

Determination of lignin content in raw materials provides information for evaluation and application of the processes. Hardness, bleachability, and other pulp properties, such as color, are also associated with the lignin content. The results of lignin of *Oxytenanthera abyssinica* is (22.47 %) and the low lignin content of bamboo indicated better unbleached pulp and decreasing of chemical solution consumption to separate lignin from fiber. The lignin values of 22.47% place bamboo at the high end of the normal range or 11-27% reported for non-woody biomass [Bagby 1971] and closely resemble the ranges reported for softwoods (24-37%) and hardwoods (17-30%) (Fengel, 1984 and Dence, 1992). This results agreed with and found in the range reportes of Judt (1993) 21-31%, Hurter (2001) (21 - 31%), Dhamodarn et al., (2003) 20 - 30%, Schott (2006) 20-30% and Yang et al 2008) 20–30%, but disagreed by Okubo et al., (2004) 32.2%.

vi. Ash content

Ash is a term generally used to refer to inorganic substances such as silicates, sulfates, carbonates, or metal ions. It has been suggested that the higher ash content in chips is mainly due to the fact that almost all silica is located in the epidermis layers (Satish et al., 1994). It is well known that transition metals such as Mn, Fe, and Cu have negative effects on the bleaching selectivity and pulp beleachability in the hydrogen peroxide bleaching stage (Loureiro *et al.* 2012).

Briefly, the ash constituents had a detrimental effect on the processing and quality of dissolving pulp. Consequently, the amount of ash in the raw material will indicate the measure to be taken on pulp processings.

Although residual ash in a dissolving pulp is considered a contaminant for the preparation of cellulose derivatives, the mineral components are not distributed homogeneously in the plant cell fractions, mainly accumulated in the parenchyma cells (Sixta 2006). Therefore, the pressure

screening of unbleached pulp and centrifugal cleaning after bleaching can be utilized to reduce the amount of harmful ash components (Wan Rosli et al. 2003).

The results of the ash content of *Oxytenanthera abyssinica* bamboo was higher (5.3%) compared to that from Afirca (1-4 %). This result in within the range of reports made by Liese (1998) 0.8 – 9.7 % and Dhamodarn et al., (2003) 1.0 – 9.0 %. However, the result of ash content of *O.abyssinica* is higher with Judt (1993) 1.7 – 4.8 %, Hurter (2001)1.7–5% Karar (2004) 4.6 % and Yang et al., (2008) 1 – 3 %. High ash content is undesirable for pulping as they affect normal alkali consumption and create problems at waste liquor recovery (Ogunsile, et al., 2009). This result indicates the soil was rich in mineral salts and inorganic matter.

4.2 Effects of cooking conditions on *Oxytenanthera abyssinica* bamboo pulp yields and kappa number

4.2.1 Experimental results

The effect of pulping time, cooking temperature and active alkali on pulp yield and kappa number was studied and evaluated for best pulping conditions. Determination of residual lignin in the pulp is the most important in all pulp analyses. It indicates the degree of delignification obtained by the cook and forms the basis of comparison for many of the cooking results, such as yield, screenings, pulp brightness; etc. It is based on measurement of a chemical reaction, such as chlorination or permanganate oxidation. These methods are more rapid and widely employed in mills, even though they have the drawback of giving only a relative figure for the lignin content and not an absolute value.

The experimental values of pulp yield and kappa number obtained under different pulping conditions are presented in table 4.2. These results were input into 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 4.2: Experimental observations

Run order	A:Temperature (^oC)	B: Active alkali (%)	C: Time (mint.)	Pulp yield (%)	Kappa number
1	200	15	180	39.21	13.5
2	175	25	60	48.11	24
3	175	15	120	50.56	28.2
4	200	25	180	32.88	17.3
5	150	25	120	49.58	22.5
6	200	15	120	48.29	17.1
7	150	20	180	51.31	14.6
8	200	20	180	40.75	12.8
9	200	25	60	42.88	16.6
10	150	15	120	51.98	32.7
11	175	25	120	47.98	12.3
12	150	15	60	52.29	44.9
13	175	15	60	51.27	35.6
14	175	15	180	48.02	23.2
15	150	20	120	49.79	20.9
16	200	20	60	43.74	21.3
17	150	25	60	49.87	34.8
18	175	20	180	48.6	14.4
19	200	15	60	49.09	22.8
20	175	20	60	49.5	30.9
21	150	20	60	50.78	36.9
22	150	25	180	48.62	11.5
23	200	25	120	39.34	13.4
24	175	25	180	44.23	10.9
25	200	20	120	40.98	15.6
26	175	20	120	49.08	25.8
27	150	15	180	51.68	20.4

The resulting data, Table 4.2; were analyzed using Design expert® 7 software to determine the effects of active alkali concentration, cooking temperature and pulping time. The dependent variables used as a response parameter were the pulp yield and kappa number. All experiments were carried out in a randomized order to minimize the effect of unexpected variability in the observed response due to extraneous factors. And the design summary for the experiment is shown in table (4.3).

Table 4.3: Design summary

Study Type	Factorial
Initial Design	Full Factorial
Center Points	0
Design Model	2FI
Runs	27
Blocks	No Blocks

Factor	Name	Units	Type	Low Actual	High Actual	
A	Temperature	^{0}C	Categoric	150	200	Levels: 3
B	Active alkali	%	Categoric	15	25	Levels: 3
C	cooking time	min.	Categoric	60	180	Levels: 3

Response	Name	Units	Obs	Analysis	Minimum	Maximum	Mean	Std. Dev.	Ratio
Y1	pulp yield	%	27	Factorial	32.88	52.29	47.05	4.77	1.59
Y2	kappa number	-	27	Factorial	10.90	44.90	22.03	8.90	4.12

4.2. 2 Adequacy check for the developed models

The adequacy of the model was checked by analysis of variance (ANOVA) and some diagnostic plots. Analysis of variance (ANOVA) is employed to test the siginificance of the developed models. Table 4.4 and, table 4.5 show the summary of the analysis of variance (ANOVA) of the two responces pulp yield and kappa number respectively. The detail ANOVA for the two responses is given at Appendix C.

Table 4.4: Analysis of variance (ANOVA) for pulp yield

Source	**Sum of Squares**	**Df**	**Mean Square**	**F Value**	**p-value Prob > F**
Model	605.19	18	33.62	26.35	< 0.0001
A-Temperature	*376.55*	*2*	*188.28*	*147.58*	*< 0.0001*
B-Active alkali	*84.25*	*2*	*42.13*	*33.02*	*0.0001*
C-cooking time	*60.52*	*2*	*30.26*	*23.72*	*0.0004*
AB	*19.21*	*4*	*4.80*	*3.76*	*0.0523*
AC	*43.7*	*4*	*10.94*	*8.57*	*0.0054*
BC	*20.91*	*4*	*5.23*	*4.10*	*0.0427*
Residual	10.21	8	1.28		
Cor Total	615.40	26			

Based on a 95% confidence level, F-Value is a test for comparing model variance with residual (error) variance. If the variances are close to each other, the ratio will be close to one and it is less likely that any of the factors have a significant effect on the response with the P- value less than 0.0500. It is calculated by Model Mean Square divided by Residual Mean Square. Also, the high F-value and a very low probability indicates that the present models are in a good prediction of the experimental results. The P- value serves as a tool for checking the siginificance of each of the coefficients. The variable with low probability levels contribute to the model, whereas the others can be neglecated and eliminated from the model. In the present study for the response pulp yield the Model F-value of 26.35 implies the model is significant. There is only a 0.01% chance that a "Model F-Value" occur due to noise.Values of "Prob > F" less than 0.0500 indicate model terms are significant.

In this study realised that the individual factors and their interaction effects are significant model terms. And for the response kappa number the Model F-value of 18.10 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 are significant model terms. Values greater than 0.1000 indicate the model terms are not significant.

Table 4.5: Analysis of variance (ANOVA) for kappa number

	Sum of Squares	**Df**	**Mean Square**	**F Value**	**p-value Prob > F**
Model	2088.22	18	116.01	18.10	0.0001
A-Temperature	*446.25*	2	*223.12*	*34.81*	*0.0001*
B-Active alkali	*317.67*	2	*158.83*	*24.78*	*0.0004*
C-cooking time	*943.38*	2	*471.69*	*73.58*	*< 0.0001*
AB	*125.18*	4	*31.30*	*4.88*	*0.0274*
AC	*235.37*	4	*58.84*	*9.18*	*0.0044*
BC	*20.37*	4	*5.09*	*0.79*	*0.5608*
Residual	51.28	8	6.41		
Cor Total	2139.50	26			

The quality of the model developed coude be evaluated from their coefficients of correlation,$\mathbf{R^2}$ (correlation coefficent) was high for both responces, a value > 0.75 indicates the aptness of the model. For a good statistical mode, the $\mathbf{R^2}$ value should be close to one. Results ensured a satisfactory adjustment of the 2FI model to the experimental data and indicated that approximately 98.34% and 97.60% of the variability in the dependent variables of pulp yield and kappa number respectively could be explained by these models and only 1.66% and 2.4% of the total variance could not explained by these models for pulp yield and kappa number respectively. The value of $\mathbf{R^2}$ for both responces is very high and close to one which indicates a good agreement between experimental and predicted values. The predicted $\mathbf{R^2}$ is in a reasonable agreement with the adjusted $\mathbf{R^2}$ for both responces.

Standard Deviation which is a square root of the residual mean square and it is the standard deviation associated with the experimental error; mean which is the dependent mean is the average of all the values for this particular response; C.V. % (Coefficient of Variation) is the error expressed as a percentage of the mean and computed as 100 x (Std Dev)/(Mean); 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; R^2 which measures the proportion of the total variability explained by the model. Whereas the adjusted R^2 statistics, defined as is a statistic that is adjusted for the "size" of the mode; that is the number of the factor. The adjusted R^2 can actually decrease if nonsiginificant terms are added to a model. Pred R Square is a measure of how good the model predicts a response value and the Adjusted R-Squared and Predicted R-Squared should be within approximately 0.20 of each other to be in "reasonable agreement." If they are not, there may be a problem with either the data or the model; Adequate precision is a measure of the range inpredicted response relative to its associated error, in other words a signal to noise ratio and its desired value is 4 or more which are listed in the table (4.6) and (4.7) for pulp yield and kappa number respectively below, are used to decide whether the model can be used or not.

Table 4.6: Model adequacy measures for pulp yield

Std. Dev	1.13	R-Squared	0.9834
Mean	47.05	Adj R-Squared	0.9461
C.V. %	2.40	Pred R-Squared	0.8111
PRESS	116.25	Adeq Precision	20.374

In this case model for pulp yield the "Pred R-Squared" of 0.8111 is in reasonable agreement with the "Adj R-Squared" of 0.9461."Adeq Precision" measures the signal to noise ratio. A ratio greater than 4 is desirable. In this case, ratio of 20.374 indicates an adequate signal. So, this model can be used to navigate the design space.

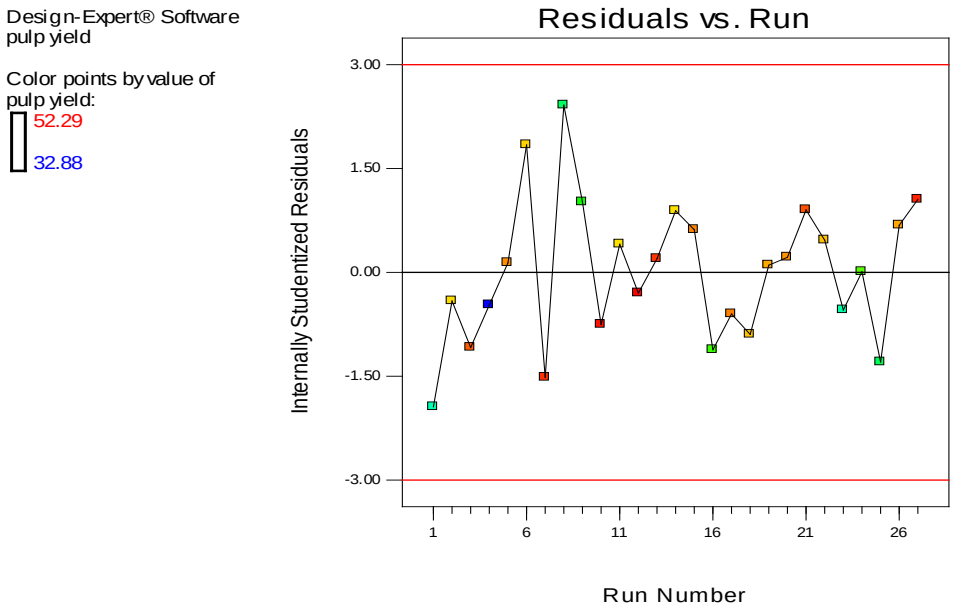
Table 4.7: Model adequacy measures for kappa number

Std. Dev.	2.53	R-Squared	0.9760
Mean	22.03	Adj R-Squared	0.9221
C.V. %	11.49	Pred R-Squared	0.7270
PRESS	584.16	Adeq Precision	16.181

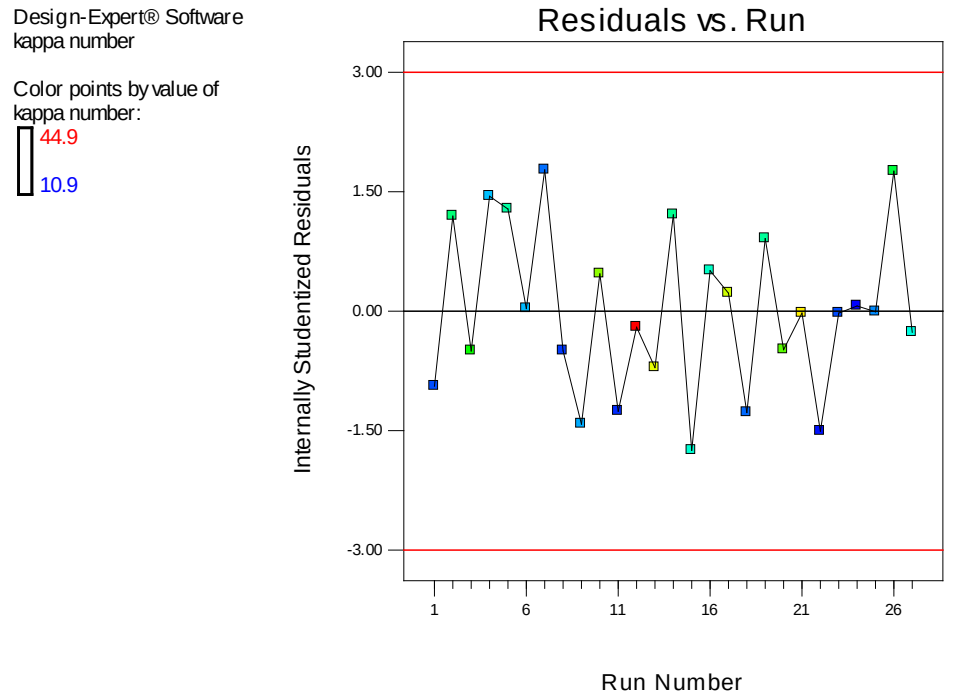
In modeling the Kappa numner adequecy the "Pred R-Squared" of 0.7270 is in reasonable agreement with the "Adj R-Squared" of 0.9221. "Adeq Precision" measures the signal to noise ratio. A ratio greater than 4 is desirable. Your ratio of 16.181 indicates an adequate signal. So, this model can be used to navigate the design space.

Additionally, the developed models for pulp yield and kappa number have been checked by using residual analysis. Residuals are usually considered as components of variations, imprecisely fitted to the model and subsequently it is predicted that they behave according to a normal distribution feature. For the evaluation of normality of the residuals, a graphical visualization of the normal probability plot is considered as the proper method. Figure 4.1 (a), and (b) are the plot of the residuals calculated against the order of experimentation. It is asserted that a tendency to have runs of positive and negative residuals indicating the existence of correlation. The normal plots for pulp yield and kappa number are shown in figure 4.2 (c) and (d) describing the data are spread approximately in a straight line, which show a good correlation between experimental and predicted values for the responces.

The plots of observed versus predicted values shows minimal variation between the observed and fitted values for both responces figure 4.2 (e) and (f). From the above ANOVA and analysis of residual plots for both responces, the model reveal adequacy and this model was used to navigate the design space to find the optimized conditions.

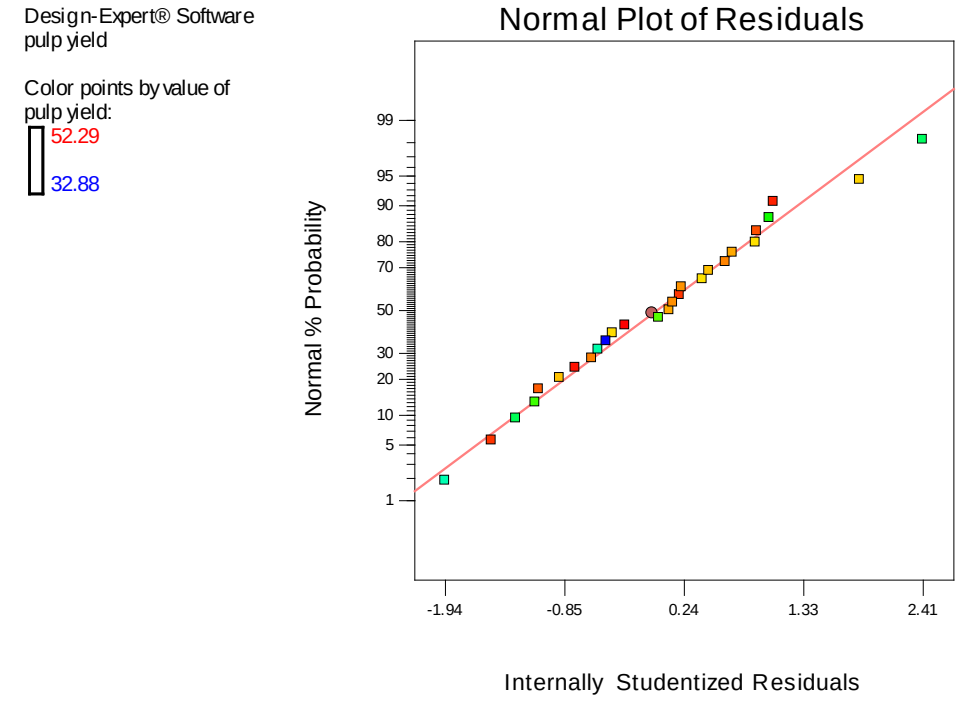


(a)

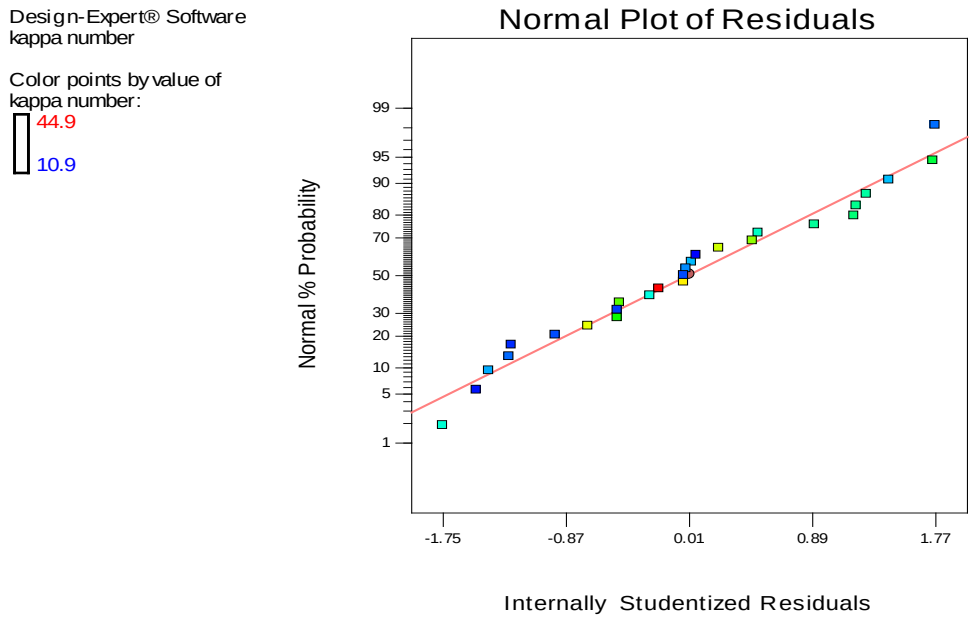


(b)

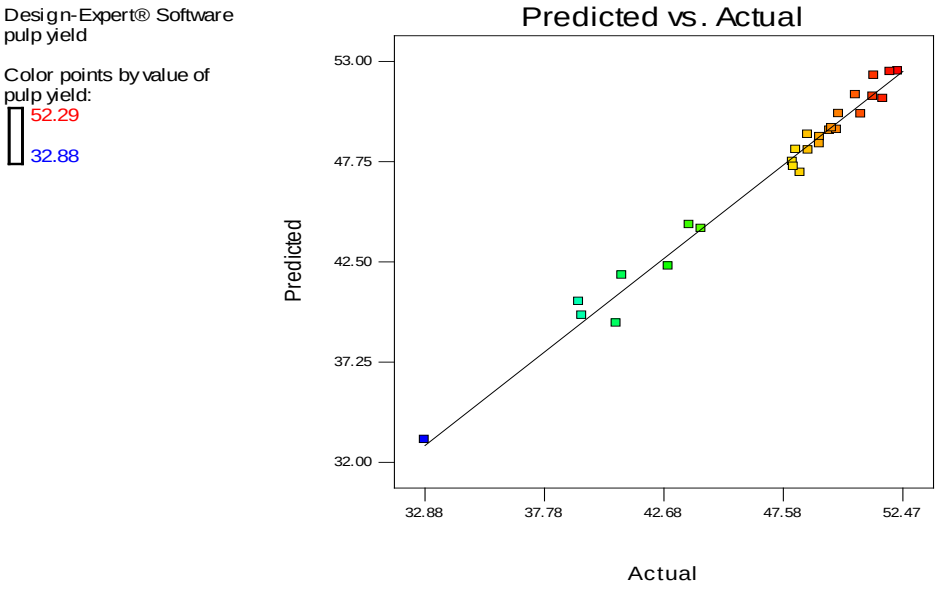
Figure 4.1 Plot of residuals versus run order of the data; (a) for pulp yield, (b) for kappa number


Design-Expert® Software
pulp yield
Color points by value of
pulp yield:
52.29
32.88
Normal Plot of Residuals
Normal % Probability
99
95
90
80
70
50
30
20
10
5
1
-1.94
-0.85
0.24
1.33
2.41
Internally Studentized Residuals

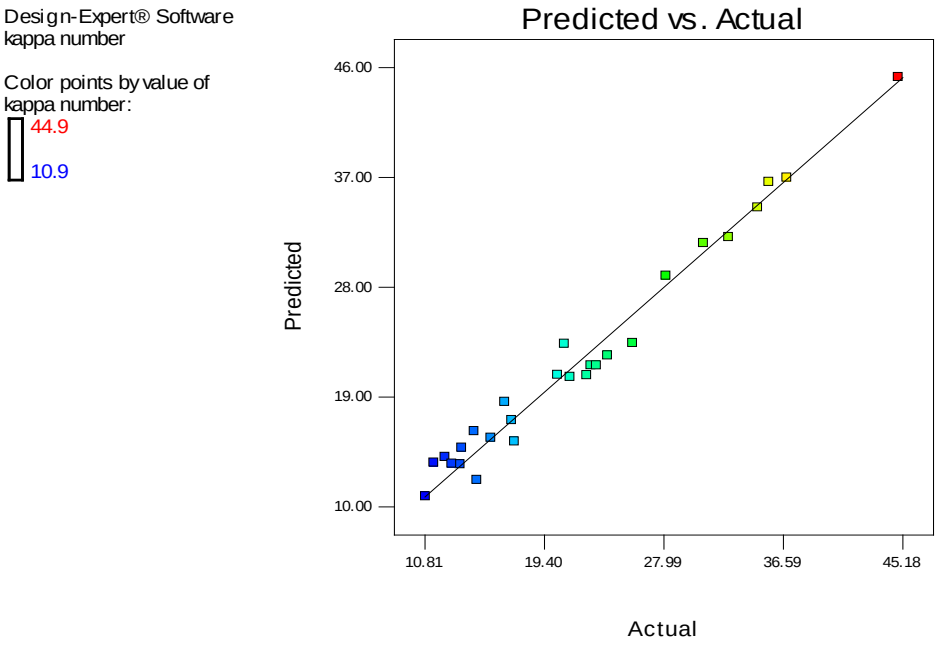
(c)


Design-Expert® Software
kappa number
Color points by value of
kappa number:
44.9
10.9
Normal Plot of Residuals
Normal % Probability
99
95
90
80
70
50
30
20
10
5
1
-1.75
-0.87
0.01
0.89
1.77
Internally Studentized Residuals

(d)



(e)



(f)

Figure 4.2 Normal probability and actual versus preidicted plots for the two responces; (c) Normal probability plot for pulp yield, (d) Normal probability plot for kappa number, (e) Actual versus predicted for pulp yield, (f) Actual versus predicted for kappa number.

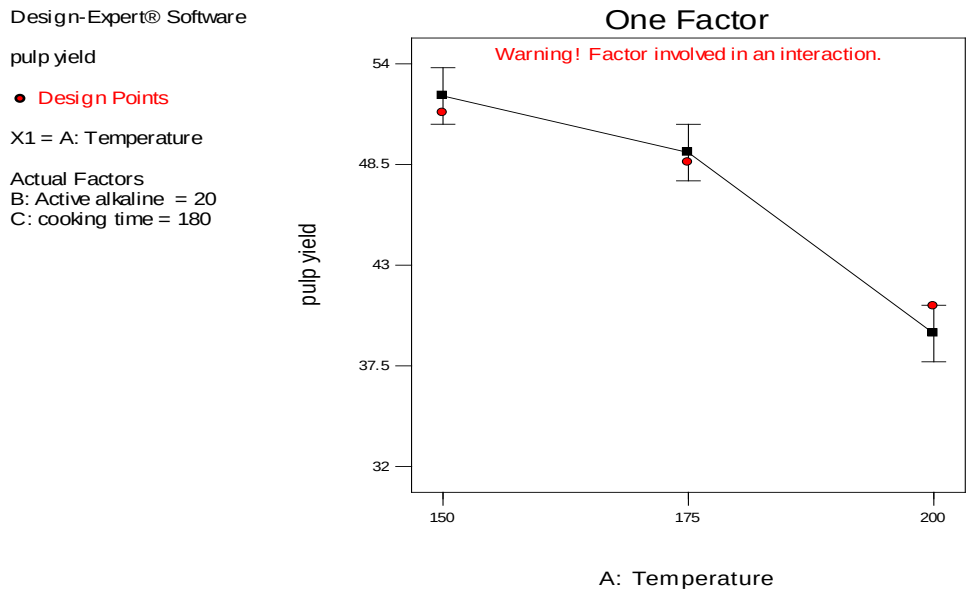
4.2.3 Effect of Pulping Process Variables

The overall screened yield for soda-AQ pulping conducted in this study. The effect of pulping time, cooking temperature and active alkali concentration on pulp yield and kappa number was studied and evaluated for best pulping conditions. Based on the analysis of variance, pulping was significantly affected by various interactions between the process variables. In addition to the interaction effect, significant individual process variables that affect the pulp yield and kappa number are cooking temperature, active alkali concentration, and reaction time. There was a general decrease in the pulp yield and kappa number (residual lignin) due to an increase in the temperature, active alkali concentration and cooking time taking uniformly the AQ concentration to 0.1% and 4:1 liquor to solid ratio.

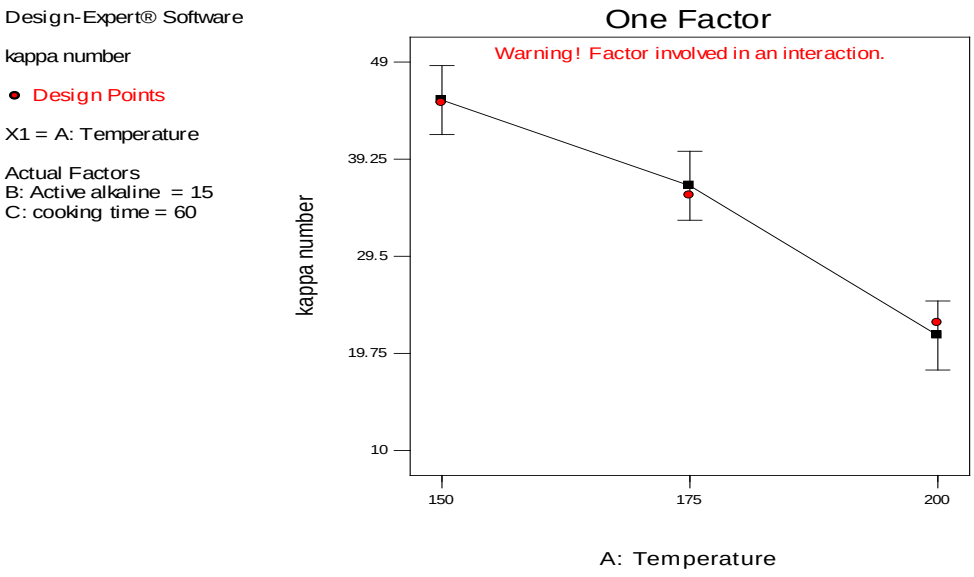
4.2.3.1 Effect of Individual Process Variables

As shown in Figure 4.3 (g) and (h) below the pulp yield and kappa number are significantly affected by reaction temperature. It can be seen from the figure that with increasing reaction temperature from 150^{o}C to 200^{o}C the pulp yield and kappa number generally decreases.

The decreasing in pulp yield and kappa number at higher reaction temperature is due to higher rate of reaction. This might be due to lignin, hemicelluloses and celluloses are dissolved out at different rates during cooking and these rates are much accelerated by increasing the temperature, and thus decreasing the pulp yield and residual lignin. Higher temperature results in higher reaction rate constant which will lead to higher rate of reaction and eventually decreases pulp yield and kappa number (residual lignin).



(g)

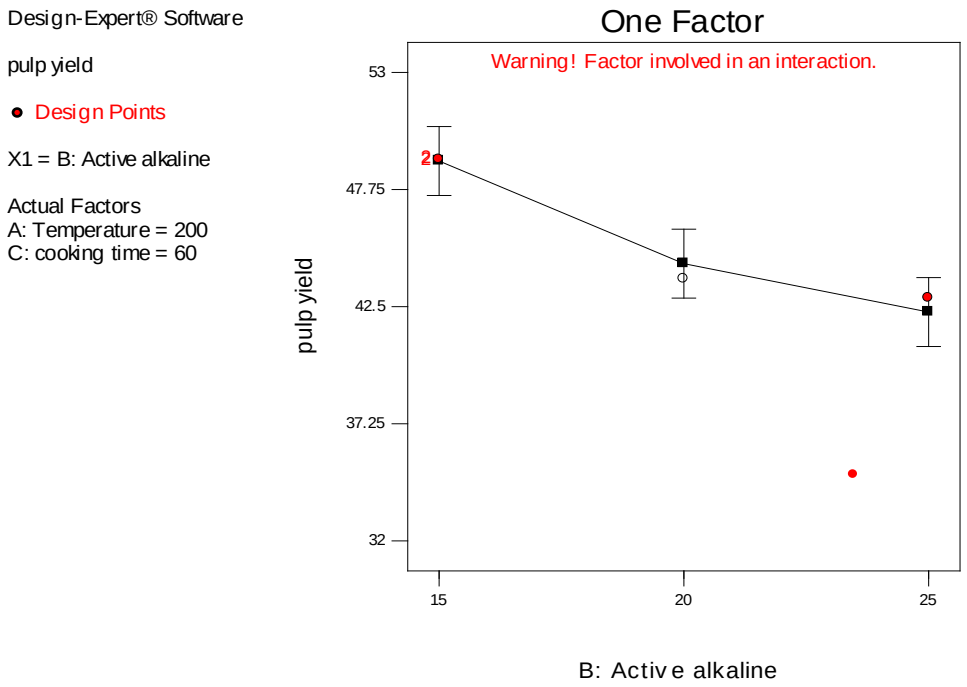


(h)

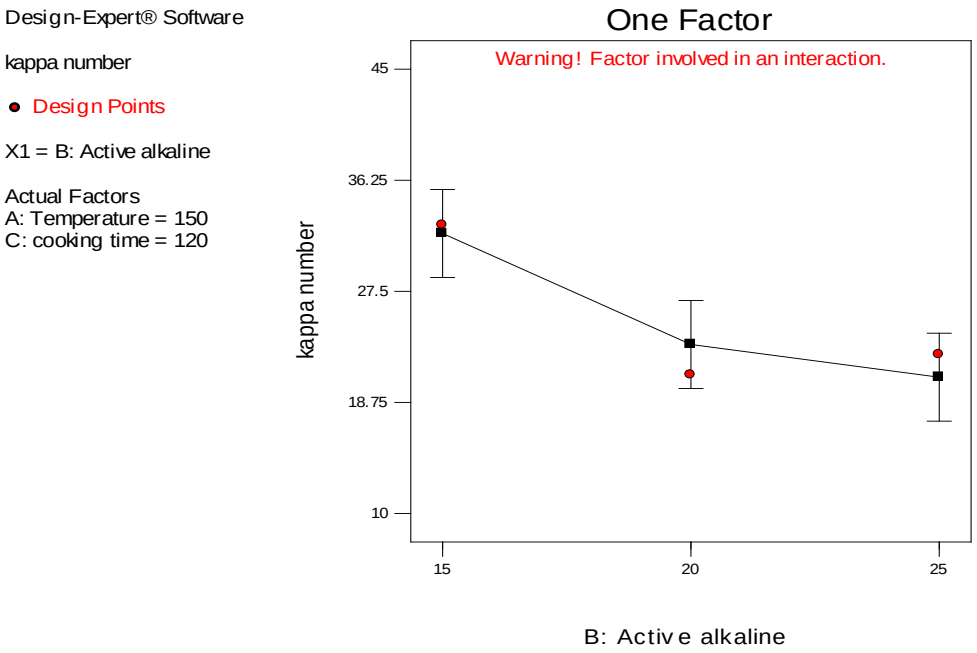
Figure 4.3 Plot of temperature versus ; (g) pulp yield at active alkali 20% and cooking time 180minutes and (h) Kappa number at active alkali 15% and cooking time 60 minutes.

Figure 4.4 (i) and (j) shows that the effects of active alkali concentration on pulp yield and kappa number (residual lignin) respectively. Increasing the amount of active alkali concentration decreases the pulp yield and kappa number significantly.

The concentration of active alkali is one of the important factors that affect the pulp yield, pulp quality and kappa number. The presence of AQ reduces the degradation effect of cellulose while enhancing the dissolution of lignin.



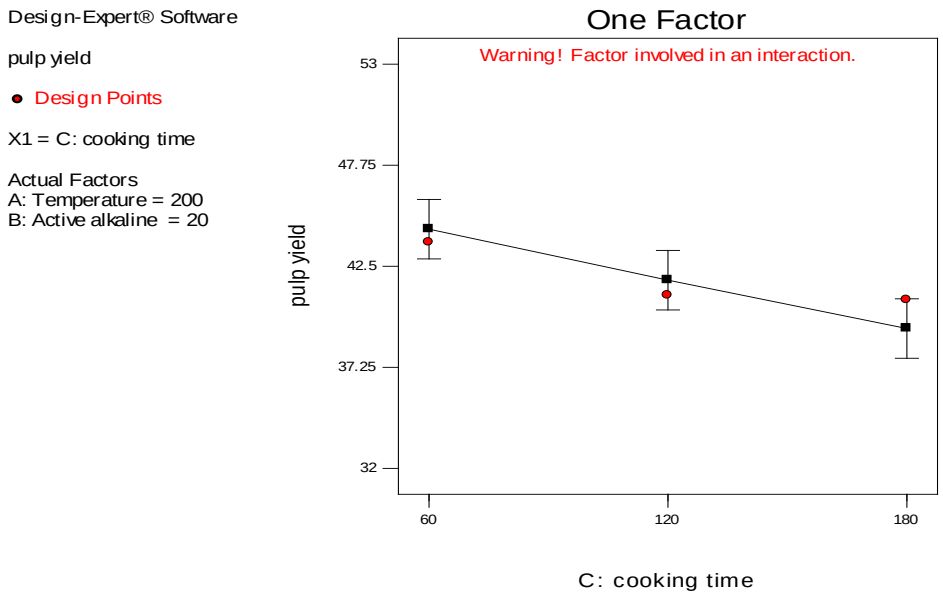
(i)



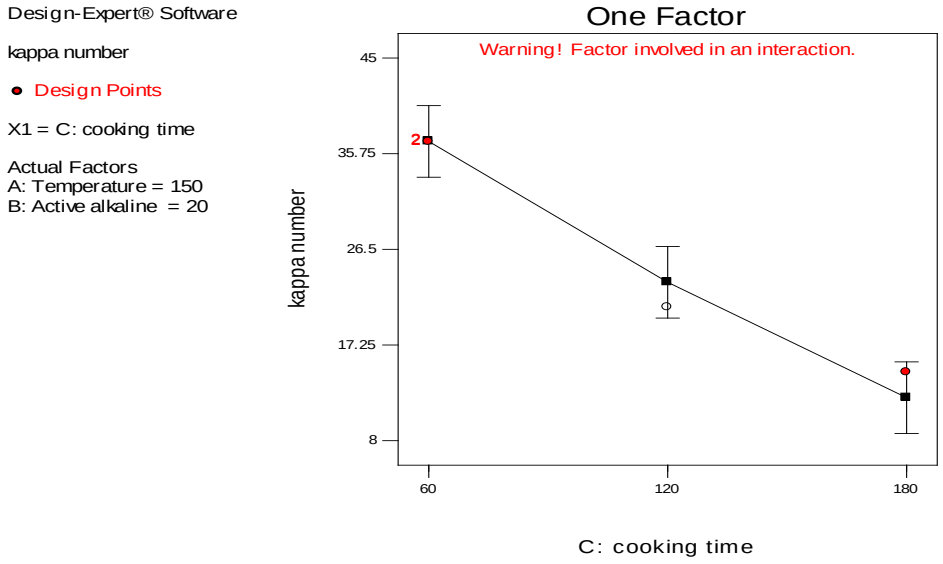
(j)

Figure 4.4 Plot of active alkali versus; (i) pulp yield at temperature of 200^{o}C and cooking time of 60 minutes and (j) Kappa number at temperature of 150^{o}C and cooking time 120minutes

Figure 4.5 (k) and (l) below illustrates the effect of pulping time on pulp yield and kappa number respectively. When the pulping time increased the pulp yield decrease slightly while the kappa number decreases highly, this is because pulping reaction gets enough time for effective delignification and dissolution of alkali soluble hemicelluloses components.



(k)



(l)

Figure 4.5 Plot of cooking time at active alkali 20% versus; (k) pulp yield at 200 ^{o}C and (l) Kappa number at 150^{o}C.

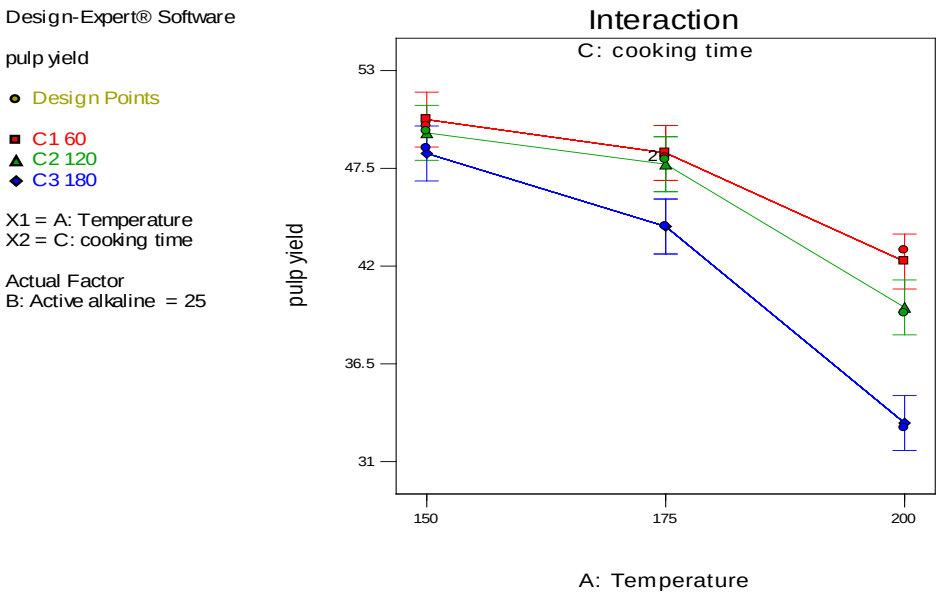
Generally, the longer the period of pulping, the higher the degree of delignification and the lower the pulp yield as a result of partial depolymerisation of cellulose chain as well as the removal of the hemicelluloses components. At a particular charge of effective alkali, pulping for 180 minutes at 200^{o}C resulted in the lowest yield while the highest yield was recorded for the pulp made for 60 minutes at 150^{o}C.

4.2.3.2 Interaction Effect Between Process Variables

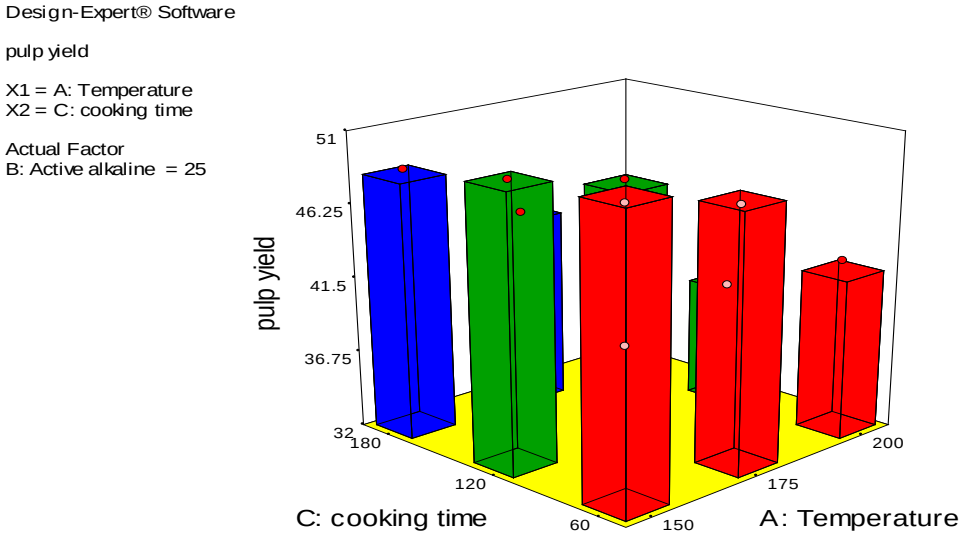
Interaction between Process Variables can affect the performance of delignification. But, as it already seen, the interaction effects of the process variables are significant. The interactions are between temperature, cooking time and active alkali concentration on pulp yield and kappa number.

Generally, an increase in reaction temperature is found to decrease the pulp yield and kappa number. This is due to similar explanation given in the previous section.

From the three interaction effects sown in the figures and 3-D plot there was a general decrease in the pulp yield and residual lignin due to an increase in the concentration of active alkali, temperature and cooking time at a uniform amount of 0.1% AQ and 4:1 liquor to solid ratio. It was noticed that nearly half of the original material was dissolved after 60 minutes of pulping and this attested the dissolving power of caustic soda as pulping liquor. The high dissolution of the initial material may also be attributed to the presence of highly soluble certain cell wall components such as fats, fatty acids, fatty alcohols, phenols, terpenes, resin acids and waxes. As observed from Table 4.2, increasing the alkali charge resulted in a decrease in the pulp yield as well as kappa number. The lignin content and pulp yield decreases slightly for the same period and markedly after high cooking time.

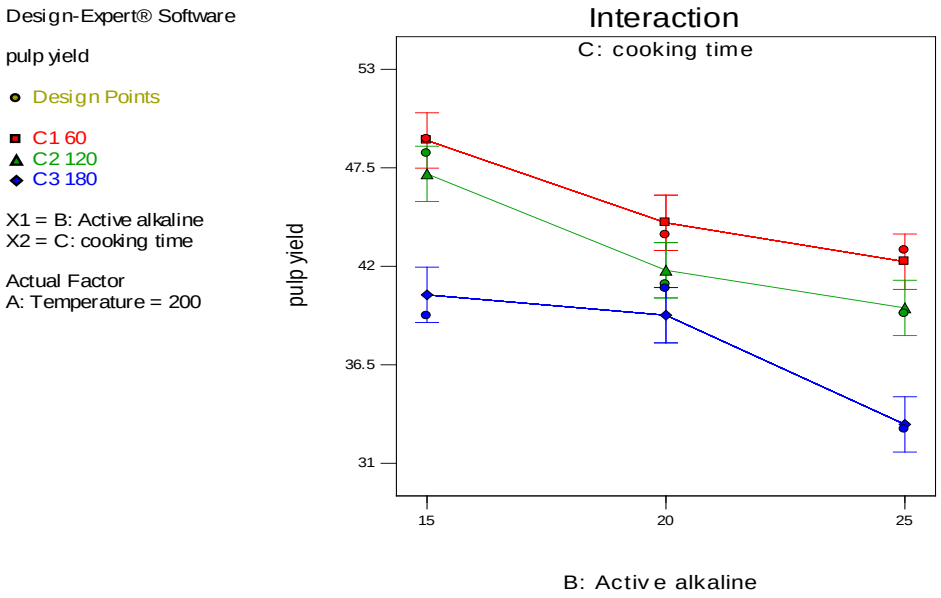


(m)

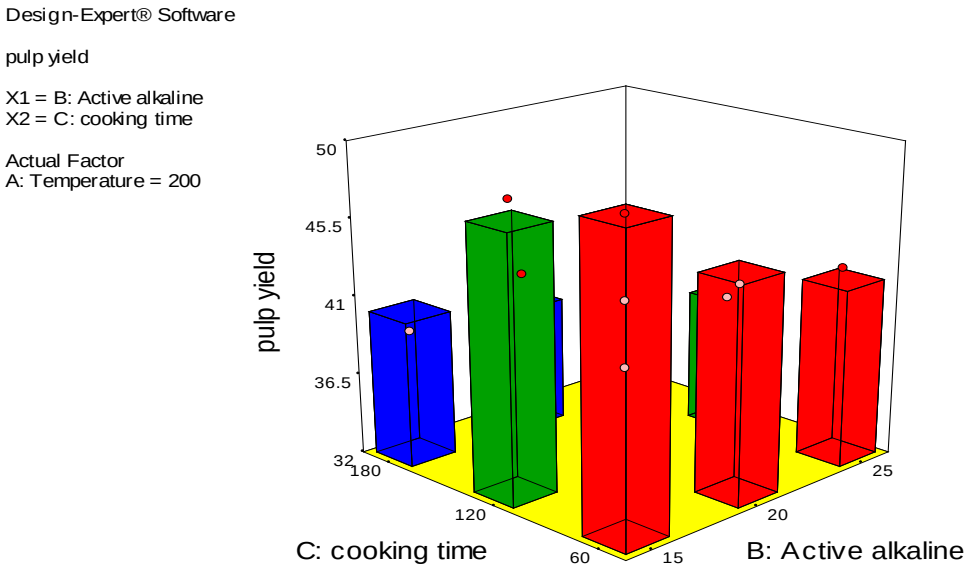


(n)

Figure 4.6 Plot of temperature and cooking time versus pulp yield when active alkali concentration is 25%; (m) interaction effect, (n) 3-D

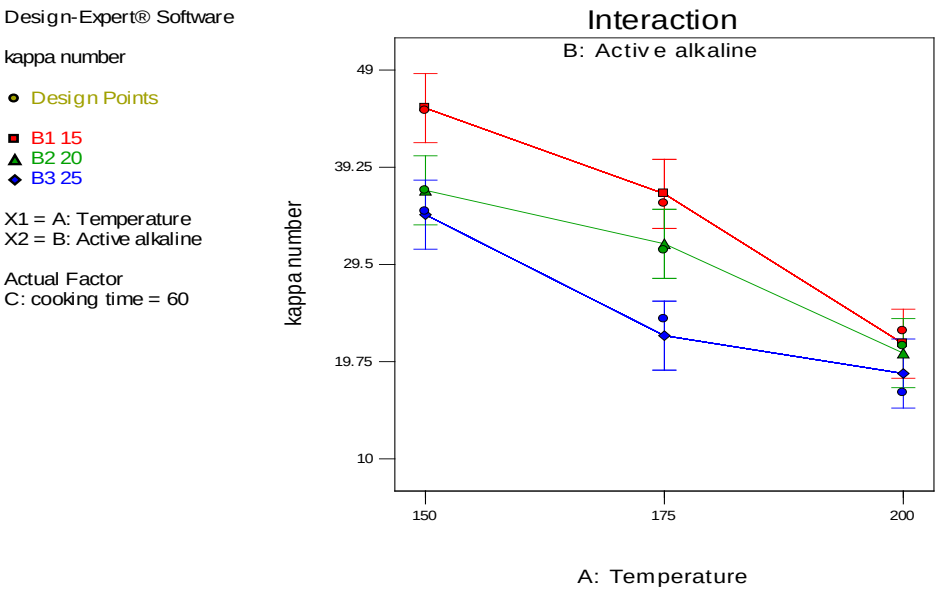


(o)

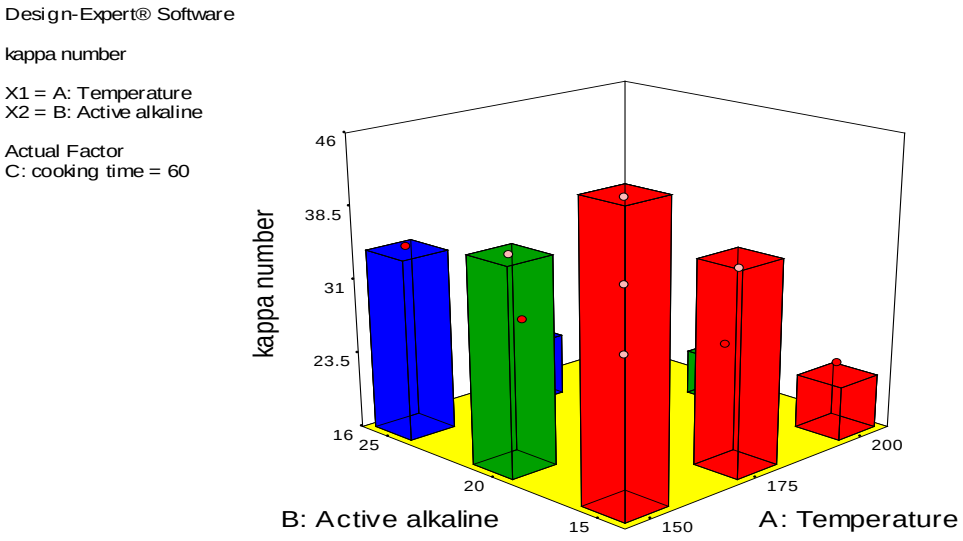


(p)

Figure 4.7 Plot of active alkali concentration and cooking time versus pulp yield when temperature is 200 ^{o}C; (o) interaction effect, (p) 3-D

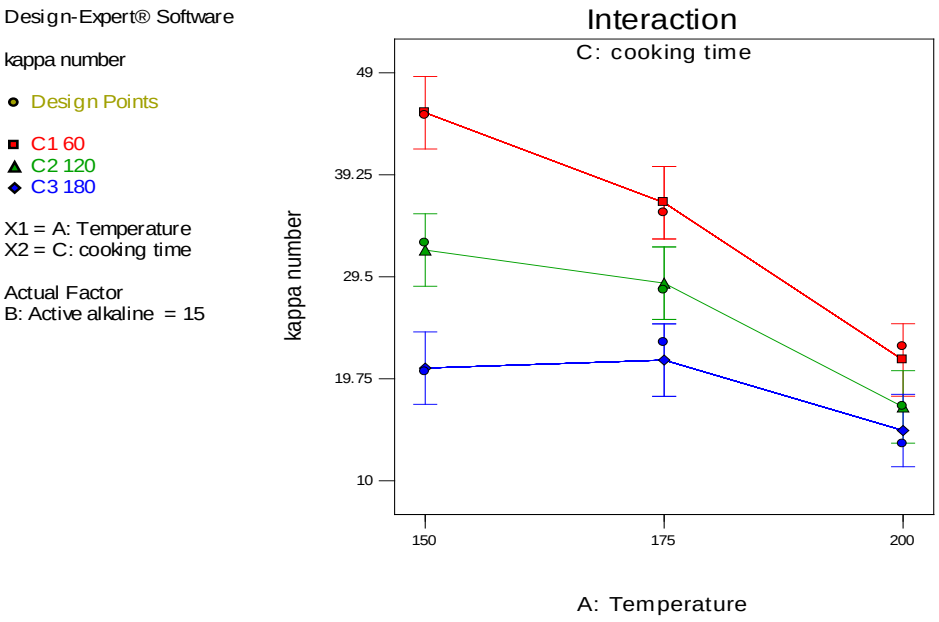


(q)

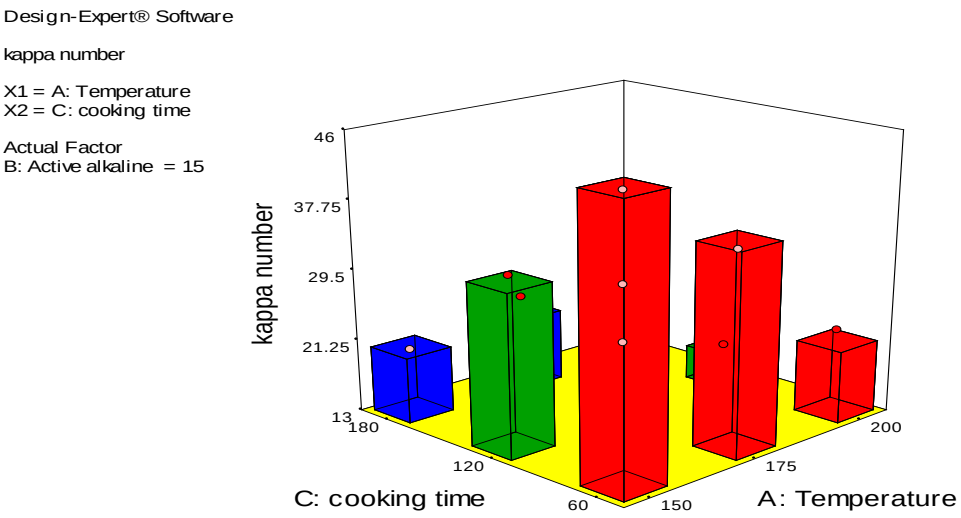


(r)

Figure 4.8 Plot of temperature and active alkali concentration versus kappa number when cooking time is 60 minutes; (q) interaction effect, (r) 3-D



(s)



(t)

Figure 4.9 Plot of temperature and cooking time versus kappa number when active alkali concentration is 15%; (s) interaction effect, (t) 3-D

4.2.4 Optimization

One of the objectives of the present study was to find the optimal process parameters for better pulp yield at minimum kappa number. The process variables such as cooking temperature, concentration of active alkali and pulping time have been optimized. In optimizing the pulping process, cooking temperature, concentration of active alkali and pulping time are a set of process parameters held to be "in range" while the pulp yield and kappa number are the two responses that need to be "maximized" for pulp yield and "minimized" for kappa number. Table 4.8 shows the summary of factors/responses and goals and the corresponding set of specific objectives that will optimize the process condition to have the highest responses. Numerical optimization was used to optimize any combination of one or more goals.

Table 4.8: Constraints applied for optimization

Factors/responces	Goal	Lower Limit	Upper Limit	Lower Weight	Upper Weight	Importance
Temperature	in range	150	200	1	1	3
Active alkali	in range	15	25	1	1	3
cooking time	in range	60	180	1	1	3
pulp yield	Maximize	32.88	52.29	1	1	3
kappa number	Minimize	10.9	44.9	1	1	3

The model capable of predicting the maximum pulp yield and the minimum kappa number value showed that the optimum values of the process variables were temperature of 150^{o}C, active alkali of 20% and cooking time of 180 minute. Under these conditions, the predicted pulp yield and kappa number were 52.2433% and 12.1556 respectively. Desirability function was used to identify the optimum levles of factors and to get maximum desirable responces. The optimized batch was selected with maximum combined desirability value i.e. 0.980 and the graph of the optimized solution for the pulping condition is shown in figure 4.10.

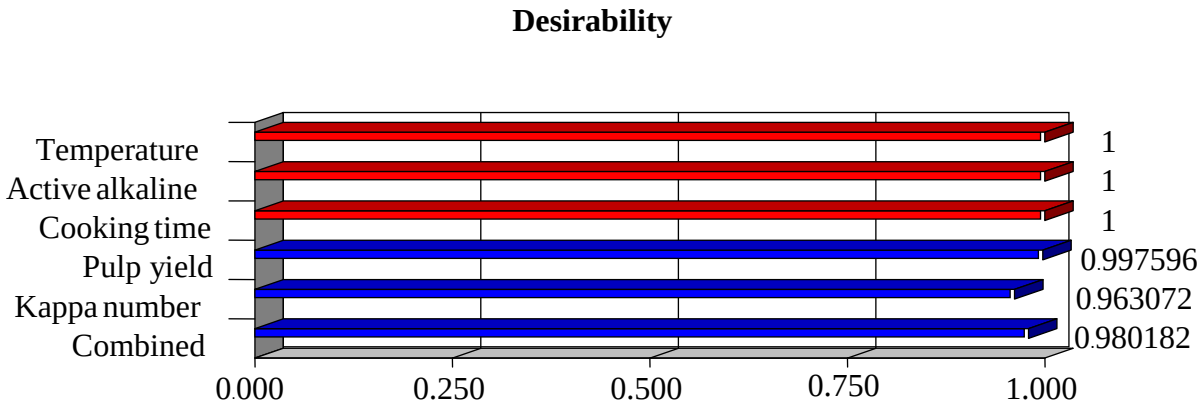


Figure 4.10 Desirability plot of optimization solution for the responses

The histogram shows how well each variables satisfied the criteria and values near one are good. The ramp plot of the optimized solution for the pulping condition is shown in figure 4.11. The ramp display combines the individual graphs for easier interpretation and the dot on each

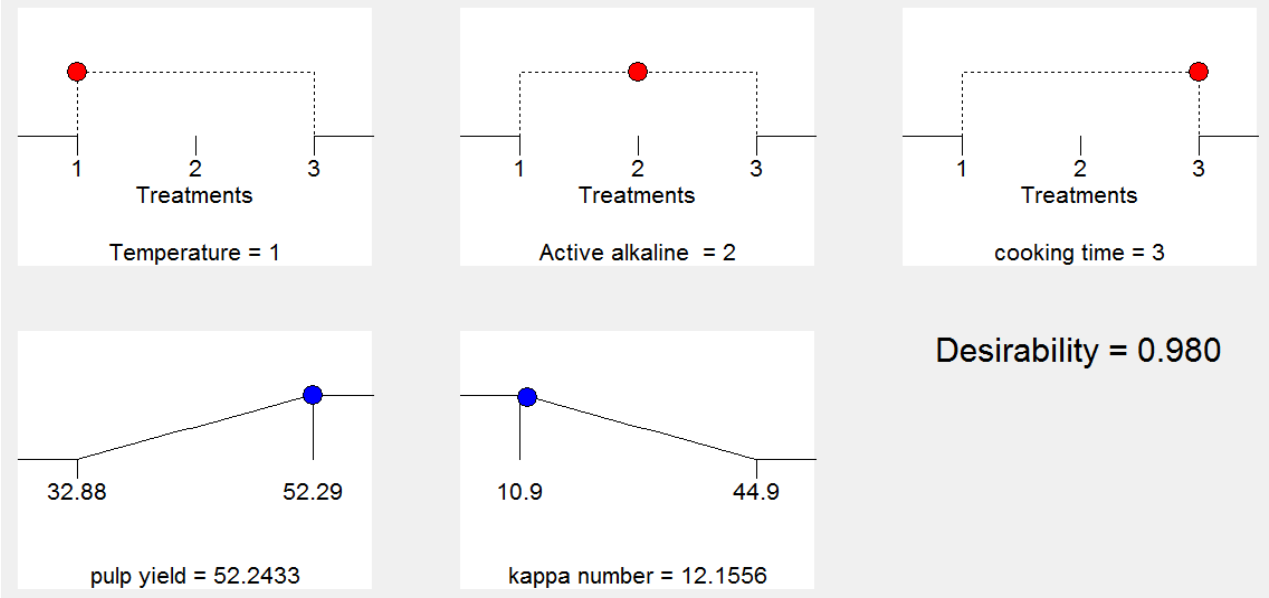


Figure 4.11: Ramp plot of optimization solution for the responces

ramp reflects the factor setting or response prediction for that solution.

The overall screened yield for soda-AQ pulping conducted in this study showed a decreasing pattern on screened yield and kappa number percentage with the increasing of the pulping conditions. The predicted highest screened yield and lowest kappa number was produced from solution of optimization at the lowest pulping temperature (150^{o}C) and moderate alkali charge percentage (20%) i.e. run number 7 where the screened yield is at 52.24% and kappa number 12.16 as summarized in table 4.9 below. In order to verify this prediction, experiments were conducted and the results were computable with the prediction. This is good in terms of cost efficiency for commercial scale, as only small amount of energy power and moderate chemicals are needed for the quality pulp production. This might be due to the low dissolvability of holocellulose parts and more lignin dissolved in higher alkaline percentage and higher temperature, and thus decreasing the pulping yield and kappa number.

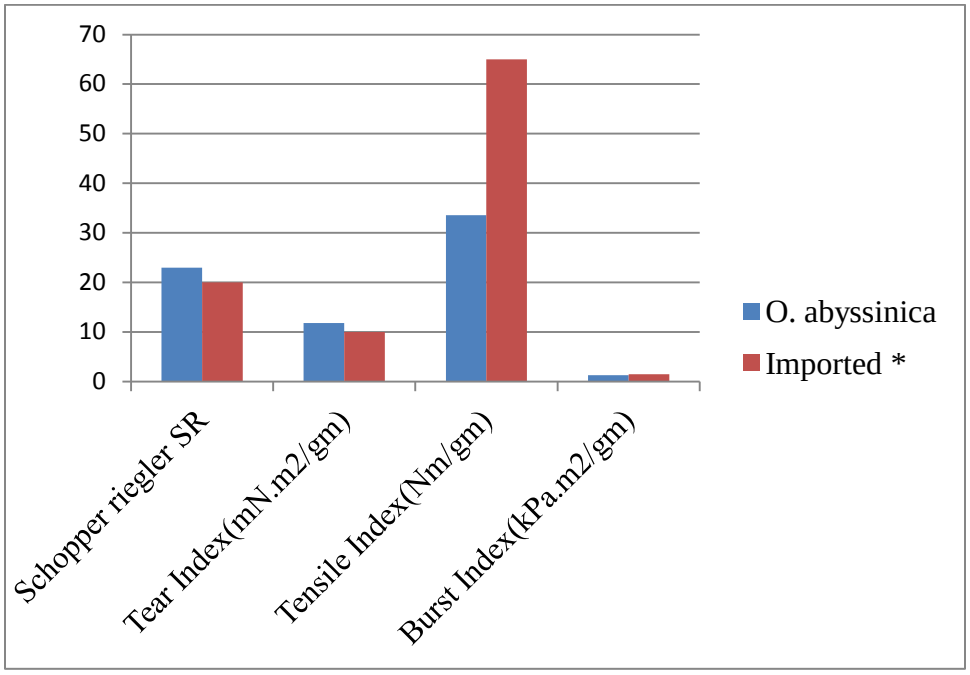
Table 4.9: Summary for optimization conditions

Pulping Temperature	Active alkali charge	Cooking Time		Pulp yield	Kappa number
150^{o}C	20%	180min.	experimental	51.31%	14.60
150^{o}C	20%	180min.	Predicted	52.24%	12.16

4.3 Characterization and comparison of *Oxytenanthera abyssinica* bamboo paper properties with other imported raw materials

4.3.1 Properties of Pulp Sheets

Unbleached pulps obtained from pulping of *Oxytenanthera abyssinica* were beaten and used to prepare paper sheets to evaluate the properties. The bamboo unbleached pulp was evaluated against the pulp specification employed for long fiber softwood pulp procurement by the Ethiopian Pulp and Paper industry share company as summarized in table 4.10. The parameters tested against this specification were freeness, tensile strength, burst strength and tear tests as shown in figure 4.12 below.



Source,* Ethiopia Pulp and Paper S.C

Figure 4.12 Comparison between Beaten O. abyssinica bamboo and imported paper properties

4.3.1.1 Tensile Index

Tensile properties describe the dimensions and strength of the individual fibers, their arrangement, and the extent to which they are bonded to each other. Papers made with long fibers generally have higher tensile strength properties than paper made of short fibers. However, the extent of inter fiber bonding is considered the most important factor contributing to tensile strength properties. Tensile index measures the paper resistance to being broken when the paper is stretch out from both sides.

In this study, the tensile index was low when compared to that of the imported softwood pulp. Fibre strength properties depend on the individual fibre strength and bonding strength between fibres. The bonding strength between fibres occurs from the physical contact with hydrogen bonding between hydroxyl groups on the fibre surface area when the fiber was beaten. The low result might be due to betting process which will make the fibre shorter and less bonding area between fibres can occurred, so less energy is needed to broke up the paper sheets and contribute to the decreasing of the tensile index. However, the tensile strength of *O. abyssinica* bamboo pulp is lower than the property of unbleached imported softwood pulp it is used for production of different types of paper and paperboard products.

4.3.1.2 Tear Index

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 is a measure of the force needed to initiate a tear. The force needed to initiate a tear may be several times the force needed to propagate the tear once it is started. Tear index is 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) (Casey, 1996).

The results of the tear resistance of Oxytenanthera abyssinica bamboo was in the interval (11.5 $mN.m^2/gm$) compared to that from imported (10-12 $mN.m^2/gm$). The tear resistance of paper made from beaten *O. abyssinica* pulp is high because there is essentially bonding to hold the

fibres together. However, increased fibre to fibre bonding eventually tends to reduce sheet flexibility and thus localized any external stress applied to the paper, so that tearing can now proceed more easily.

4.3.1.3 Burst Index

Bursting strength is perhaps the most commonly measured strength property of paper. The test apparently originated from the old time practice of the papermaker who, in a hands-on quality control evaluation of paper strength, would attempt to push his thumb through the sheet (Anon, 1988). Burst index is obtained by dividing the bursting strength in kPa by the grammage of the paper in g/m2. The bursting strength measures the paper resistance to being burst when hydraulic pressure is applied to the paper. The results of the burst strength of *Oxytenanthera abyssinica* bamboo pulp is low but nearly close to the specification of imported softwood pulp.

Table 4.10: Ethiopia Pulp and Paper SC Pulp procurement specification and *O. abyssinica* bamboo physical properties of pulp sheet

	Schopper riegler SR	Tear Index(mN.m2/gm)	Tensile Index(Nm/gm)	Burst Index(kPa.m2/gm)
O. abyssinica	23	11.8	33.58	1.3
Imported *	20-25	10-12	65-80	1.5-5

*source: Ethiopia pulp and paper share company

CHAPTER FIVE

5 CONCLUSION AND RECOMMENDATION

5.1 Conclusion

This work was intended to study the chemical composition of the raw material, the influence of pulping parameters (active alkali (soda), cooking temperature, and time on the pulp yield and kappa number and characterization of paper Sheets Properties of *Oxytenanthera abyssinica* bamboo pulp.

Variability of these operating conditions was the pre-dominant factors for the pulp yield and quality of *Oxytenanthera abyssinica* bamboo pulp.

There are different methods of pulping from *Oxytenanthera abyssinica* bamboo culms. In this thesis, soda-anthraquinone pulping method was used. In soda-anthraquinone pulping the liquor used for the pulping was NaOH-AQ solution. In this study based on the analysis of experimental results, it is realized that the individual factors and their interaction effects are significant model terms on pulp yield and kappa number. This shows that the capability of the design of the experimental analysis is successfully capturing these effects. The maximum pulp yield and minimum kappa number obtained was 52.24% and 12.16 respectively were achieved under the optimum conditions; at the active alkali of (20%), cooking temperature of 150^{o}C and the cooking time of 180 min with high value of combined desirability, i.e. 0.98. This is good in terms of cost efficiency for commercial scale, as only small amount of energy power and moderate chemicals are needed for the quality pulp production.

The observed quantitative difference in the quantity and quality of the pulp was due to active alkali, cooking temperature and time variability. Thus, determination of the appropriate amount of the active alkali, optimal temperature and time for the recommended particle size needs to have a consideration to get the maximum amount of the required product.

The potential use of *Oxytenanthera abyssinica* bamboo that it is a fast growing plant, with short harvesting time and good chemical composition properties make it cost effective and sustainable feedstock for pulp and paper production.

Based on the studies conducted, it was found that the paper mechanical properties for the optimum condition (20% of alkali charge and 150^{o}C of pulping temperature) are as follows. Tensile index at 33.55 Nm/g, bursting index at1.303 kPa.m^2/g, and tearing index at 11.5 mN.m^2/g. It can be concluded from these findings that comparable moderate strength paper can be produced from *O. abyssinica* bamboo pulp with more environmentally friendly pulping process.

Finally it can be concluded that *Oxytenanthera abyssinica* bamboo has a great potential for substitution of imported pulp in paper and paper products processing industry.

5.2 Recommendation

- Here in the experimental work the age, position and site effects on the pulp yield and kappa number of *Oxytenanthera abyssinica* bamboo has not been studied. This is due to the time constraint during this thesis work.
- From the point of application of *Oxytenanthera abyssinica* bamboo:
    - Since rural areas of the Ethiopian people use *Oxytenanthera abyssinica* resource for construction of traditional houses, low-grade furniture, household utensils, beehives, fences, and handicrafts. The people need to be fully aware of which parts of the bamboo to use for their specific purpose.
    - It is advisable to use *Oxytenanthera abyssinica* bamboo for pulp production in Ethiopia since it contains higher cellulose content and has good pulping characteristics which make bamboo a preferred raw material for pulping.
    - The paper mechanical properties from this study shows that *Oxytenanthera abyssinica* bamboo fiber can be good material for paper and paper product industry.

Additionally, I recommend that preliminary design of pilot plant, process development and scale up has to be performed.

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APPENDICES

Appendix A: Vital pictures during the research work

i. Sample preparation of *Oxytenanthera abyssinica* bamboo

(a) Air dry

(b) cutting

(c)Milling

(d) sieving

(e) plastic packing

ii. Chemical composition analysis *Oxytenanthera abyssinica* bamboo

(f) hot-water determination

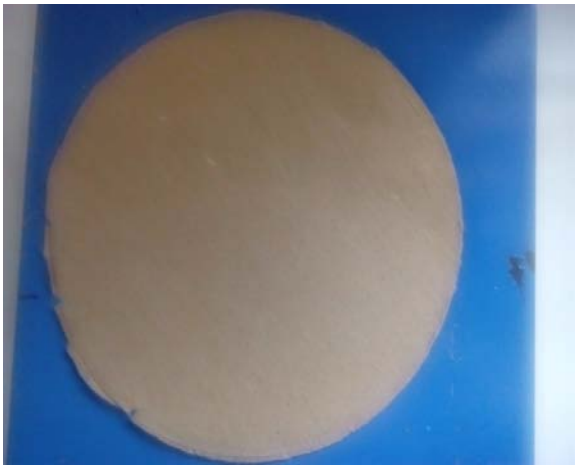
(g) cellulose determination

(h) alcohol-toluene determination

iii. Pulping *Oxytenanthera abyssinica* bamboo



(i) Cooking (j) stage one washing (k) stage two washing

(l) Final washing (m) unbleached pulp



(n) Kappa number determination (o) bleached pulp

Appendix B: Model fit summary for the two responses (pulp yield and kappa number)

Table 4.3 Design summary

Study Type	Factorial
Initial Design	Full Factorial
Center Points	0
Design Model	2FI
Runs	27
Blocks	No Blocks

Factor	Name	Units	Type	Low Actual	High Actual	
A	Temperature	Oc	Categoric	150	200	Levels: 3
B	Active alkali	%	Categoric	15	25	Levels: 3
C	cooking time	min.	Categoric	60	180	Levels: 3

Response	Name	Units	Obs	Analysis	Minimum	Maximum	Mean	Std. Dev.	Ratio
Y1	pulp yield	%	27	Factorial	34.02	52.29	47.03	4.64	1.54
Y2	kappa number	-	27	Factorial	10.90	44.70	22.02	8.83	4.10

Appendix C: ANOVA for the two responses (pulp yield and kappa number)

Response 1: pulp yield

ANOVA for selected factorial model

Analysis of variance table [Classical sum of squares - Type II]

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	
Model	605.19	18	33.62	26.35	< 0.0001	significant
A-Temperature	*376.55*	*2*	*188.28*	*147.58*	*< 0.0001*	
B-Active alkaline	*84.25*	*2*	*42.13*	*33.02*	*0.0001*	
C-cooking time	*60.52*	*2*	*30.26*	*23.72*	*0.0004*	
AB	*19.21*	*4*	*4.80*	*3.76*	*0.0523*	
AC	*43.74*	*4*	*10.94*	*8.57*	*0.0054*	
BC	*20.91*	*4*	*5.23*	*4.10*	*0.0427*	
Residual	10.21	8	1.28			
Cor Total	615.40	26				

The Model F-value of 26.35 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, AC, BC are significant model terms.

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.

Std. Dev.	1.13	R-Squared	0.9834
Mean	47.05	Adj R-Squared	0.9461
C.V. %	2.40	Pred R-Squared	0.8111
PRESS	116.25	Adeq Precision	20.374

The "Pred R-Squared" of 0.8111 is in reasonable agreement with the "Adj R-Squared" of 0.9461."Adeq Precision" measures the signal to noise ratio. A ratio greater than 4 is desirable. Your ratio of 20.374 indicates an adequate signal. This model can be used to navigate the design space.

Term	Coefficient Estimate	df	Standard Error	95% CI Low	95% CI High
Intercept	47.05	1	0.22	46.55	47.55
A[1]	3.60	1	0.31	2.89	4.31
A[2]	1.54	1	0.31	0.83	2.25
B[1]	2.10	1	0.31	1.39	2.81
B[2]	0.12	1	0.31	-0.59	0.83
C[1]	1.56	1	0.31	0.85	2.27
C[2]	0.46	1	0.31	-0.25	1.17
A[1]B[1]	-0.77	1	0.43	-1.78	0.23
A[2]B[1]	-0.75	1	0.43	-1.75	0.26
A[1]B[2]	-0.15	1	0.43	-1.15	0.86
A[2]B[2]	0.35	1	0.43	-0.65	1.35
A[1]C[1]	-1.24	1	0.43	-2.24	-0.24
A[2]C[1]	-0.53	1	0.43	-1.53	0.47
A[1]C[2]	-0.66	1	0.43	-1.66	0.34
A[2]C[2]	0.16	1	0.43	-0.85	1.16
B[1]C[1]	0.17	1	0.43	-0.84	1.17
B[2]C[1]	-0.73	1	0.43	-1.73	0.28
B[1]C[2]	0.67	1	0.43	-0.34	1.67
B[2]C[2]	-1.01	1	0.43	-2.01	-7.485E-003

Final Equation in Terms of Coded Factors:

Pulp yield =+47.05+3.60 * A[1]+1.54 * A[2]+2.10 * B[1]+0.12 * B[2]+1.56 * C[1]+0.46 * C[2] -0.77 * A[1]B[1]-0.75 * A[2]B[1]-0.15* A[1]B[2]+0.35 * A[2]B[2]-1.24 * A[1]C[1]-0.53 * A[2]C[1]-0.66 * A[1]C[2]+0.16 * A[2]C[2]+0.17 * B[1]C[1]-0.73 * B[2]C[1]+0.67 B[1]C[2] -1.01* B[2]C[2]

where A- temperature

B- active alkali

C- cooking time

Final Equation in Terms of Actual Factors: Not available, because this model contains more than 12 categorical equations.

Response 2: **kappa number**

ANOVA for selected factorial model

Analysis of variance table [Classical sum of squares - Type II]

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	
Model	2088.22	18	116.01	18.10	0.0001	significant
A-Temperature	*446.25*	*2*	*223.12*	*34.81*	*0.0001*	
B-Active alkaline	*317.67*	*2*	*158.83*	*24.78*	*0.0004*	
C-cooking time	*943.38*	*2*	*471.69*	*73.58*	*< 0.0001*	
AB	*125.18*	*4*	*31.30*	*4.88*	*0.0274*	
AC	*235.37*	*4*	*58.84*	*9.18*	*0.0044*	
BC	*20.37*	*4*	*5.09*	*0.79*	*0.5608*	
Residual	51.28	8	6.41			
Cor Total	2139.50	26				

The Model F-value of 18.10 implies the model is significant. There is onlya 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 are significant model terms.

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.

Std. Dev.	2.53	R-Squared	0.9760
Mean	22.03	Adj R-Squared	0.9221
C.V. %	11.49	Pred R-Squared	0.7270
PRESS	584.1	Adeq Precision	16.181

The "Pred R-Squared" of 0.7270 is in reasonable agreement with the "Adj R-Squared" of 0.9221. "Adeq Precision" measures the signal to noise ratio. A ratio greater than 4 is desirable. Your

ratio of 16.181 indicates an adequate signal. This model can be used to navigate the design space.

Term	Coefficient Estimate	df	Standard Error	95% CI Low	95% CI High
Intercept	22.03	1	0.49	20.91	23.16
A[1]	4.54	1	0.69	2.96	6.13
A[2]	0.78	1	0.69	-0.81	2.37
B[1]	4.46	1	0.69	2.87	6.04
B[2]	-0.57	1	0.69	-2.16	1.02
C[1]	7.72	1	0.69	6.13	9.31
C[2]	-1.09	1	0.69	-2.68	0.50
A[1]B[1]	1.63	1	0.97	-0.61	3.88
A[2]B[1]	1.73	1	0.97	-0.51	3.98
A[1]B[2]	-1.88	1	0.97	-4.13	0.37
A[2]B[2]	1.46	1	0.97	-0.79	3.70
A[1]C[1]	4.57	1	0.97	2.32	6.81
A[2]C[1]	-0.37	1	0.97	-2.61	1.88
A[1]C[2]	-0.12	1	0.97	-2.37	2.13
A[2]C[2]	0.38	1	0.97	-1.87	2.63
B[1]C[1]	0.22	1	0.97	-2.03	2.47
B[2]C[1]	0.51	1	0.97	-1.74	2.76
B[1]C[2]	0.60	1	0.97	-1.65	2.85
B[2]C[2]	0.39	1	0.97	-1.86	2.64

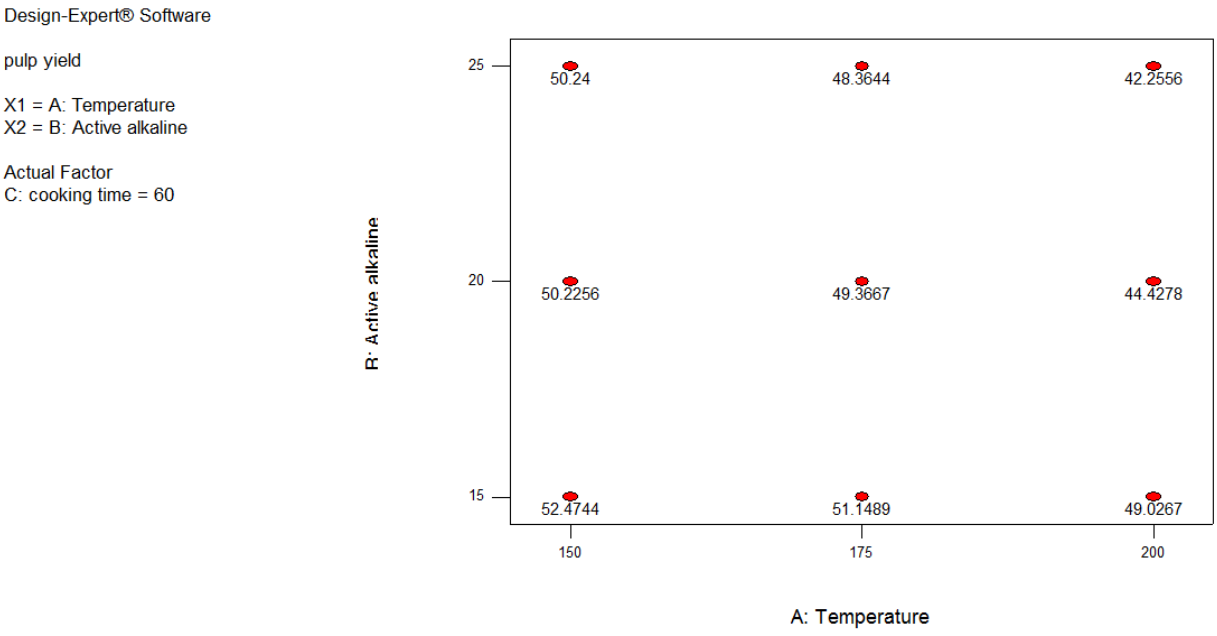
Final Equation in Terms of Coded Factors:

Kappa number = +22.03+4.54* A[1]+0.78* A[2]+4.46* B[1]-0.57* B[2]+7.72 * C[1]-1.09* C[2]+ 1.6* A[1]B[1]+1.73* A[2]B[1]-1.88* A[1]B[2]+1.46 * A[2]B[2]+4.57* A[1]C[1]-0.37 * A[2]C[1]- 0.12* A[1]C[2]+0.38* A[2]C[2]+0.22* B[1]C[1]+0.51 * B[2]C[1]+0.60 * B[1]C[2]+0.39 * B[2]C[2]

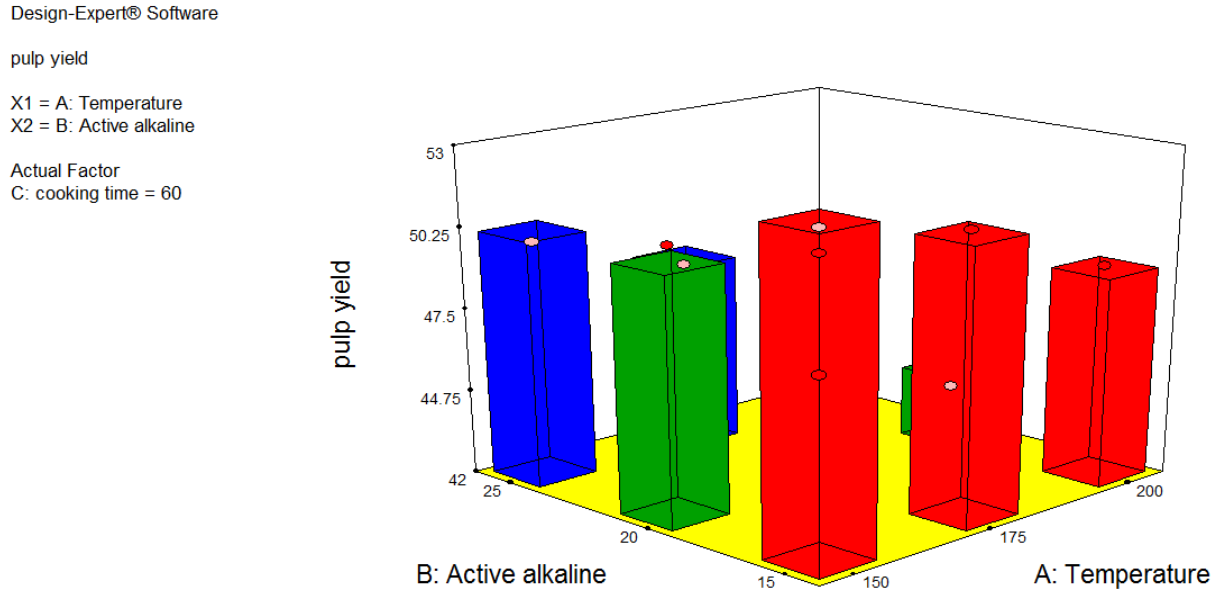
Final Equation in Terms of Actual Factors: Not available, because this model contains more than 12 categorical equations.

Appendix D: 3D and contour plots for the two responses (pulp yield and kappa number)

1. 3D and contour plots for the response pulp yield



(a)



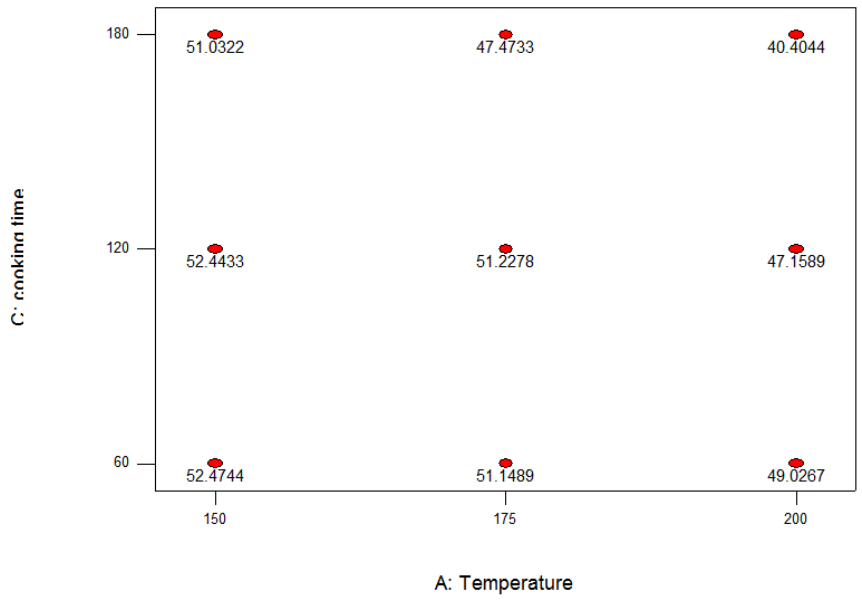
(a)

Design-Expert® Software

pulp yield

X1 = A: Temperature
X2 = C: cooking time

Actual Factor
B: Active alkaline = 15



(b)

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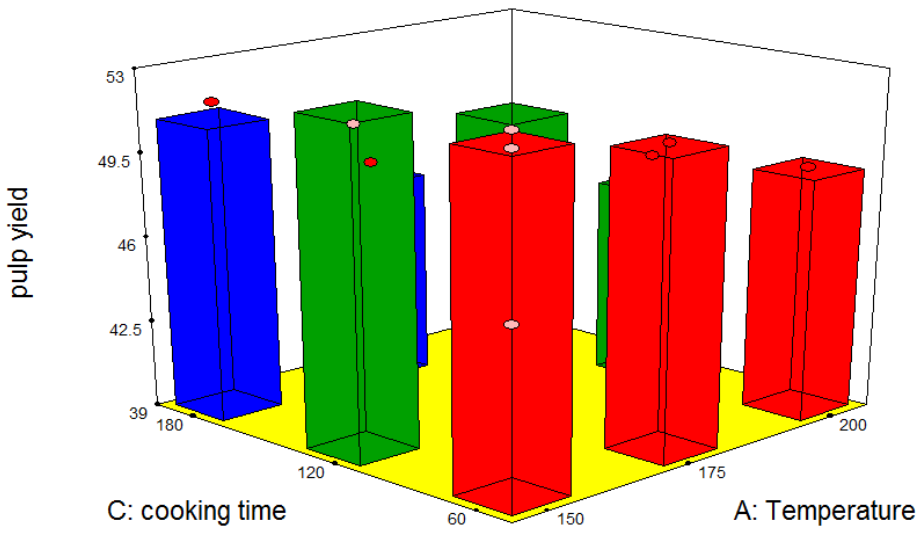
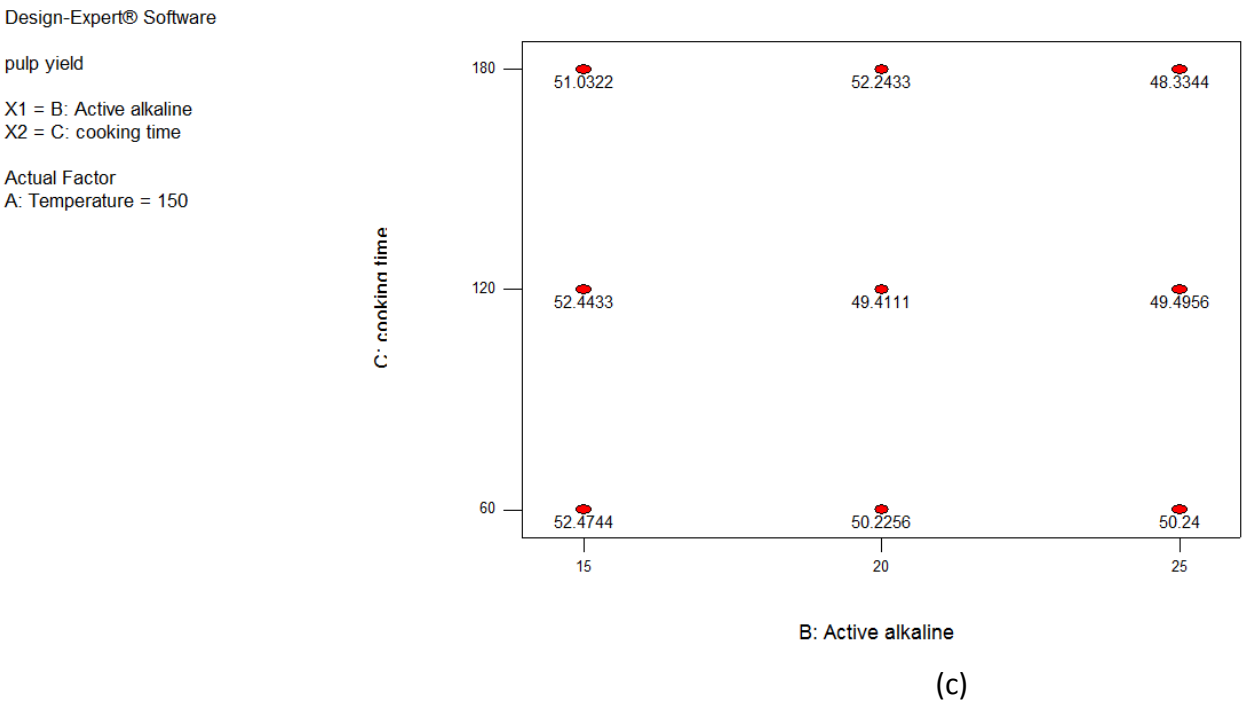
pulp yield

X1 = A: Temperature
X2 = C: cooking time

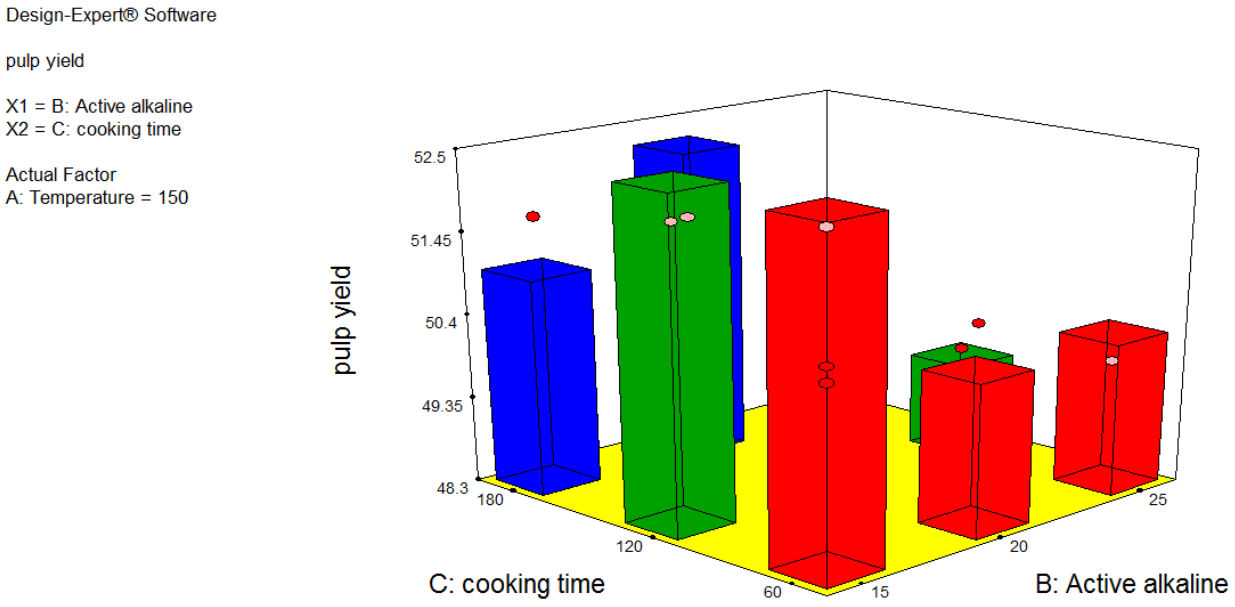
Actual Factor
B: Active alkaline = 15



(b)



(c)



(c)

Figure 1: contour and 3D plots of pulp yield of the samples studied as a function of (a) temperature and active alkali, cooking time fixed at 60 min. (b) temperature and cooking time, active alkali fixed at 15% (c) active alkali and cooking time, temperature fixed at 150^{o}C

2. 3D and contour plots for the response kappa number

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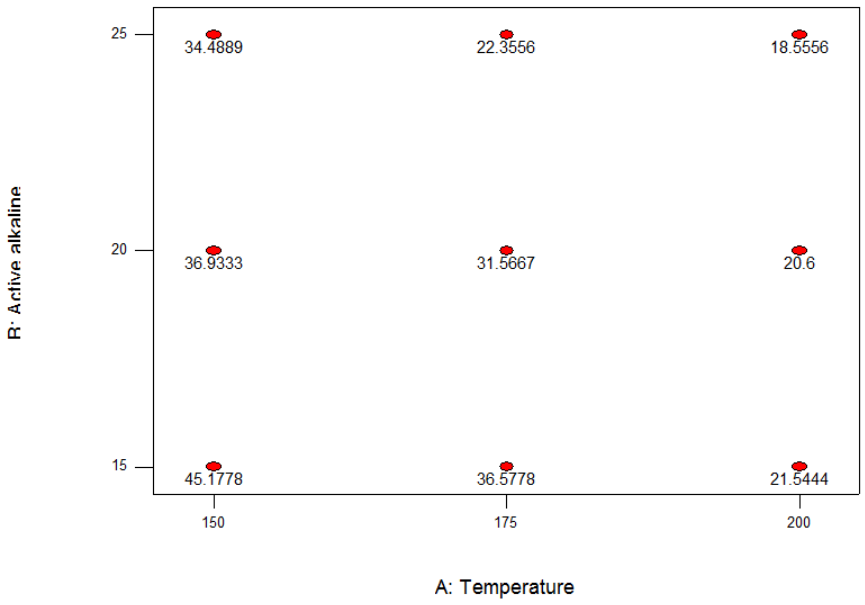
kappa number

X1 = A: Temperature
X2 = B: Active alkaline

Actual Factor
C: cooking time = 60



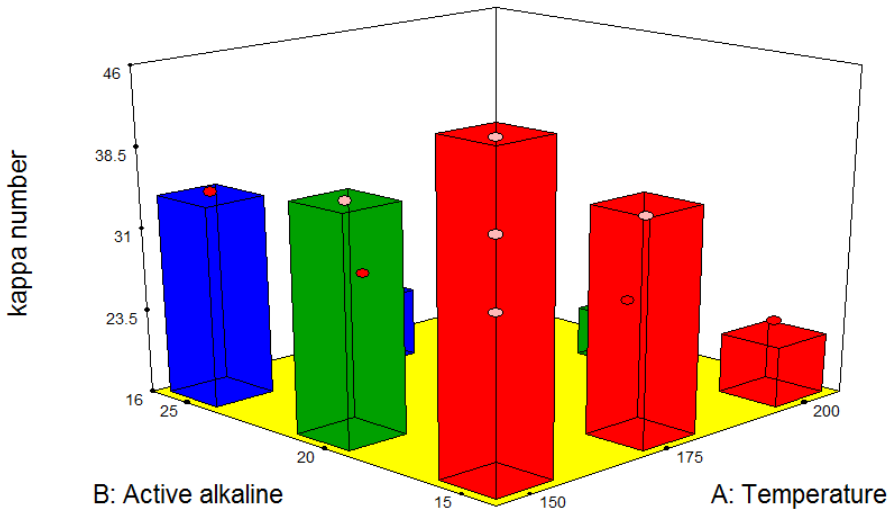
(d)

Design-Expert® Software

kappa number

X1 = A: Temperature
X2 = B: Active alkaline

Actual Factor
C: cooking time = 60



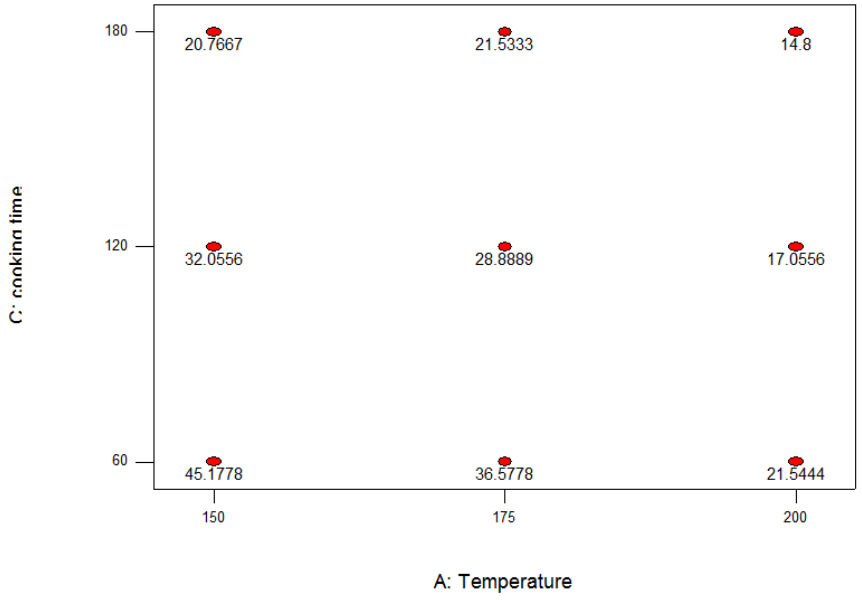
(d)

Design-Expert® Software

kappa number

X1 = A: Temperature
X2 = C: cooking time

Actual Factor
B: Active alkaline = 15



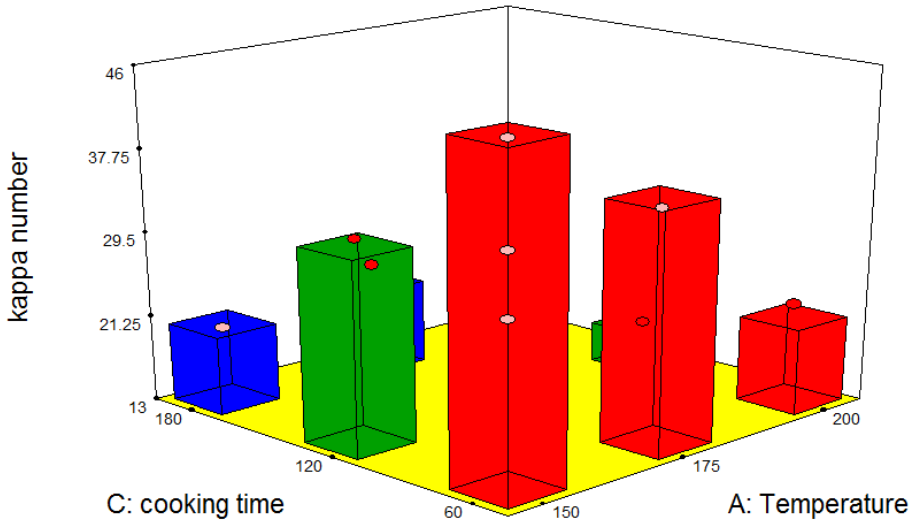
(e)

Design-Expert® Software

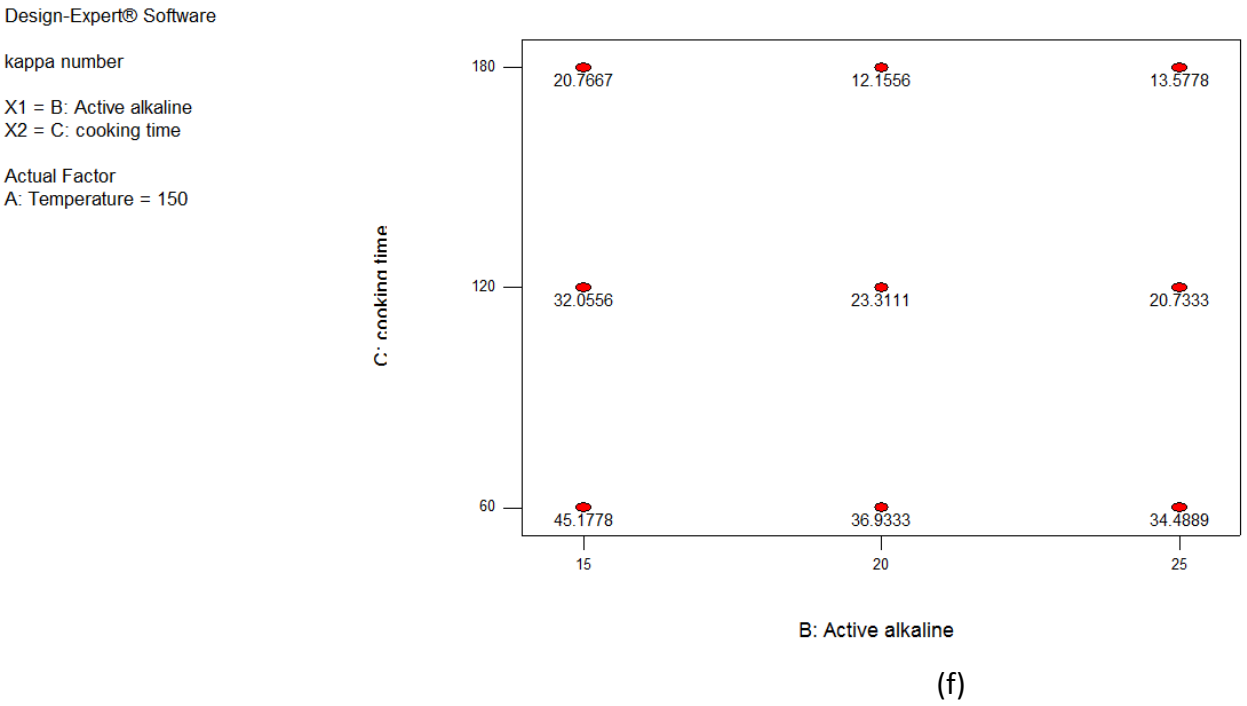
kappa number

X1 = A: Temperature
X2 = C: cooking time

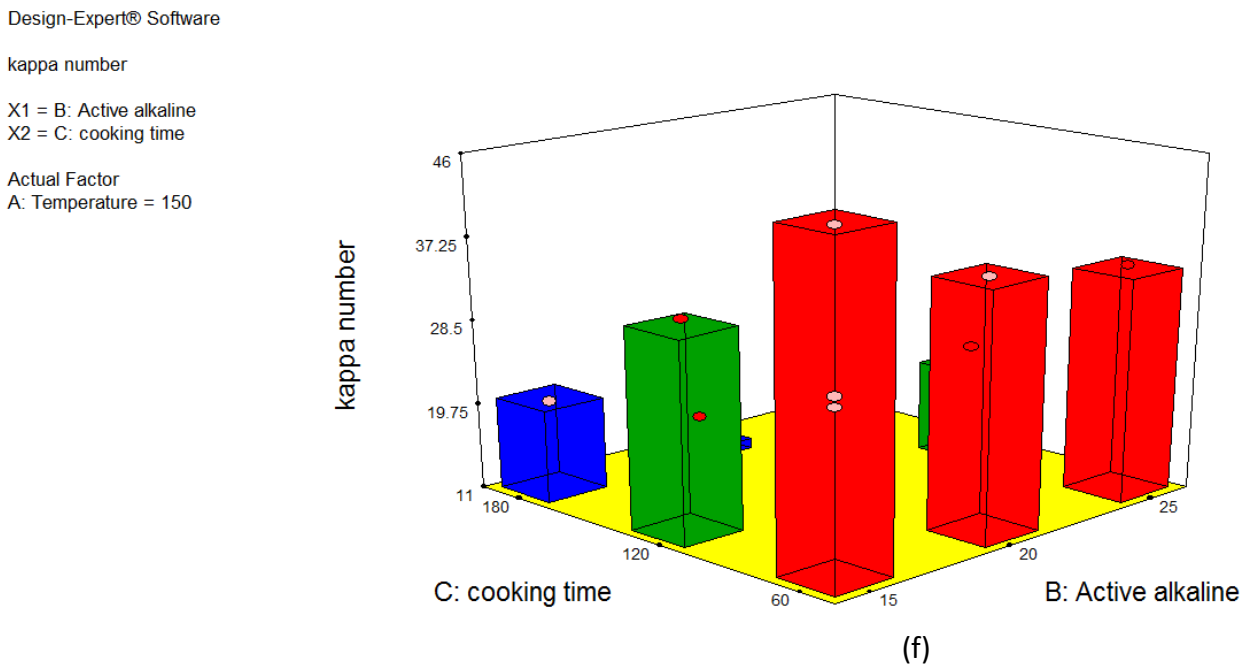
Actual Factor
B: Active alkaline = 15



(e)



(f)



(f)

Figure 2: contour and 3D plots of kappa number of the samples studied as a function of (d) temperature and active alkali, cooking time fixed at 60 min. (e) temperature and cooking time, active alkali fixed at 15% (f) active alkali and cooking time, temperature fixed at 150^{o}C.

Declaration

I declare that the thesis 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, that all resources of materials used for this thesis have been duly acknowledged.

Name: Amsalu Tolessa Mossissa

Signature: _____

Date of submission: _____

This thesis has been submitted for examination with my approval as a university advisor.

Name: Dr. Ing Belay Woldeyes

Signature:_____

Date: _____