Addis Ababa University
Addis Ababa Institute of Technology
School of Chemical and Bio Engineering

(M.Sc. program in Process Engineering)

Pulp Production from Cotton Stalks using Kraft Pulping

A thesis Submitted to the Research and Graduate School 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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(M.Sc. Thesis)

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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, and that all resources of materials used for this thesis have been duly acknowledged.

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ABSTRACT

The study aimed at optimizing pulping variables and selecting suitable delignification conditions for the production of pulp from cotton stalk. The influence of operational variables on the pulp yield and lignin dissolution of cotton stalks was studied. Cotton stalks chips were delignified in a laboratory pulpwood according to the Kraft pulping process. The conditions used were: Active alkali charge (5- 25%), sulfidity (10-50%), cooking temperature (155-175^{o}C and cooking time (30 – 150 minutes). The cotton stalks chip size and liquor to solid ratio were kept constant at 2cmX0.5cmX0.5cm on average and 5L to 1kg, respectively. Experimental data were fitted into a central composite design and a quadratic equation has developed. Model prediction for pulp yield and kappa number showed good agreement with experimental data with error values less than 5%. Optimum pulp percent yield (39.79%) was obtained using at 16.65% of active alkali, 20% of sulfidity, 163^{o}C temperature and 60 minutes of cooking time. The study shows that pulping at low temperatures for a short cooking time with high concentration of pulping liquor gives the best compromise for both pulp yield and kappa number/residual lignin content. The results of morphology analysis and pulp hand sheet physical tests shows that cotton stalks has similar fiber dimension and paper quality with eucalyptus.

ACRONYMS

AA	Active alkali
ANOVA	Analysis of Variance
BLO	Black liquor oxidation
CMP	Chemi-mechanical pulping
CS	Cotton Stalks
CSF	Canadian standard of freeness
DCE	Direct contact evaporator
ETIDI	Ethiopian Textile Industries Development Institute
ESP	Electrostatic precipitator
EPPSC	Ethiopian Pulp and paper Share Company
gpl	gram per liter
LSD	Least Significant Difference
MEEs	Multiple Effect Evaporators
NDCE	Non-direct contact evaporator
NSSC	Neutral sulfite semi-chemical
S	Sulfidity
SDT	Smelt dissolving tank
SNNP	South nations and nationalities people
TAPPI	Technical Association of Pulp and Paper Industries
TMP	Thermo Mechanical pulping
TRS	Total reduced sulfur
RMP	Refiner mechanical pulping

1. INTRODUCTION

1.1 Background

The demand and use of pulp and paper have marked the levels of civilization and development of many societies. As a result many developed nations use plenty of pulp and paper. 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. Paper in society is used in education, information storage, advertising, communication, in protection, 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 [2]. However, 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 [1].

As environment related climatic changes have become national and international challenges, possible sources of vital human needs, paper inclusive must be looked for from alternative extraordinary sources that offer less adverse impact on the environment. In most cases the non-wood materials such as agricultural food crop residues, grasses and tree leaves which do not have immediate beneficial applications in many communities have been proposed to be potential sources of pulp. Since all these plant materials contain cellulose in form of fibers, they stand to be potential sources for pulp manufacture with less environmental degradation threat [2].

Besides, the narrow issue of raw material availability, there are other driving forces behind the growing interest in non-wood pulping. In Europe, the overproduction of food and the large subsidies delivered to the agriculture sector have resulted in a need to find alternative uses for grain fields. Non-wood fibers provided the bulk of raw material supplies for paper makers over many centuries, and they still play an important role. Environmentalists claim that non-wood papermaking is more sustainable and environmentally friendly than wood-based paper production. It is an undeniable fact that both Europe and America share a large, untapped papermaking fiber resource. It should also be kept in mind that fibers harvested annually have a high biomass production potential. Some non-wood plants even give more pulp per hectare than

wood. From a marketing perspective, the environmental perceptions related with papers containing non-wood pulp are very positive [3]. Globally, non-wood pulp production is based primarily on straw (46%), bagasse (14%) and bamboo (6%). Agricultural by-products account for 73% of the world's non-wood pulp capacity, while natural plants such as reed and bamboo account for 18% and the remainder consists mainly of industrial crops [4]. In the future, the main non-wood fiber sources will be agricultural by-products such as straw and bagasse, or naturally growing plants like reed. No significant increase can be foreseen in the production of bamboo pulp because of the various other uses open to people using the fiber. In Europe, pulp capacity is based mainly on straw. Industrial crops are the second most important raw material source in the European non-wood pulp industry, especially in the form of cotton linters. Political, economic and environmental issues favor growing special plants. More advanced utilization techniques and logistics of reed canary grass, miscanthus, sorghum, kenaf and hemp are also being developed in Europe [4]. In 2013, 403 million tonnes of paper was produced. Among this 11% was produced from non-wood fibers. Per capita consumption was 57, 8 and 1.56 kg/yr globally, in Africa and in Ethiopia respectively [32].

The supply of paper in Ethiopia is dominated by imported products. The only paper producing factory in Ethiopia is Ethiopian Pulp and Paper Share Company which is located at Wonji. This factory imported pulp wood raw material and produces10, 000tonne of paper and 11,470tonne of corrugated paper annually. Unfortunately this covers only 0.1% of 203,859 tonne, which is current demand of the country. Ethiopia is rich in non-wood fiber materials. Almost all categories of non-wood fiber are found in the country. Residues of both agricultural and industrial process, naturally occurring uncultivated crops and on purpose or dedicated crops are found in different regions of the country with a significant amount. These include straw (e.g. from wheat, barley or rice), bagasse, maize stalks, bamboo, cotton stalks, lint and fluff, rags (from cotton material), hemp and sisal from old ropes and jute. Therefore utilizing these materials as raw material for pulp and paper production is recommended in many ways. In this work pulp was produced from one of the agricultural residues, cotton stalks, and tested for its quality.

1.2 Statement of the problem

The increasing/growing demand for paper products in Ethiopia and the foreign exchange amount expended for imports calls for the production of pulp and paper in the country. Finding input raw material sources for production of pulp is of paramount importance. In Ethiopia, there is an enormous potential for the production of cotton following its suitable agro-ecological zones and the availability of water. According to Ethiopian investment authority, the total potential area for farming cotton is estimated to be 3,000,810 hectares [9]. These areas are found in Amhara, Oromiya, SNNP, Gambella, Afar, Somalia, Benshangule Gumuz and Tigrai regions. By the year 2014/15 there is an expectations of 231,250 tonnes of raw cotton production and in plan to increase this capacity [10]. The Ethiopian Textiles Industry Development Institute (ETIDI) is one of the catalysts towards achieving the textile industry sub-sector's goals set by the Government in its five years Growth & Transformation Plan (GTP). The packaging industries are other driving forces for expansion of cotton production. Thus the farming of cotton would increase in the coming years.

On the other hand, the only pulp and paper industry in Ethiopia is Ethiopian pulp and paper Share Company located in Wenji. The factory importing pulp and convert to desired paper product. The country is totally dependent on imported pulp. Tiret PLC is on the way to install pulp and paper factory around Bahir Dar, using eucalyptus tree (bahir zaf) as raw material. In these factories paper is produced from wood fibers. However, trees as raw material are not preferable due to ecological effects and cost. Therefore, looking for raw material other than trees is the question of environment and cost.

Cotton stalks could be one promising material for paper production. Cotton stalk is rich in fiber, having cellulose content of 45.5%. This is similar to coniferous tree (the main raw material for paper) which has cellulose 42-51% and can be used as a raw material for paper production [23]. Therefore, investigating the pulp yielding potential of cotton stalk is timely.

1.3 Objectives

1.3.1 General objectives

The general objective of this study was to develop an optimal process for Kraft pulping of cotton stalks.

1.3.2 Specific objectives

- To analyze physical characteristics/morphological analysis/ of cotton stalks fiber and compare with those of wood fiber
- To look in to the effects of sulfidity used on quality and quantity of pulp
- To investigate the effects of cooking time on yield of pulp
- To investigate the effects of active alkali amount on pulp yield
- To investigate the effects of the cooking temperatures on the quality and quantity of pulp
- To determine the optimal pulping conditions for good quantity of pulp

1.4 Significance of the study

- This study show that cotton stalk can serve as an alternative raw material source for pulp and paper production.
- This work will show the possibility of minimizing environmental load emissions.
- Cotton production would get more recognition and cotton growers will be beneficial from selling of cotton stalks.
- Land coverage for cultivation of trees of raw material for paper manufacturing can be used for other purpose.
- Collection of cotton stalks from the fields and reaching them to factories for the production of pulp will generate rural employment.

2. LITERATURE REVIEW

2.1 History of paper production

Wood, as a papermaking fiber is a relative newcomer. For 90% of its existence of almost 2000 years, paper has been made exclusively from non-wood plant fibers. The first true paper, credited to Ts'ai Lun in 105 AD in China, was apparently made from true hemp (Cannabis Sativa). First among the papermaking fibers were hemp and China grass (Ramie, Boehmeria nivea). As demand for paper grew, so did the search for other suitable raw materials. The first suitable raw fiber that Chinese found (i.e.straight from the plant) apparently was the inner bark of Mulberry (Broussonetia papyrifera). Another raw material used was Bamboo [12].

During the next several centuries, the art of papermaking grew far and wide from Japan in the east, to Siam (now Thailand) in the south, to Chinese Turkestan in the west. In Turkestan, in 751 AD, papermaking was learned by the Arabs who brought it westward over their trade routes. Papermaking reached Samarkand, Baghdad (793 AD), Damascus, Cairo (900 AD), and Fez (1100 AD). From there it spread to Spain in 1151 AD then to France in 1348 AD and later on to Germany in 1390 AD. In the region where paper mulberry, bamboo and China grass were not available, replacement raw materials such as linen and cotton rags were used [12].

In 1450, the invention of printing using movable type in Germany resulted in a great reduction in the cost of book publishing. This created a demand for printing surfaces which parchment could not meet. During the next 150 years, mills for making paper by hand were built in nearly every country in Europe [12]. As printing costs declined, the literacy rates increased and many schools and universities were founded. This increase in literacy led to increase in publishing and in particular, the first newspapers around the year 1600 AD.

The resulting increase in demand could not be met only from rags and old ropes. Therefore, the search for alternative raw materials was intensified. Laboratory experiments were conducted on hundreds of vegetables, leaves, barks, weeds and wood. Trial copies of books were actually printed on paper made from asbestos (in 1727), lime tree bark (in 1786), marshmallow, swamp moss (in 1799) and straw (in 1800) [12]. With the advent of Fourdrinier continuous web paper machine in 1805 followed by the cylinder machine in 1809, increased the speed of paper production thus resulting in an increased production at lower cost. This further improved the demand for raw materials [12].

In 1827, straw was brought into successful commercial use. However, some straw alone could not satisfy demand for all grades, experiments on other raw material continued. Between1840 and 1885, experiments on wood yielded four commercially successful pulping processes. Pulps from these processes proceeded to displace straw from a number of paper grades. However, straw held its place as a major raw material for corrugated board for some time and reached its peak in 1940 with a production of 2/3 million tons. Since then, due to the economics of supply and high labor cost of collection, non-wood plant fibers have been almost entirely replaced by wood as papermaking raw material in most developed countries [12].

Today, the highest ratio of non-wood to total papermaking pulp capacities is found in the developing market economies of Asia, Africa and Latin America, as well as the centrally planned economies of Asia. Some of these regions have more non-wood plant pulping capacities than wood pulping capacities. China has more than twice as much. Further, total non-wood plant pulping capacity worldwide is increasing faster than the wood pulping capacity. Their respective annual rates of increase were 6% annually for non-wood as compared to 2% annually for wood pulp during the period from 1988 to 1993. It is expected to be 2.5% annually for non-wood and 1% for wood during the period from 1993 to 1998. As a result, non-wood plant pulping capacity (as a percentage of total papermaking pulp capacity) has increased from 6.7% in 1970 to 10.6% in 1993[13]. Of the total 20,887,000 metric tons of non-wood plant fiber pulp produced in 1995, 15,957,000 metric tons were produced in China. This accounts for over 76 percent of total world non-wood plant fiber pulp production and over 83% of total Chinese pulp production [14].

Due to the expected shortage and rising prices of wood for papermaking in the US, non-wood fibers are expected to be a source of papermaking fibers in the US in the near future [15]. At the same time, Europe has a shortage of short fibered hardwood pulp and is thus an importer of this kind of pulp. Some of the non-wood fibers have the properties to replace these fibers. The use of non-wood fibers for papermaking is thus also expected to grow in Europe.

2.2 Pulp and Paper Technologies

Pulp and paper are manufactured from raw materials containing cellulose fibers, which generally include wood, recycled paper, and agricultural residues. Paper is made by pulping wood, bleaching this pulp and then spreading it out into sheets to make it into paper. At various stages of the process, chemicals are used to give the paper particular properties, such as the bleaching chemicals that make paper white and which also enable it to subsequently be coloured.

The manufacturing of paper or paperboard can be divided into six main process areas, which are discussed further in the sections below: (1) wood/raw material preparation; (2) pulping; (3) bleaching; (4) chemical recovery; (5) pulp drying (non-integrated mills only); and (6) papermaking. Figure 2.1 presents a flow diagram of the pulp and paper manufacturing process. Some pulp and paper mills may also include converting operations like coating, box making, etc.; however, these operations are usually performed at separate facilities. Some integrated pulp and paper mills perform multiple operations (e.g., chemical pulping, bleaching, and papermaking; pulping and unbleached papermaking; etc.). Nonintegrated mills may perform either pulping (with or without bleaching), or papermaking (with or without bleaching) [16].

2.2.1 Wood Preparation

Wood is the primary raw material used to manufacture pulp, although other raw materials can be used. Wood typically enters a pulp and paper mill as logs or chips and is processed in the wood preparation area, referred to as the wood yard. In general, wood yard operations are independent of the type of pulping process. If the wood enters the wood yard as logs, a series of operations converts the logs into a form suitable for pulping, usually wood chips. Logs are transported to the slasher, where they are cut into desired lengths, followed by debarking, chipping, chip screening, and conveyance to storage. The chips produced from logs or purchased chips are usually stored on-site in large storage piles [16].

2.2.2 Pulping

During the pulping process, wood chips are separated into individual cellulose fibers by removing the lignin (the intercellular material that cements the cellulose fibers together) from the wood. There are five main types of pulping processes: (1) chemical; (2) mechanical; (3) semi-chemical; (4) recycle; and (5) other (e.g., dissolving, non-wood). Chemical pulping is the most common pulping process.

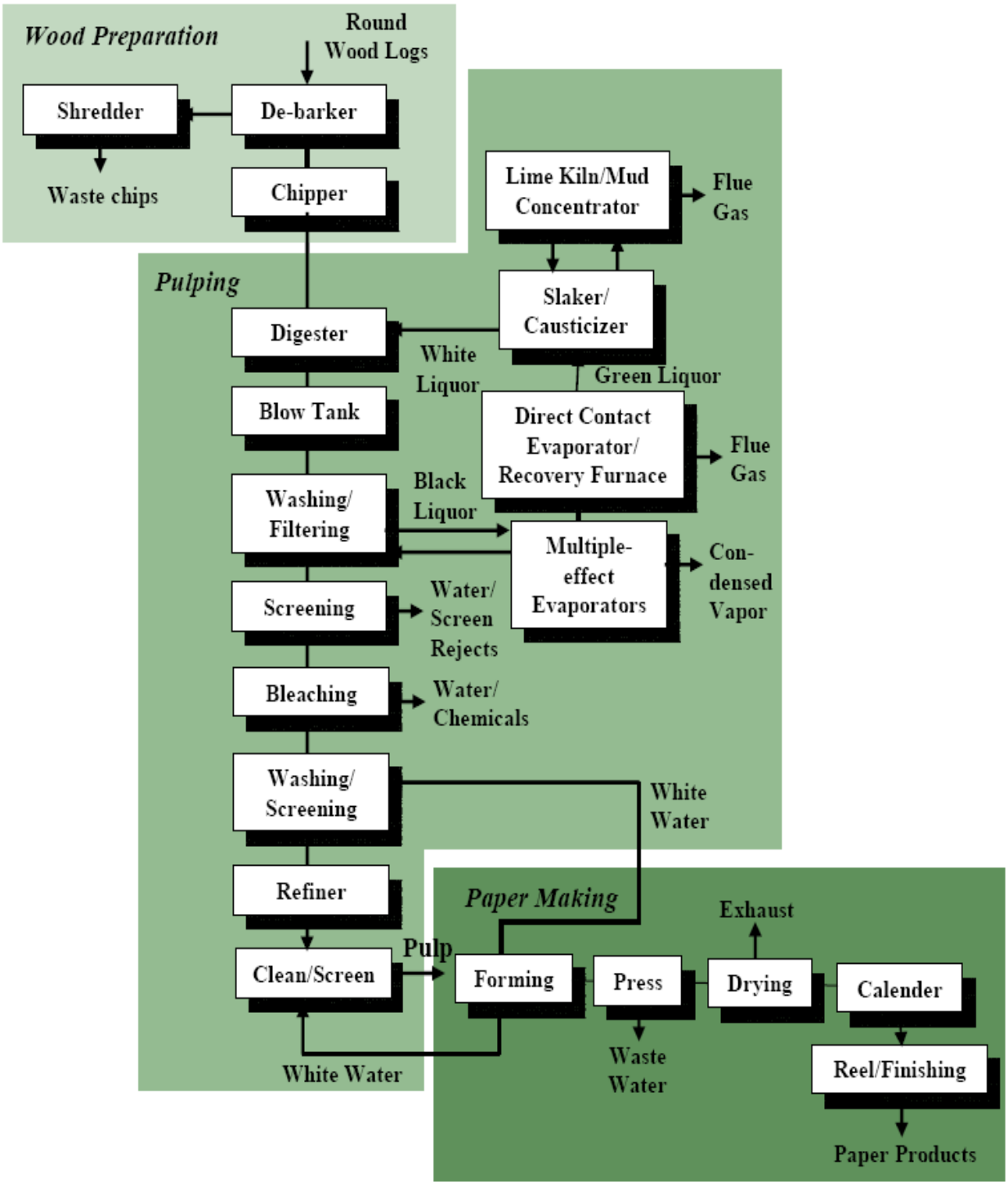


Figure 2.1: Flow Diagram of the Pulp and Paper Manufacturing Process [17]

Chemical (i.e., kraft, soda, and sulfite) pulping involves "cooking" of raw materials (e.g.,wood chips) using aqueous chemical solutions and elevated temperature and pressure to extract pulp fibers. Kraft pulping is by far the most common pulping process used by plants in the U.S. for virgin fiber, accounting for more than 80 percent of total U.S. pulp production. The kraft pulping process uses an alkaline cooking liquor of sodium hydroxide (NaOH) and sodium sulfide (Na_2S) to digest the wood, while the similar soda process uses only NaOH. This cooking liquor is mixed with the wood chips in a reaction vessel (digester). After the wood chips have been "cooked," the contents of the digester are discharged under pressure into a blow tank. As the mass of softened, cooked chips impacts on the tangential entry of the blow tank, the chips disintegrate into fibers or "pulp." The pulp and spent cooking liquor are subsequently separated in a series of brown stock washers [16 - 18].

The cooking liquor in the sulfite pulping process is an acidic mixture of sulfurous acid (H_2SO_3) and bisulfite ion (HSO_3^-). In preparing sulfite cooking liquors, cooled sulfur dioxide (SO_2) gas is absorbed in water containing one of four chemical bases - magnesium (Mg), ammonia (NH_3), sodium (Na), or calcium (Ca). The sulfite pulping process uses the acid solution in the cooking liquor to degrade the lignin bonds between wood fibers. Sulfite pulps have less color than kraft pulps and can be bleached more easily, but are not as strong. The efficiency and effectiveness of the sulfite process is also dependent on the type of wood furnish and the absence of bark. For these reasons, the use of sulfite pulping has declined in comparison to kraft pulping over time [16 - 18].

In mechanical pulping (i.e., refiner mechanical pulping [RMP], thermo-mechanical pulping [TMP], chemi-mechanical pulping [CMP]), pulp fibers are separated from the raw materials (e.g., round wood, wood chips) by physical energy such as grinding or shredding, although some mechanical processes use thermal and/or chemical energy to pretreat raw materials [16]. Semi-chemical pulping uses a combination of chemical and mechanical (i.e., grinding) energy to extract pulp fibers. Wood chips first are partially softened in a digester with chemicals, steam, and heat. Once chips are softened, mechanical methods complete the pulping process. The pulp is washed after digestion to remove cooking liquor chemicals and organic compounds dissolved from the wood chips. This virgin pulp is then mixed with 20 to 35 percent recovered fiber (e.g., double-lined kraft clippings) or re pulped secondary fiber (e.g., old corrugated containers) to enhance machinability.

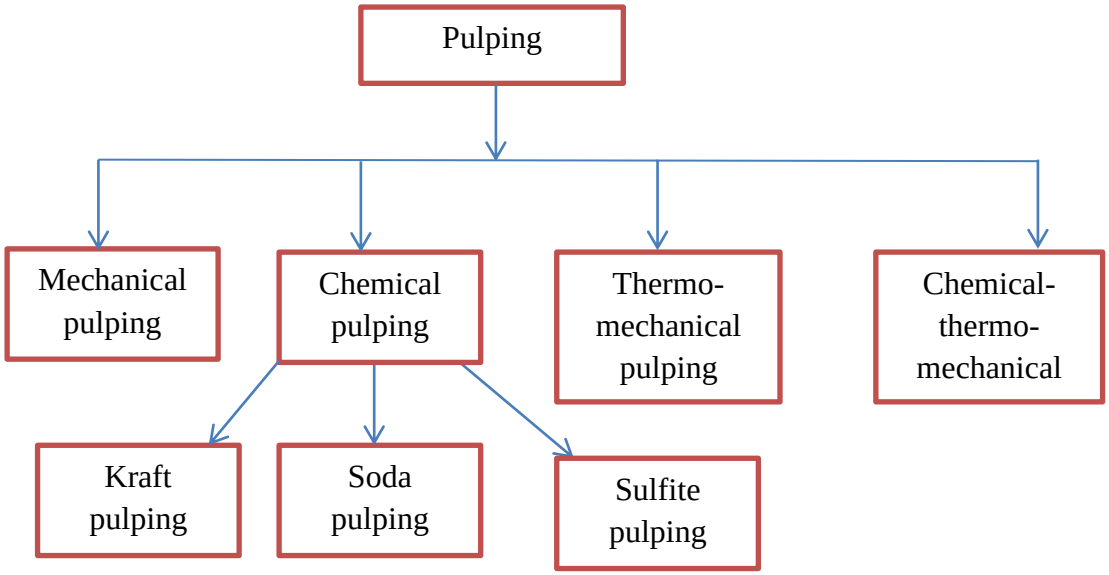


Figure 2.1: Types of wood pulping methods

The chemical portion (e.g., cooking liquors, process equipment) of the pulping process and pulp washing steps are very similar to kraft and sulfite processes. At currently operating mills, the chemical portion of the semi-chemical pulping process uses either a non-sulfur or neutral sulfite semi-chemical (NSSC) process. The non-sulfur process uses either sodium carbonate (Na_2CO_3) only or mixtures of Na_2CO_3 and NaOH for cooking the wood chips, while the NSSC process uses a sodium-based sulfite cooking liquor [16 - 18].

In the recycle (i.e., secondary fiber) pulping process, pulp fiber from previously manufactured products (e.g., cardboard, office paper) are recovered by hydration and agitation. Secondary fibers include any fibrous material that has undergone a manufacturing process and is being recycled as the raw material for another manufactured product. Secondary fibers have less strength and bonding potential than virgin fibers. The fibrous material is dropped into a large tank, or pulper, and mixed by a rotor. The pulper may contain either hot water or pulping chemicals to promote dissolution of the paper matrix. Debris and impurities are removed by "raggers" (wires that are circulated in the secondary fiber slurry so that debris accumulates on the wire) and "junkers" (bucket elevators that collect heavy debris pulled to the side of the pulper by centrifugal force) [16 - 18].

Dissolving kraft and sulfite pulping processes are used to produce highly bleached and purified wood pulp suitable for conversion into products such as rayon, viscose, acetate, and cellophane [16]. Non-wood pulping is the production of pulp from fiber sources other than trees. Non-wood

fibers used for papermaking include straws and grasses (e.g., flax, rice), bagasse (sugar cane), hemp, linen, ramie, kenaf, cotton, and leaf fibers. Pulping of these fibers may be performed by mechanical means at high temperatures or using a modified kraft or soda process [19].

2.2.3 Bleaching

Pulp cooking can safely dissolve up to about 90 percent of the lignin without degrading the cellulose fiber. Additional delignification is done by bleaching. Bleaching of high-yield chemical pulps is achieved by decolorizing with either an oxidizing agent or a reducing agent. The bleaching process removes color from the pulp (due to residual lignin) by adding chemicals to the pulp in varying combinations, depending on the end use of the product. The same bleaching processes can be used for any of the pulping process categories. The most common bleaching chemicals are chlorine, chlorine dioxide, hydrogen peroxide, oxygen, caustic, and sodium hypochlorite. Concerns over chlorinated compounds such as dioxins, furans, and chloroform have resulted in a shift away from the use of chlorinated compounds in the bleaching process to chlorine free bleaching chemicals. Bleaching chemicals are added to the pulp in stages in bleaching towers. Spent bleaching chemicals are removed between each stage in washers. Washer effluent is collected in seal tanks and either re-used in other stages as wash water or sent to wastewater treatment [19].

Bleaching sequences generally contain two phases with in each sequence:

1) A delignification segment, whose function is to remove the lignin from produced pulp; and
2) A brightening segment, whose principal function is to increase the brightness of the pulp.

The efficiency of the bleach cycle (related to its cost effectiveness), also depends on controlling the operating environment within each bleaching stage.

Bleaching is achieved through chemical reactions. Operating conditions are related to temperature, time, chemical concentrations, and degree of acidity or alkalinity. These factors must be kept in balance to achieve the desired degree of bleaching, while at the same time minimizing damage to the cellulose fiber. In addition, the “consistency” (amount of fiber being bleached in relation to the volume of liquid) of the fiber slurry being bleached affects chemical penetration and therefore must also be controlled. Computerization and improved sensors now

allow nearly real-time control over the operating environment in all stages of the pulping and bleaching processes [20].

2.2.4 Chemical Recovery

For economic and environmental reasons, chemical and semi-chemical pulp mills employ chemical recovery processes to reclaim spent cooking chemicals from the pulping process. At kraft and soda pulp mills, spent cooking liquor, referred to as "weak black liquor," from the brown stock washers is routed to the chemical recovery area at kraft and soda pulp mills. The chemical recovery process involves concentrating weak black liquor, combusting organic compounds, reducing inorganic compounds, and reconstituting the cooking liquor. The typical kraft chemical recovery process consists of the general steps described in the following paragraphs [16, 18].

Black liquor concentration: Residual weak black liquor from the pulping process is a dilute solution (approximately 12 to 15 percent solids) of wood lignins, organic materials, oxidized inorganic compounds (sodium sulfate [Na_2SO_4], Na_2CO_3), and white liquor (Na_2S and NaOH). The weak black liquor is first directed through a series of multiple-effect evaporators (MEEs) to increase the solids content to about 50 percent to form "strong black liquor." The strong black liquor from the MEE system is either oxidized in the black liquor oxidation (BLO) system if it is further concentrated in a direct contact evaporator (DCE) or routed directly to a Non-direct contact evaporator (NDCE), also called a concentrator. Oxidation of the black liquor prior to evaporation in a DCE reduces emissions of odorous total reduced sulfur (TRS) compounds, which are stripped from the black liquor in the DCE when it contacts hot flue gases from the recovery furnace. The solids content of the black liquor following the final evaporator/ concentrator typically averages 65 to 68 percent. The soda chemical recovery process is similar to the kraft process, except that the soda process does not require BLO systems, since it is a non-sulfur process that does not result in TRS emissions [16].

Recovery furnace: The concentrated black liquor is then sprayed into the recovery furnace, where organic compounds are combusted, and the Na_2SO_4 is reduced to Na_2S. The black liquor burned in the recovery furnace has a high energy content (13,503 to 15,362 kJ/kg of dry solids), which is recovered as steam for process requirements, such as cooking wood chips, heating and evaporating black liquor, preheating combustion air, and drying the pulp or paper products. The

process steam from the recovery furnace is often supplemented with fossil fuel-fired and/or wood-fired power boilers. Particulate matter (PM) (primarily Na_2SO_4) exiting the furnace with the hot flue gases is collected in an electrostatic precipitator (ESP) and added to the black liquor to be fired in the recovery furnace[16].

Additional makeup Na_2SO_4, or "salt cake," may also be added to the black liquor prior to firing. Molten inorganic salts, referred to as "smelt," collect in a char bed at the bottom of the furnace. Smelt is drawn off and dissolved in weak wash water in the smelt dissolving tank (SDT) to form a solution of carbonate salts called "green liquor," which is primarily Na_2S and Na_2CO_3. Green liquor also contains insoluble unburned carbon and inorganic impurities, called dregs, which are removed in a series of clarification tanks. Causticizing and calcining. Decanted green liquor is transferred to the causticizing area, where the Na_2CO_3 is converted to NaOH by the addition of lime [16].

The green liquor is first transferred to a slaker tank, where CaO from the lime kiln reacts with water to form calcium hydroxide ($Ca(OH)_2$). From the slaker, liquor flows through a series of agitated tanks, referred to as causticizers, that allow the causticizing reaction to go to completion (i.e.$Ca(OH)_2$ reacts with Na_2CO_3 to form NaOH and calcium carbonate ($CaCO_3$)). The causticizing product is then routed to the white liquor clarifier, which removes $CaCO_3$ precipitate, referred to as "lime mud." The lime mud is washed in the mud washer to remove the last traces of sodium. The mud from the mud washer is then dried and calcined in a lime kiln to produce "reburned" lime, which is reintroduced to the slaker. The mud washer filtrate, known as weak wash, is used in the SDT to dissolve recovery furnace smelt. The white liquor (NaOH and Na_2S) from the clarifier is recycled to the digesters in the pulping area of the mill [16].

2.2.5 Pulp Drying/Papermaking

After pulping and bleaching, the pulp is processed into the stock used for papermaking. At non-integrated mills, market pulp is dried, baled, and then shipped off-site to paper mills. At integrated mills, the paper mill uses the pulp manufactured on-site. The processing of pulp at integrated mills includes pulp blending specific to the desired paper product desired, dispersion in water, beating and refining to add density and strength, and addition of any necessary wet additives (to create paper products with special properties or to facilitate the papermaking process). Wet additives include resins and waxes for water repellency; fillers such as clays,

silicas, talc, inorganic/organic dyes for coloring; and certain inorganic chemicals (calcium sulfate, zinc sulfide, and titanium dioxide) for improved texture, print quality, opacity, and brightness [18].

The papermaking process is similar for all types of pulp. The pulp is taken from a storage chest, screened and refined (if necessary), and placed into a head box of the paper machine. From the head box, slurry of pulp is created using water, usually recycled whitewater (drainage from wet pulp stock in pulping and papermaking operations). The pulp slurry is put through a paper machine and then passed through a press section, where the whitewater is drained and the sheet forming process is begun. The paper sheet is then put through a dryer and a series of booths for coating and drying. The finished product then goes through a calendar (where the sheet is pressed to reduce thickness and smooth the surface) and is wound onto storage reels. [19]

2.3 Effects of Fiber Properties on Quality of Paper

Fibers are particles that have one dimension significantly larger than the other two. Fibers are often characterized or selected according to their aspect ratio, i.e., the ratio of the large dimension to one of the small dimensions. If no other criteria are used, then materials that might not normally be considered fibrous may contain a fraction of particles that meet the criteria for fibers.

Short fibers do not produce good surface contact and fiber-to-fiber bonding. The value of fiber diameter affects the tear resistance as the ratio of fiber length to the fiber diameter increases the tear resistance. Fibers with large lumen and thin walls tend to flatten to ribbons during paper making with enhanced inter-finer bonding between fibers and consequently having good strength characteristics. The smaller fiber lumen width results the poorer pulp beating because of liquids into empty spaces of the fibers. The Larger the fiber lumen width better, will be the beating of pulp, because of penetration of liquid into empty space between the fibers. Thin walled cells on the other hand, collapse readily to form dense, well-boded paper, low in tear but high in other strength properties. The Runkel ratio and flexibility coefficient are important indices to determine the suitability of material for pulp and papermaking. Low Runkel ratio is expected to have an inevitably positive effect on tensile and bursting strengths as well on folding endurance [30].

2.4 Pulp Technology Selection

The Kraft or sulphate pulping process evolved from the soda process in the period of 1870 to 1885. Few technologies that are over 100 years old still dominate an industry as does Kraft pulping. About 70% of the world pulp production is still manufactured by the Kraft process and this process still dominates due to expansion in new pulping capacity. Some of the key features that contribute to this longevity are:

1. The wide variety of unbleached and bleached products that can be produced from the same basic process ranging from high strength linear board to high chemical purity dissolving and specialty pulps.
2. The ability to readily pulp any commercial wood species and produce a stronger pulp than most other chemical or mechanical process.
3. The high efficiency and economical chemical recovery system that regenerates both pulping chemicals and needed process energy and steam for pulp mill operations.
4. The opportunities for continuous improvement of the Kraft process to produce stronger and more uniform pulp, to increase pulp yield, to reduce energy usage and to meet current and future environmental restrictions.

In the last few years, we have seen substantial process improvements and technology developments in: fiber raw material preparation and chip quality, batch and continuous digester mechanics, achieving strength potential of pulps, heat recovery and cold blow systems, catalysts and additives, extended delignification and cooking liquor sequencing, process control systems and sensors, quality control. Each of these areas has allowed mills worldwide to continue to rely on Kraft pulping as the major process. There for the foreseeable future Kraft pulping with its recent engineered improvements will dominate the industry for many more decades [25].

2.4 The Kraft Process

The kraft process is presently the most widely used cooking technology because of the following advantages:

- all wood species can be used
- the process is tolerant to bark
- the pulp fibers have the highest strength
- the pulping chemicals and energy are recovered at high efficiency
- the cooking time is relatively short
- it generates valuable side-products such as tall-oil

The Kraft pulping solution called white liquor is a strongly alkaline solution (pH-14) of mostly NaOH and Na_2S. It also contains small amounts of Na_2C0_3, Na_2S0_4, $Na_2S_20_3$ and NaCl. The active delignification species in the kraft cooking liquor are the OH^- and HS^- ions formed by hydrolysis of NaOH and Na_2S by the following equilibria:

$$NaOH + H_2O \longleftrightarrow Na^+ + OH^- + H_2O \quad (2.1)$$

$$Na_2S + H_2O \longleftrightarrow 2Na^+ + S^{-2} + H_2O \quad (2.2)$$

$$S^{-2} + H_2O \longleftrightarrow HS^- + OH^- \quad (2.3)$$

2.4.1 Lignin Reactions

Although the delignification reactions of the alkaline Kraft process are not exactly known, it is generally agreed that cleavage of the non-phenolic P-aryl ether bonds are mainly responsible for the solubilization of lignin. The presence of hydrogen sulfide ions significantly affects the delignification due to their strong nucleophilicity in comparison with hydroxyl ions [28]. Both hydroxyl and hydrogen sulfide ions promote the cleavage of ether linkages [28]. During the kraft process, white liquor (a blend of sodium hydroxide and sodium sulfide) promotes lignin dissolution and consequent fiber liberation. Kraft pulping occurs in three distinct kinetic phases: the initial phase, bulk phase, and residual phase. During the bulk reaction phase, 60% to 68% of the total delignification of the wood occurs. The use of sodium hydroxide and sodium sulfide offers a number of advantages when compared to other processes, especially in terms of fiber strength. However, there are also disadvantages; the major one being the loss in pulp yield caused

by carbohydrate instability and degradation during the alkaline reaction. Typically, for hardwood pulps, delignification reactions are about 13 times faster than carbohydrate degradation reactions [26]. Easier lignin breakdown during pulping could potentially result in less drastic process condition requirements, leading to carbohydrate preservation. In order to achieve the structural breakdown and solubilization of lignin, wood chips need to first be impregnated with alkali. The impregnation process consists of transportation of cooking liquor through the surface of the chip, followed by diffusion into the interior. As the chip heats up, lignin chemical reactions start to occur. When chips are being pulped at elevated temperatures, the rate of liquor diffusion into the wood is the rate determining step. Delignification reactions tend to be faster than the diffusion rate [27]. This event is followed by diffusion of degradation products to the exterior of the chip and transportation of those products to the cooking liquor. While penetration is the flow of white liquor to the chip interior (driven by hydrostatic pressure), diffusion is the flow of white liquor ions through the water (present in the chips), which occurs via concentration gradients.

Kraft delignification occurs by modifying the structure of lignin in two different ways to enhance its dissolution. The first is to degrade the lignin into smaller units by cleaving inter unit linkages as shown in figure 2.2. The second is to introduce hydrophilic groups into the polymer and cleaved fragments, making the lignin more soluble in the cooking liquor, figure 2.3. These phenomena occur when linkages holding the phenyl propane units together are cleaved, thereby generating free phenolic hydroxyl groups. The presence of these hydroxyl groups increases the hydrophilicity of the lignin and lignin fragments. Thus, the solubility of the lignin in the cooking liquor is increased. Meanwhile, the carbon-carbon linkages, being more stable, tend to survive the kraft pulping process.

The reaction mechanism

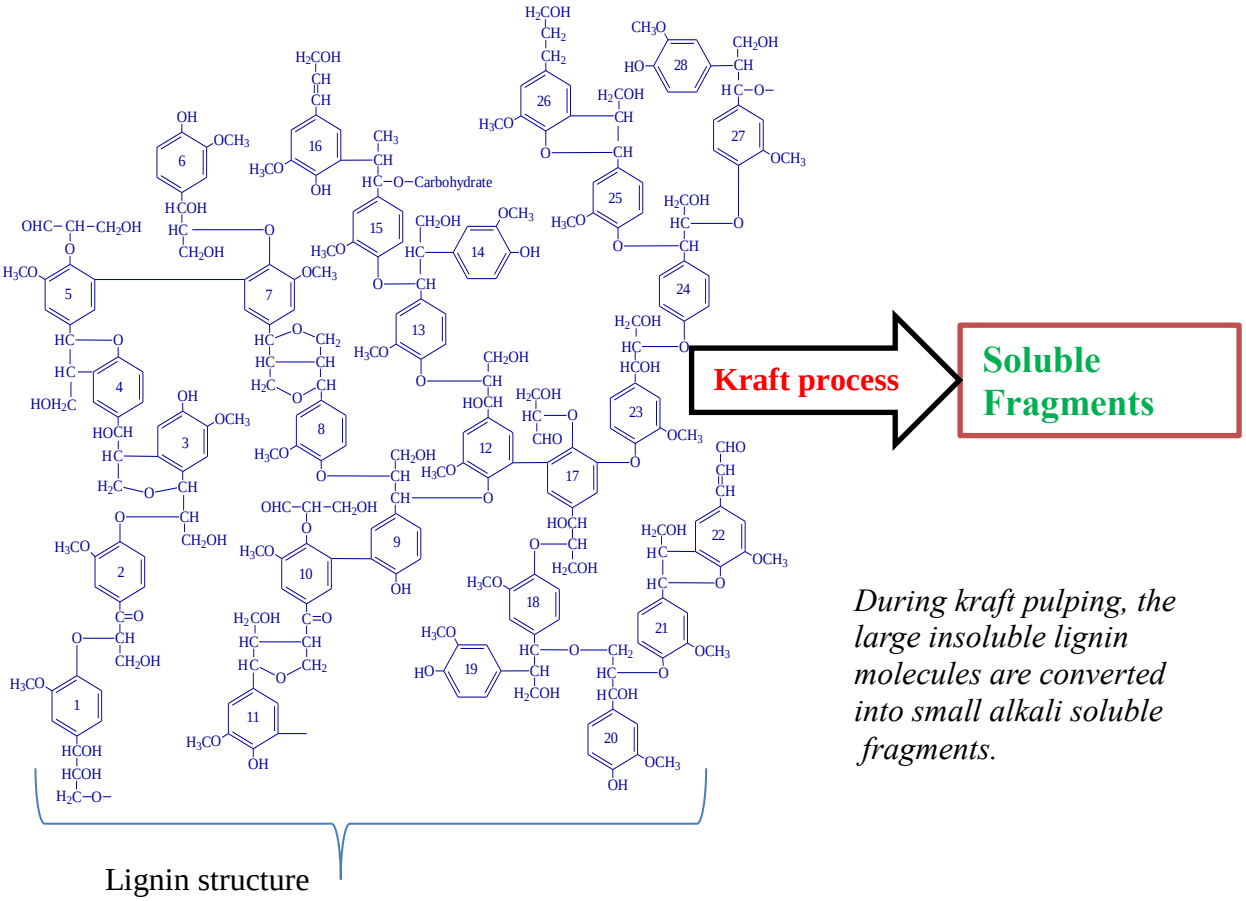


Figure 2.3: Reaction mechanism of lignin and Kraft chemical.

The goal in kraft pulping is the cleavage of lignin into alkali soluble fragments. Cleavage is affected by the following factors:

- Type of linkage
- Presence of free phenolic hydroxyl group
- Functional groups (benzyl hydroxyl, carbonyl)
- Type and amount of nucleophiles (OH-, HS-)
- Reaction temperature

Sites for Nucleophilic Attack

The cooking chemicals used in kraft cooking (NaOH and Na_2S: OH^- and HS^-) both act as nucleophiles, because of their free pair of electrons. Sites for nucelophilic attack in lignin are those areas of reduced electron density (partially positive sites).

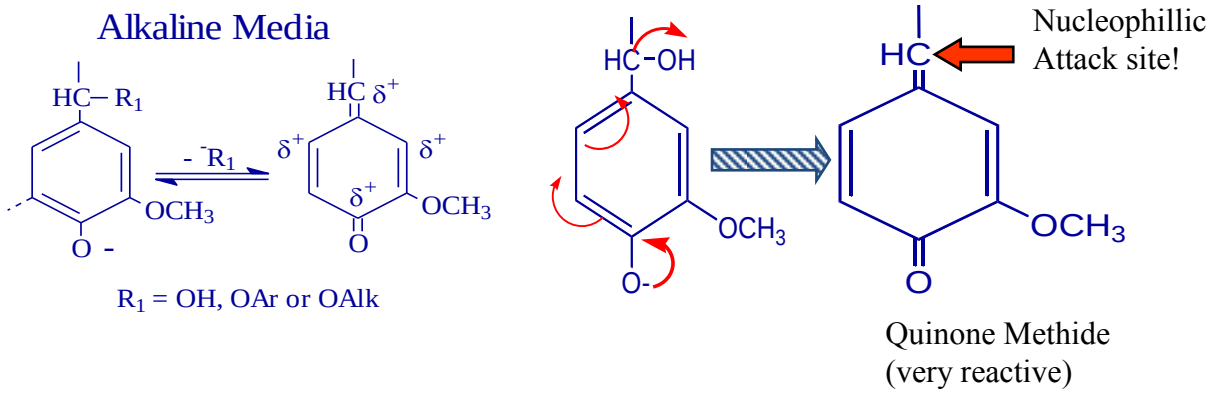


Figure2.4: Nucleophilic Attack Site for Lignin Reaction

A free phenolic hydroxyl group is needed for the formation of a quinone methide. The oxygen of the quinone group (carbonyl) attracts the electron density on the double bond thus making the carbon more positive. This in turn shifts the electron densities of the other bonds on this conjugated system.

2.4 Applications of pulp and paper

The range of possible uses of paper seems almost limitless. New ways of using it are being devised daily. This evolution will continue because paper is an expression of everyday living.

Paper may be impregnated, enameled, metallized, made to look like parchment, creped, water-proofed, waxed, glazed, sensitized, bent, turned, folded, twisted, crumpled, cut, torn, dissolved, macerated, molded, and embossed. It may be colored, coated, printed or even written on. It can be laminated with fabric, plastic and metal. It can be opaque, translucent or transparent.

It is naturally combustible, or can be made fire retardant. It may be a carrier or a barrier or a filter. It may be made tough enough to withstand acid, or soft enough for a baby's skin. It can be re-used and recycled and it is made from a renewable, sustainable source [21]. Paper has many applications in many sectors some are listed in the table below.

Table 2.1: Applications of pulp and paper in different sectors [21]

Sectors	Applications
Agriculture	Sacks, seed packets, and animal bedding.
Building	Wallpaper, damp-proof courses, roofing, flooring, flame resistant papers, plasterboard, and decorative laminates for furniture.
Business	Receipts, circulars, catalogues, filing systems, sales and service manuals, brochures, and letter heading.
Cars	Fascia boards, door and roof liners, filters, the Highway Code, and driving licenses.
Communications	Writing pads, envelopes, newspapers, magazines, greeting cards, calendars, diaries, telephone directories, labels, business and passports.
Domestic Products	Tissues, paper plates and cups, toilet paper, kitchen towels, table napkins, wallpaper and lampshades.
Education	Books, exercise books, wall charts, flip charts, and report cards.
Electrical	Special insulating boards, electrolytic condenser paper, wrapping and identification for electrical cables, printed circuits, and battery separators.
Entertainment	Menu cards, paper hats, crackers, fireworks, wrapping paper, programs, playing cards, board games, kites, model aircraft, and race cards.
Filtration	Filters for water, air, coffee, tea bags, medicine, beer, oil, and mechanical uses.
Impregnated Papers	Polishing, waxing, and cleaning.
Industry	Protection for manufactured goods, in transport, transfer sheets for decorating chinaware, display boards; point of sale materials and in storage.
Medical	Wrapping to keep instruments and equipment sterile, bandages, first aid bands, clothing for nurses, face masks, surgeons' caps, disposable bed pans, sheets, and pillowcases.

Money; Finance; Security	Bank notes, insurance forms, cheek books, stamps, cash bags and security papers that contain special markings which are only visible when subjected to ultra-violet light.

2.6 Pulp and Paper Demand in Ethiopia

Ethiopia does not produce its own pulp, but only paper. There is one paper-producing factory in Ethiopia, which is located in wenji. The paper mill uses imported pulp and waste paper as its raw material. The mills produce some 12,490 metric tons per annum of different qualities of finished paper and 10,241 metric tons of corrugated paper. However, the paper demand of the country cannot be satisfied by domestic production only. Therefore, Ethiopia imports not only pulp but also finished papers and corrugated papers too. According to Ethiopian central statistical authority, pulp wood used by the mill is imported at an annual cost of about 148 million Birr, and about 2.2 billon Birr is needed to import finished paper products per year.

Table 2.2: The amount of pulp and paper commodities imported and costs incurred [35]

	Year					
Commodity imported	2010/11		2011/12		2012/13	
	Amount, tone	Cost, '000 Birr	Amount, tone	Cost, '000 Birr	Amount, tone	Cost, '000 Birr
Pulp wood	5,583	44,850	10,346.3	119,193.3	12,637	147,082.2
Paper & paper board	73,345	1,221,765	83,188.2	1,785,735	99,642	2,128,721.2

Forecasting demand

The demand for pulp and paper products as an all-purpose product is related with the overall economic development of the country. Both service providers and manufacturers usage of new products of paper is one of the reasons for the ever increasing demand for pulp and paper. Education expansion policies and freedom of press can be driving forces for stationery and news print papers. Growth anticipated in the manufacturing and agro-industries will result in more

demand for suitable packaging. Average growth rates of 53. 72 % and 16.6% have achieved in pulp wood and paper imported during the three consecutive years. From this we can predict demand to be imported by the year 2015/16 as 45,903tone pulp and 157,956.7 tons of paper and paper board.

2.7 Cotton Cultivation in Ethiopia

Cotton has been grown and used for a very long time in Ethiopia. It has been used in hand spinning and weaving. Now days, the establishments of large textile industries has resulted in to cotton supply and demand in balance. However, starting from 2006 E.C Ethiopian Textile Industry Development Institute (ETIDI) has taken responsibility of cotton development activity by establishing cotton development directorate. Thus, it is expected that cotton cultivation and productivity will increase and fulfill the requirements of textile factories.

Cotton is grown under both rain-fed (peasant smallholdings) and irrigated (large-scale commercial farms) in Ethiopia. The methods of production and problems vary considerably between the two types of farms. There is a vast potential to grow cotton both under rain fed and irrigated conditions in the country. There are about 3,000,810 ha of land that is potentially suitable for cotton production.

Table2.3: Potential areas of cotton cultivation [10]

Region	High productive land (hectare)	Medium productive land (hectare)	Total land available for cotton production (hectare)
Tigray	208,830	60,300	269,130
Amhara	544,030	134,530	678,710
SSNP	385,400	215,530	600,930
Oromiya	205,490	201,930	407,420
Gambella	262,850	53,600	316,450
Benshangule	79,930	223,240	303,170
Afar	150,000	50,000	200,000
Somalia	150,000	75,000	225,000
Total	1,986,530	1,014,280	3,000,810

Cotton grows in 8 regions of Ethiopia. Large amounts of row cotton supplies are covered by, Tigray, Afar, Gambela and Benishangule regions. In Oromia and Somali regions, there is no satisfactory activity on cotton cultivation. Cotton production and productivity mainly depend on climatic factors, agricultural inputs, agricultural management practice, agricultural technology, Soil type and etc.

Table 2.4: Cotton cultivation type [10]

S/N	Parameters	Water source	
		Rain fall	Irrigation
1	Planting period(average)	Late June- July	April – may
2	Harvesting period(average)	November – December	September - October
3	Productivity (average)	1.5tons/ha	2.5tones/ha

Table2.5: Status of the Ethiopian Cotton Production in the last Six Years [11]

Area/Production	2009/10	2010/11	2011/12	2012/13	2013/14	2014/15 (estimated)
Total area , ha	82,600	99,250	143,160	81,080	59,000	125,000
Total row cotton, tons	123,900	148,870	214,730	121,620	94,590	231,250
Lint, t/ha	0.55	0.55	0.56	0.56	0.59	0.68
Total lint ,tons	45,845	55,081	79,452	45,000	35,000	85,560

2.5 Previous Works on Cotton Stalk Pulping

So far scientists conducted several researches to utilize cotton stalks for raw material of pulp and paper. Physical and chemical analysis of cotton stalks is one work done by Tutus et al 2010[23]. According to their work, cotton stalk has the following characteristics:

Table 2.6: Chemical analysis of cotton stalks (*Gossypium hirsutum* L.) [23]

Chemical content	**Percentage /%/**
Holocellulose	75.6
Cellulose	45.5
α-cellulose	39.8
Lignin	18.2
Ash	2.52
Silica	0.48
Alcohol-benzene soluble	6.1
1%NaOH soluble	30.9
Cold water soluble	11.7
Hot water soluble	15.3

Table 2.7: Dimensional analysis of cotton stalks fibers [23]

Fiber dimension	**Data**
Fiber lengths (mm)	0.81
Fiber width (µm)	24.98
Lumen width (µm)	16.75
Cell wall thickens(µm)	4.12

Cotton stalk pulping had been conducted by [24]. The pulping condition was active alkali 10-20% of oven dry fiber, cooking time temperature was from 150-165^{o}C and liquor to solid fiber source ratio and the following results were obtained from the result.

Table 2.8: Results of pulping of both American and Egyptian cotton stalks [24]

	NaOH%	Kappa no	Total yield, %	Screened yield, %	Rejects, %	Residual alkali, gpl/Na_2O
American	12	95.4	37.4	30.9	7.00	1.40
	18	22.5	34.0	32.9	1.10	6.94
Egyptian	12	89.7	44.5	34.9	10.3	1.20
	18	21.5	39.4	39.0	0.43	8.10

3. MATERIALS AND METHODS

3.1 Materials

The major raw material used during the experimental works was cotton stalks. Cotton stalks were acquired from Ethiopian Agricultural Research Institute site at Werer, Afar region, in December 2014. The chemicals and analytical reagents grade used were sodium hydroxide, sodium sulfide, hydrogen peroxide, acetic acid, distilled water, sulfuric acid, potassium permanganate, safarine and ethanol, bought from different chemical stores in Addis Ababa.

3.2 Equipments

The equipments used during the experimentations includes laboratory autoclave, microscope equipped with a camera, spectroscopy , water bath, hacksaw, separating funnel, balance, oven, magnetic stirrer, different size conical and Erlenmeyer flasks, beakers, measuring cylinders, burette, zipper bags, hammer and tensile, burst and tear machines.

The experimental work was started in January and ended in May; a total five months was spent for the laboratory works. Morphological analysis of cotton stalks fiber was done at Forest Products Utilization Research Center, Addis Ababa. Kraft pulping of cotton stalks and kappa number determination of cotton stalks pulps were done at School of Chemical and Bio Engineering Laboratory, AAiT and the pulp hand sheet physical strength tests were conducted in the laboratory of Ethiopian Pulp and Paper Share Company, Wenji. The overall structure of the experimental works is shown in Figure (3.1).

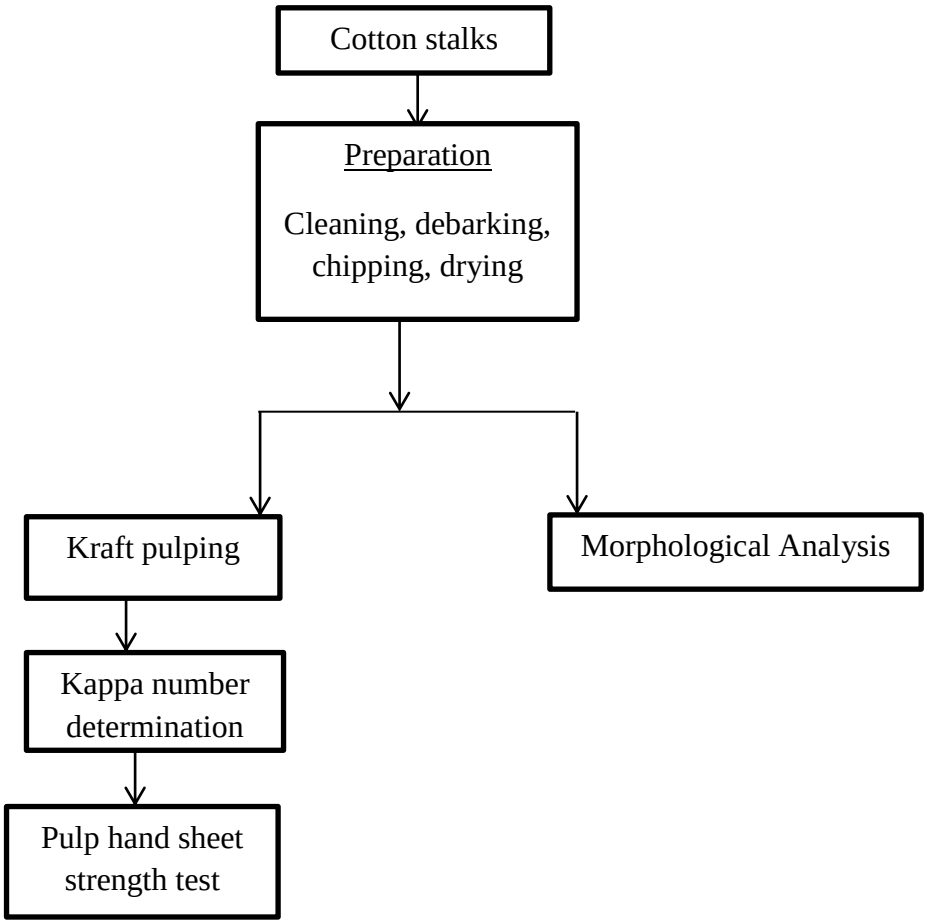


Figure 3.1: Frame work of the experiment

3.3 Experimental Method

3.3.1 Morphological Analysis of Cotton Stalks Fiber

Cotton stalks were collected from the Ethiopian Agricultural Research Institute site at Werer in December 2014 and were air dried. From the collected raw materials, some parts of cotton stalks are taken randomly and cut in to 2cm length X 0.5mm width pieces after cleaning from roots, leaves and soil. For cell wall thickness, fiber diameter, lumen diameter the cotton stalk pieces are then immersed in cold water in a flask for four days. Then the stalks were boiled for 24 hours in order to soften them and make easy for slicing [29]. From the water macerated stalks 20 micro meters slices from cross sectional (for cell wall thickness, fiber diameter, lumen diameter) parts were taken by slicer and macerated in 1% safarine solution for 5 minutes. Then washed by 50%, 65%, 75%, 85% and 97% ethanol on petri dishes to remove excess safarine solution that cause invisibility of cells. Then the slices were placed on a slide (standard of, 7.5cm X 2.5cm) and

covered by a cover clip after dropping hematoxylin as binder. After the prepared sample is dried, cell visual were obtained by motic microscope at 100X magnification. Motic microscope has camera and computer accessory to capture images. Motic images advanced 3.2 version is used to measure fiber dimensions directly from captured images. For fiber length measurement: longitudinal slices from bottom, middle and top parts of stalk were taken and immersed in a mixture 1:1 v/v of 30%H_2O_2 and glacial acetic acid and heated in water bath at 90^oC for two days[29]. The immersed slices were then shaken by hand and macerated fiber suspension was placed on a slide (standard, 7.5 cm × 2.5 cm) by means of a medicine dropper to measure dimensions using a calibrated electrical motic microscope. Once the visual is obtained images are taken from the microscope by connecting to computer. Motic images advanced 3.2 version was used to measure fiber dimensions. Fiber length measured from longitudinal slices with 40X magnification. Fiber diameter and lumen diameter are viewed with 100X magnification from cross sectional slices in order to increase visual of the cell. Cell wall thickness was calculated according to equation (3.1).

$$cell\ wall\ thicness = \frac{fiber\ diameter - lumen\ diameter}{2} \quad (3.1)$$

At least 20 fibers were measured for each dimension from the fiber suspension to take the average value of each dimension and to keep the error below 5% for a 95% confidence level. Four derived values including slenderness ratio, flexibility coefficient, runkel ratio and wall rigidity were evaluated using fiber dimensions.

$$slenderness\ ratio = \frac{fiber\ length}{fiber\ diameter} \quad (3.2)$$

$$flexibility\ coefficient(\%) = \frac{lumen\ diameter\ of\ fiber}{diameter\ of\ fiber} * 100 \quad (3.3)$$

$$Runkel\ ratio = \frac{2*cell\ wall\ thickness}{lumen\ diameter} \quad (3.4)$$

$$wall\ regidity(\%) = \frac{cell\ wall\ thickness}{fiber\ diameter} * 100 \quad (3.5)$$

The cotton stalk dimensions and derived values then were compared to those of non- woods, woods and cotton stalks from other countries to assay the acceptability of the cotton stalk for pulp and paper production.

3.3.2 Kraft pulping of cotton stalks

3.3.2.1 Raw material preparation

Raw material, cotton stalks from Werer Agricultural Research Center, were collected and cleaned from roots, leaves and soil. Then cut by axes in to an approximate size of 5cm length and dried by air for a week. After that cotton stalks loaded into two sacks each having 30kg weight and transported to Addis Ababa Institute of Technology. 2kg of cotton stalks from the sacks were then taken and cut into an average length of 2cm using hacksaw in Mechanical Engineering laboratory. Then the barks of cotton stalks are easily removed and the thickness of cotton stalks reduced manually by hammer till it had 0.5cm diameter. Now the samples size became ready for pulping (i.e 2cmX0.5cmX0.5cm) and this was weighed to know the amount of cotton stalks required for pulp making. The chipped and debarked cotton stalks were then made free from moisture in an oven at 105^{o}C. The moisture content was also determined by the following formula.

$$Moisture\ content(\%) = \frac{W1-W2}{W2} * 10 \qquad (3.6)$$

Where,

W1 = mass of chipped and debarked cotton stalks before drying

W2 = mass of chipped and debarked cotton stalks after drying

The weight was measured at every 2 hours interval. Weight measuring was continued until constant weight was obtained.

Then the oven dry cotton stalks chips are ready for pulping. 60g of cotton stalks loaded in to 0.5 liter flask with 300ml solution containing cooking chemicals, mixture of sodium hydroxide, sodium sulfide and distilled water. The flask containing sample and cooking chemicals are then inserted in laboratory autoclave and cooked with the required cooking condition.

3.3.2.2 Cooking conditions preparation and settings

1) White liquor preparation

Cooking liquor or white liquor was prepared using different ratios of NaOH, Na_2S and distilled water. Nine (9) different kinds of white liquor were prepared and some of them were repeated based on the response surface methodology central composite design (CCD) of the experiment.

Active alkali (AA) charge: the weight percentage of NaOH and Na_2S to the oven dry cotton stalk basis at 5%, 10%, 15% and 20%.

Sulfidity (S): the weight percentage of Na_2S to active alkali charge at 10%, 20%, 30% and 40%.

Table 3.1: White liquor combination and repetitions for the pulping experiment

	Active alkali (%)	Sulfidity (%)	Repetitions
1	10	20	4
2	20	20	4
3	10	40	4
4	20	40	4
5	5	30	1
6	25	30	1
7	15	10	1
8	15	50	1
9	15	30	10
Total			30

2) Cooking Temperature Settings:

The cooking temperature as one factor was set differently as per our desire temperature in a laboratory autoclave's temperature settings. The temperature setting of the equipment ranges from 20^{o}C to 400^{o}C. But for our Kraft pulping experiment temperature setting was done at five different levels and some of them were repeated. 155^{o}C, 160^{o}C, 165^{o}C and 170^{o}C were set as per the design of experiment [24]. Among these temperatures 160, 165 and 170 degree Celsius temperatures were repeated 8 times, 12 times and 8 times respectively.

3) Cooking time:

The other factor studied in Kraft pulping is the holding time at maximum temperature. Thus after the desired cooking temperature was set in the autoclave, switch is on and temperature increases dramatically to its set point then stop further increasing. Cooking time at maximum temperature started to count at the time when cooking temperature reaches to maximum set point temperature. Then cooking/Kraft pulping continued to the desired cooking time. When the required cooking time reached, the power switched off let to cool for 20 minutes in order to with draw the sample. Therefore, five levels were used for setting cooking time. These are 30minutes, 60minutes, 90minutes, 120 minutes and 150 minutes. From these 60 minutes, 90 minutes and 120minutes were set repeatedly 8 times, 12 times and 8 times respectively.

3.3.2.3 Pulping Experiment procedures

Once the white liquor and cotton stalks are prepared, 500 ml capacity heat resistant glass flask was used as a sample container where Kraft pulping takes place. Inside the flask, the amount of distills water and oven dry cotton stalks was kept constant at 5L to 1kg (i.e 300ml and 60gram) respectively. However, Active alkali and sulfidity was varied as per the design. Then the flask was tied by aluminum foil after chemicals, distilled water and cotton stalks were added to protect loss of white liquor and cotton stalks due to eruption. 300 ml water poured in to an autoclave to generate steam for cooking. Then the prepared flask inserted in to the autoclave and fastened with bolts to protect gas leakage. The desired temperature then set and power switched on. As it can be observed from the experiments the time taken to raise the temperature from room temperature up to maximum temperature was an average of 65 minutes. Then the prepared cotton stalk chips were pulped using Kraft method, by varying the parameters sulfidity, active alkali charges, cooking time and cooking temperature. Liquor to solid ratio kept 5L: 1kg. Pulping was performed in a laboratory autoclave. During cooking, the autoclave was de-gassed for a period of 5 minutes at every 1-hour interval [8]. After each cook, 20 minutes gas down period is allowed before the black liquor ejection. All produced pulps were disintegrated and washed with cold water on a standard size 1mm x 1 mm netted sieve. Then after washed and screened the produced pulp, drying in oven and moisture freed of pulp is followed.

3.3.2.4 Pulp Yield Determination

The objective of this experiment was to produce pulp. And pulp ideally it needs to be pure fiber. That is why we try to remove lignin and extract cellulose. When lignin removed from cotton stalks we got fibers suitable for paper making called pulp. Since cotton stalks are made of many chemical compositions like other woody species, it is unthinkable to get 100% pulp yield. Unfortunately in cotton stalks it is less than 46%, because it contains 46% of cellulose. We expect the loss of pulp yield due to cellulose degradation and fiber loss with rejects. Pulp yield expressed as percentage of the oven dry weight of the chips was determined. The pulp yield was determined by the method as per Tappi standards [22].

$$pulp\ yield\ (\%) = \left(\frac{moisture\ free\ weight\ of\ screened\ pulp\ from\ digester}{moisture\ free\ weight\ of\ cotton\ stalks\ feed\ for\ pulping}\right) * 100 \quad (3.7)$$

3.3.3 Kappa Number Determination

The Kappa number is an indication of the residual lignin content or bleach ability of wood pulp by a standardized analysis method. Therefore, kappa number of pulp is one of the important parameters in pulp manufacturing because it relates to the bleach ability, or degree of delignification, of the pulp. The kappa number is defined as the volume of 0.02 mole/L (0.1normality) potassium permangate solution consumed by one gram of moisture-free pulp in an acidic medium through the following reactions, depending on the acidity of the medium:

$$MnO4^- + 8H^+ + 5e \longrightarrow Mn^{2+} + 4H_2O \quad (3.8a)$$

$$MnO4^- + 4H^+ + 3e \longrightarrow MnO_2 + 2\ H_2O \quad (3.8b)$$

The *kappa number* is the volume (in milliliters) of 0.1*N* potassium permanganate solution consumed by one gram of moisture-free pulp under the conditions specified in (TAPPI T236cm-85) test method. The method calculates the volume of 0.02 mole/L (0.1 N) potassium permanganate consumed by one gram of moisture-free pulp by the difference between the initial and the final excess volumes of potassium permanganate after a 10-minute reaction at 25^{o}C under weakly acidic conditions. The final excess volume of potassium permanganate after the 10-minute oxidation reactions is determined by titrimetric using a standard thiosulfate solution after

adding an excess of potassium iodide to the slurry to react with the excess permanganate to form iodine.

$$k = \frac{p*f}{w} \quad (3.9)$$

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 0.1 N permanganate actually consumed by the test specimen, mL

b = amount of the thiosulfate consumed in the blank determination, mL

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

N = normality of the thiosulfate

However, TAPPI test method has the following short comings and supposed to be obsolete [31].

1) Thiosulfate titration of iodine is tedious because a blank experiment (without pulp, and using exactly the same procedures) is needed to reduce the experimental error in the titration due to the high volatility of iodine.
2) The thiosulfate titration requires that the reaction be kept under weakly acidic conditions, which causes large variations in kappa measurements.
3) The 10-minute oxidation reaction time is arbitrary and can cause errors in determining kappa numbers for various pulps because permanganate can be both oxidized and decomposed by other organic materials in pulp the actual oxidation time is much shorter than 10 minutes.
4) The method requires that the volume of consumed permanganate after the 10-minute reaction should be around 50% of the initial volume to obtain good measurements; this is impossible because the final excess permanganate volume can only be known after the kappa number has been determined
5) The non-constant correction factor is purely empirical, derived through experimental calibration, and can cause errors and
6) Compounds other than lignin in a pulp, such as significant amount of hexenuronic acid in bleached pulps, can be oxidized by permanganate in the first 10-minute reaction.

In order to overcome these short comings, X.S. Chai and J.Y. Zhu [31] developed a spectrophotometric method for the rapid determination of pulp kappa number through direct

measurements of the permanganate concentrations in pulp-permanganate reaction solutions. They proposed the use of strong acidification to prevent the precipitation of MnO_2. As a result, spectral interference from the precipitated MnO_2 was eliminated and reaction (3.8a) then becomes the dominant oxidation reaction. Furthermore, they determined the representative pulp oxidation reaction time and the final excess permanganate concentration in the reacting solution from the measured permanganate absorption spectral intensities. Then they directly determined pulp kappa number using the permanganate absorption data without calibration and corrections. Because of strong acidification, the effect of the amount of excess permanganate or the mass of the pulp sample on measured kappa number was eliminated. As a result, spectroscopic method was used to determine pulp kappa number in this work.

Mathematically pulp kappa number is defined as:

$$K = \frac{P}{w} \tag{3.10}$$

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

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

$$P = a - b = a(1 - \frac{b}{a}) \tag{3.11}$$

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

$$Ao = \varepsilon.l.Co = \varepsilon.l.(\frac{0.1a}{VT}) \tag{3.12}$$

and

$$Ae = \varepsilon.l.Ce = \varepsilon.l.(\frac{0.1b}{VT}) \tag{3.13}$$

where:

VT is the total volume of the reaction solution, which includes the addition of sulfuric acid. $\mathbf{A_0}$ and **Ae** are the permanganate absorbance (or spectral intensity) in the beginning blank solution and at end of the oxidation reactions in the solution, **ε** and **l** are the molar absorptivity of the

solution and the optical path-length of the cell, respectively. From Eqns. (3.10) to (3.13), we can determine the kappa number using the following expression:

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

From equation (3.9) we can conclude that that kappa number can be calculated from the ratio of the permanganate absorption spectral intensities at a given wavelength at the beginning and end of the permanganate-pulp reaction. The percentages of remaining lignin content in the pulp can be estimated as:

$$Lignin\ (\%) \cong Kappa\ number * 0.15 \quad (3.15)$$

Experimental Procedures:

5ml of 0.1N concentration potassium permanganate solution was first measured for its spectral intensity at beginning A_0. Then 20ml of standardized sulfuric acid 2mol/L concentration added to the permanganate solution in order to make strong acidic reaction solution. Then 150mg oven dry of pulp was added to the prepared reaction solution and stirred by magnetic stirrer. After three (3) minutes reaction time filtration was done and the filtrate reaction solution measured for spectral intensity at the end, A_e. Then kappa number was calculated by equation (3.14).

Kappa number is determination of relative hardness, bleach ability or degree of delignification of pulp. It is important parameter of unbleached pulp which is to be bleached. Low Kappa pulps are easier to bleach. High Kappa pulps usually require more energy in refining, but often produce stronger paper or board (particularly with regard to tear strength). A fully bleached pulp can have Kappa number as low as one (1) and very high yield unbleached pulp may have kappa number as high as 100.

Table 3.2: Typical kappa number requirement of some pulps [32]

Pulp	Kappa number
Hardwood Pulp for Bleaching	10 - 20
Softwood Pulp for Bleaching	20 - 30
Wood pulp to be used Unbleached	40 -100

3.3.4 Pulp Hand Sheet Preparation

Dry cotton stalks pulp produced from optimized pulping condition was used for sheet preparation procedures. 400g of oven dry pulp was mixed with 23 liters of water to make pulp slurry with consistency of 1.7%. Pulp slurry was added in to a beating machine and beat up by circulating it. Freeness of slurry was checked out at each ten minutes beating interval. This was done by taking 128ml of slurry from the beater (this contains 2gm of moisture free fiber) and then dilute to 1000ml with distilled water and measured freeness value. When the freeness of pulp is 30CSF, 800ml sample was taken from beater and diluted to 2liters of water (0.62% consistency) and disintegrated at 1500rpm for five minutes. The beated and disintegrated pulp suspension was taken from the disintegrator and diluted to 4liters of water and agitated well by hand. 404ml from the diluted suspension was taken 60gm/m^2 was prepared by sheet forming machine. Ones the sheets are prepared two stage pressing was followed by applying 0.47MPa pressure for four minutes by pressing machine. Then the stocks are removed from the press and attached to the drying plates in order to dry by oven at 130^{o}C for 45 minutes.

The prepared sheets were then tested for the following properties:

Tensile Strength of Pulp:

This is not the tensile strength of individual fiber, which is even higher than or comparable with steel. The tensile strength discussed here is maximum strength of randomly oriented pulp fiber when formed in a sheet. This tensile strength gives an indication of the maximum possible strength of pulp beaten under ideal condition. This again an indication of what level of tensile strength can be achieved in real paper making environment.

Burst strength of Pulp:

It is the capacity of a material (such as a paper or textile) or object (such as a metal pipe) to maintain in continuity when subjected to pressure; broadly**:** the pressure often expressed in pounds per square inch required to rupture such a material or object under rigidly controlled conditions. It is a pressure measured at which a pulp sheet will burst, used as a measure of resistance to rupture. Burst strength depends largely on the tensile strength of extensibility of the material/pulp sheet/.

Tear strength of pulp:

Tear strength is a measure of how well a material can withstand the effects of tearing. More specifically however it is how well a material resists the growth of any cuts when under tension. To measure the tear strength the sample is held between two holders and a uniform pulling forces applied until the aforementioned deformation occurs. Tear resistance is then calculated by dividing the force applied by the thickness of the material. Materials with low tear resistance tend to have poor resistance to abrasion and when damaged will quickly fail.

3.5 Pulping experiment Process flow Diagram

The inputs of the cotton stalk pulping are cotton stalks pulp, sodium hydroxide, sodium sulfide and electrical energy to heat the white liquor and the cotton stalks. The outputs are cotton stalk pulp as the desired product and black liquors and rejects as by product.

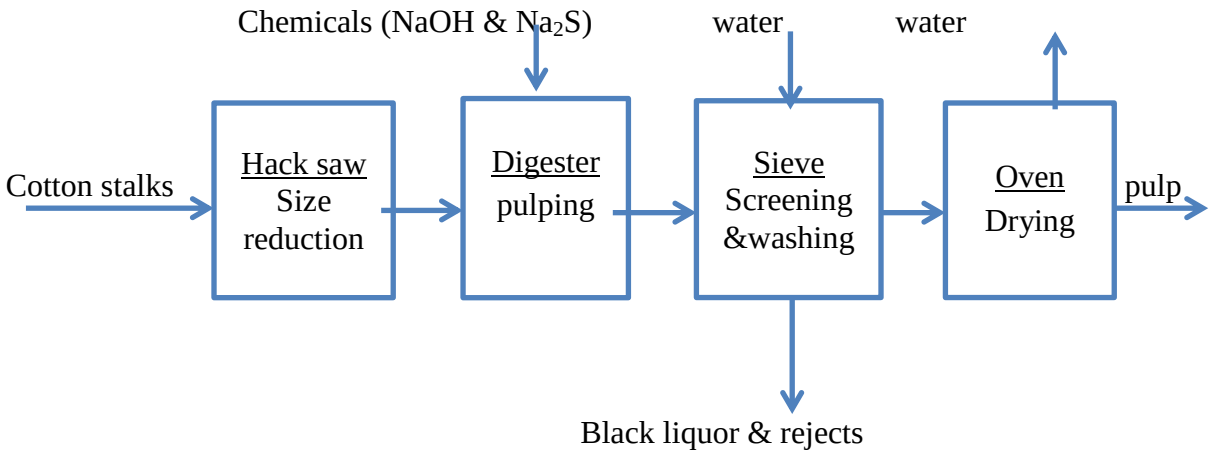


Figure 3.2: Experimental pulping of cotton stalks flow diagram

3.5 Design of Experiments

Data analysis was performed by DESIGN EXPERT software using response surface methodology with central composite design (CCD) method. The response variable is pulp yield expected to be greater than 30% of the feed. For Kraft pulping of cotton stalks there were four factors with two levels for each. Cooking temperature (160^{o}C & 170^{o}C), sulfidity {Na_2S/(NaOH + Na_2S)} (40% & 20%), cooking time at maximum temperature (1 and 2 hours) and Active alkali (NaOH + Na_2S) percentage on od cotton stalk charge 10% and 20% levels [34].This design of the experiment would be helpful to differentiate the significance of the main and the interaction factors.

Table 3.3: Design Experiments factors and levels

Factor	-2	-1	0	+1	+2
Active alkali (%)	5	10	15	20	25
Sulfidty (%)	10	20	30	40	50
Temperature(^{o}c)	155	160	165	170	175
Time (minutes)	30	60	90	120	150

4. RESULTS AND DISCUSSIONS

4.1 Analysis of Cotton Stalk Fiber Morphology

The average measured values of cotton stalks fiber dimension, obtained from the experiment are presented in Table4.1. Derived values were computed by equation (3.2) to (3.5) and the results are presented in Table 4.2. These results were compared to those of some non-wood plants, softwoods and hardwoods.

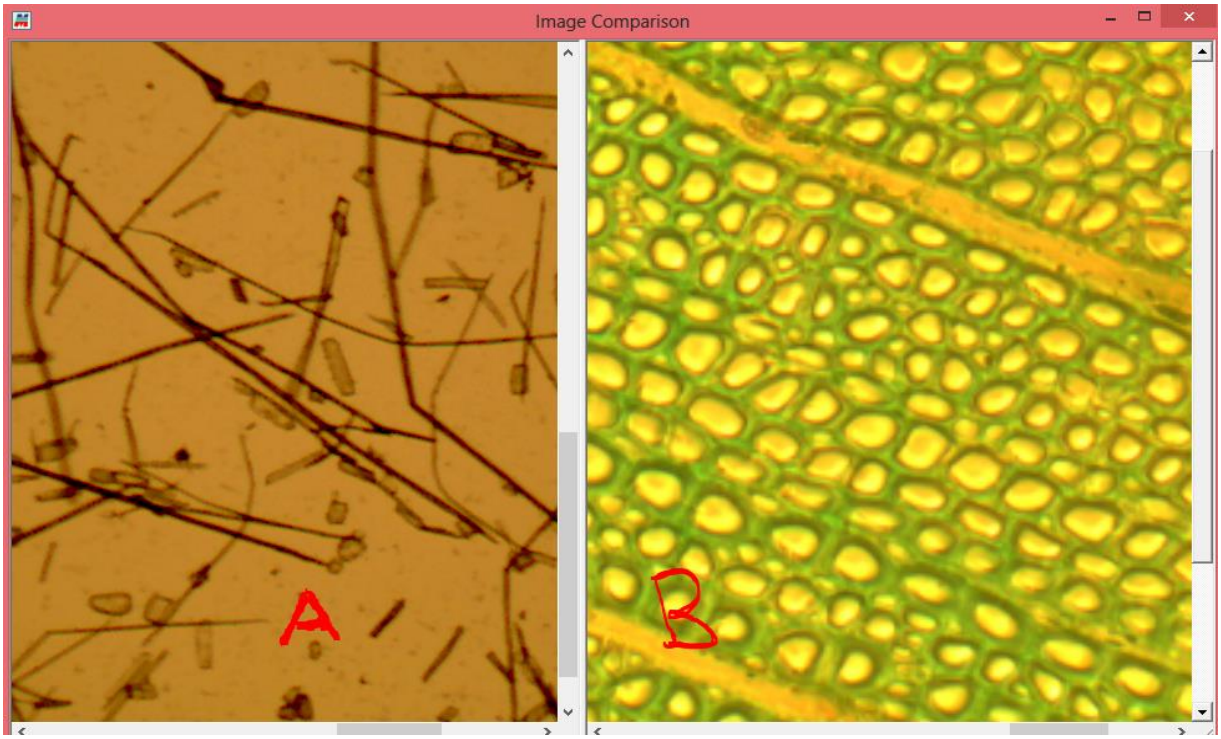
Cotton stalks fibers dimensions and their derived values, falls within the same range as eucalyptus. Now day eucalyptus is a promising source of short fibers. Therefore, the morphological analysis so indicates cotton stalk can be used as a source of fiber like hard woods. Cotton stalks have low slenderness ratio, but still very good flexibility and Runkel ratios, which can yield pulps with acceptable breaking length, tear and burst indices suitable for newsprint paper production.

Table 4.1: Fiber dimensions of cotton stalk

Fiber dimension	**Symbol**	**Average value**
Fiber length (mm)	L	0.83
Fiber diameter(µm)	D	24.38
Cell wall thickness(µm)	CW	4.37
Lumen width	LW	15.65

Table 4.2: Derived values

Derived indices	**Formula**	**Average value**
Slenderness ratio	L/D	34.04
Runkel ratio	2CW/LW	0.54
Flexibility coefficient (%)	LW/D *100	64.20
Wall rigidity (%)	**CW/D *100**	17.92



(A) ⊢—40X magnified (B) ⊢—100X magnified

Figure 4.1: Cotton stalks fiber images obtained from motic microscope; (A) fiber length, (B) fiber diameter, lumen width and cell wall thickness

Table 4.3: Comparison of morphological characteristics of local cotton stalks and other plants

Name of plant	L,mm	D,µm	CW, µm	LW, µm	L/D	2CW/LW	LW/D	2LW/D
Cotton stalk from local ---	0.83	24.38	4.37	15.65	34.04	0.54	0.64	0.17
Cotton stalk from Sudan **	0.79	18.2	3.3	11.6	43.4	0.56	0.63	0.54
Eucalyptus species *	0.6-1.2	13-27	2.3-5.2	5-15	55.18-25.28	0.4-1.64	0.34-0.72	0.28-0.62
Pinus kesiya *	2.3	40.7	5.9	34.8	56.51	0.34	0.85	0.03

* ([30]), ** ([23]), --- (determined)

4.2 Kraft pulping of cotton stalks

4.2.1 Sample Analysis

a) Mass loss during Size reduction and debarking

In order to prepare raw materials for pulping, size reduction and debarking was conducted on cotton stalks and the following mass loss was observed.

Table 4.4: Cotton stalk mass loss during size reduction and debarking

Run	Cotton stalks mass before size reduction and debarking (kg)	Cotton stalks mass before size reduction and debarking (kg)	Mass loss (kg)
1	2	1.56	0.44
2	2	1.62	0.38
3	2	1.58	0.42

As it can be seen from the above table, the average mass loss is 0.42kg from 2 kg of cotton stalks. Therefore, (0.42/2)*100 = 21% of mass loss was obtained during size reduction and debarking of cotton stalks.

b) Moisture content determination of cotton stalks

The cotton stalks were collected in December, 2014, after two months the moisture content of cotton stalks was determined using equation 3.1 and the results are presented in table 4.5. Drying time required to get constant weight was 8 hours.

Table 4.5: Moisture Content of Cotton Stalks

Run	Mass before drying(kg)	2hrs drying	4hrs drying	6hrs drying	Mass after 8hrs drying(kg)	Moisture content (%)
1	1	0.9562	0.9423	0.9355	0.9354	6.9
2	1	0.9558	0.9418	0.9328	0.9328	7.2
3	1	0.9554	0.9412	0.9336	0.9337	7.1
4	1	0.9560	0.9420	0.9321	0.9319	7.3
5	0.70	0.6830	0.6680	0.6519	0.6517	7.4

From this tabulated data it can be calculated that the average moisture content of cotton stalks, 7.18%.

4.2.2 Cotton stalk pulp yield

Percent yield of cotton stalk pulp was calculated by equation (3.7). The results are presented in table 4.6.

Figure 4.2: Cotton stalk pulps dried by oven

Table 4.6: Percent yield of cotton stalks pulp

		Factors				
Run n.o	Code	Active alkali (%)	Sulfiditiy (%)	Maxi- Pulping temp. (^{o}C)	Time @ max-temp. (minute)	Yield (%)
1	-1,-1,-1,-1	10	40	160	60	38.5
2	1,-1,-1,-1	20	40	160	60	40.2
3	-1, 1,-1,-1	10	20	170	60	36.2
4	1, 1,-1,-1	20	20	170	60	40.2
5	-1,-1, 1,-1	10	40	170	60	38.7
6	1,-1, 1,-1	20	40	170	60	37.2
7	-1, 1, 1,-1	10	20	170	60	37.9
8	1, 1, 1,-1	20	20	170	120	38.6
9	-1,-1,-1, 1	10	40	160	120	38.5
10	-1,-1,-1, 1	20	40	160	120	39.5
11	-1, 1,-1, 1	10	20	160	120	37.2
12	-1, 1,-1, 1	20	20	160	120	40.5
13	-1,-1, 1, 1	10	40	170	120	38.3
14	1,-1, 1, 1	20	40	170	120	36
15	-1, 1, 1, 1	10	30	170	120	38.3
16	1, 1, 1, 1	20	30	170	120	38.3
17	-2, 0, 0, 0	5	10	165	90	34.6
18	2, 0, 0, 0	25	50	165	90	36.5
19	0,-2, 0, 0	15	30	165	90	37.8
20	0, 2, 0, 0	15	30	165	90	38
21	0, 2, 0, 0	15	30	155	90	41.6
22	0, 0, 2, 0	15	30	175	90	39.7
23	0 ,0, 0,-2	15	30	165	30	39.6
24	0 ,0, 0, 2	15	30	165	150	39.5
25	0, 0, 0, 0	15	40	165	90	39.7
26	0, 0, 0, 0	15	40	165	90	39.7

27	0, 0, 0, 0	15	30	165	90	39.6
28	0, 0, 0, 0	15	30	165	90	39.5
29	0, 0, 0, 0	15	30	165	90	39.7
30	0, 0, 0, 0	15	30	165	90	39.7

The maximum pulp yield obtained was 41.6% at the cooking conditions of 15% and 30% of active alkali and sulfidity respectively and at 155^{o}C temperature and 90 minutes of holding time. The minimum pulp yield 34.6% was found at 5% active alkali charge and 10% sulfidity cooked at 165^{o}c for 90 minutes.

Effects of Active alkali charge on pulp yield

Percent yield of cotton stalks pulp is affected by active alkali charge, sulfidity, temperature, and holding time at maximum temperature. Active alkali charge plays a great role on the percentage yield of cotton stalk pulp. Figure 4.3 shows that the pulp yield increases as the active alkali charge increases from 5% to 15% of oven dry cotton stalks. But unfortunately pulp yield decreases as active alkali charges increases above 15%.

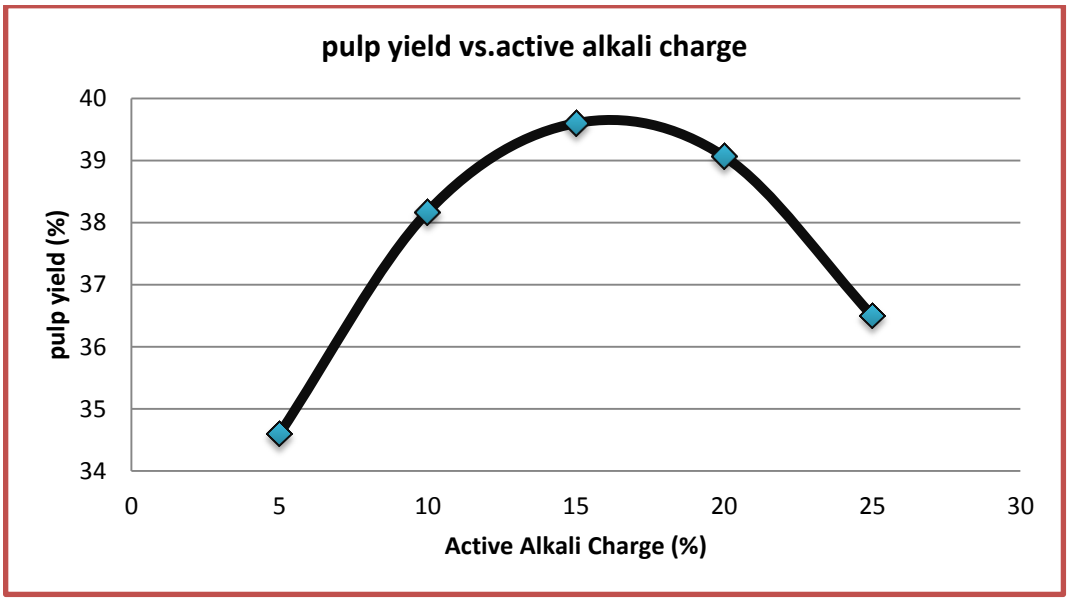


Figure 4.3: Effects of active alkali charge on pulp yield of cotton stalks

Even though Active alkali charge (NaOH + Na_2S), concentrations of chemical in white liquor, had a positive effect on delignification, it had negative impact on pulp yield when charged at higher concentrations. Higher Active Alkali concentration accelerates the delignification rate and in contrast degrades cellulose which is the main content of pulp.

Effects of sulfidity on pulp yield

In Kraft pulping, sodium sulfide (Na_2S) acts as a catalyst and interference of other side reactions. As it can be seen from figure 4.3, increasing sulfidity from 10% to 30% increases pulp yield from 37.8% to 39.1%. However, increments of sulfidity from 30% to 50%, decreases the pulp yield from 39.1% to 38%. Off course active alkali, temperature and time was kept at their central points.

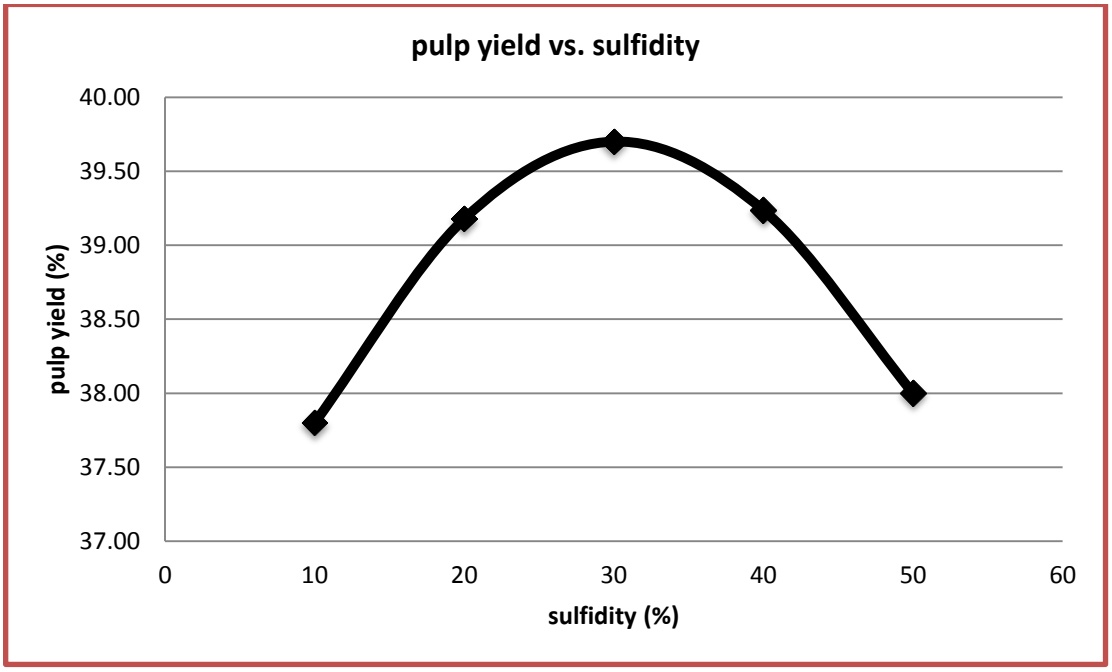


Figure 4.3: Effects of sulfidity on pulp yield of cotton stalks

This is because at lower concentrations of sodium sulfide, the speed of the reaction will slower and it takes longer time to extract lignin from the wood. The other reason is that at lower concentrations of sodium sulfide there is a chance for side reactions to occur. On the other hand at higher percentage of sulfidity, Kraft pulping will completed in shorter time and farther cooking will damage the product then yield reduced.

Effects of temperature on pulp yield

As it can be observed from figure 4.4, temperature has a negative effect on pulp yield of cotton stalks. When temperature increases from 155^{o}C to 175^{o}C by keeping other three factors at their central point's pulp yield of cotton stalks decreases from 41.6% to 39.27%. Temperature has a significant impact on both the diffusion rate and reaction rate of kraft cooking chemicals. As the temperature in the early portion of the cook increases, significantly more alkali is consumed by chemical reaction at the expense of chemical diffusion in to fiber. As the rate of alkali consuming reactions is highest at the beginning of the cook, increased temperatures in the impregnation stage will significantly reduce the amount of alkali available for diffusion. In addition when wood is heated, changes in cellulose, hemicellulose, lignin and extractives can modify its hygroscopic, stability, diffusibility or permeability. Higher temperature cooking of cotton stalks damages pulp yield. This is because rate of delignification is much higher at higher temperature as compared to lower temperature and at higher temperature we get lower yield because higher temperature also affects and damages the fiber which contributes in decreasing the yield. Higher temperature also affects the lignin condensation because at higher temperature, chemical penetration takes place rapidly which also reduces the yield.

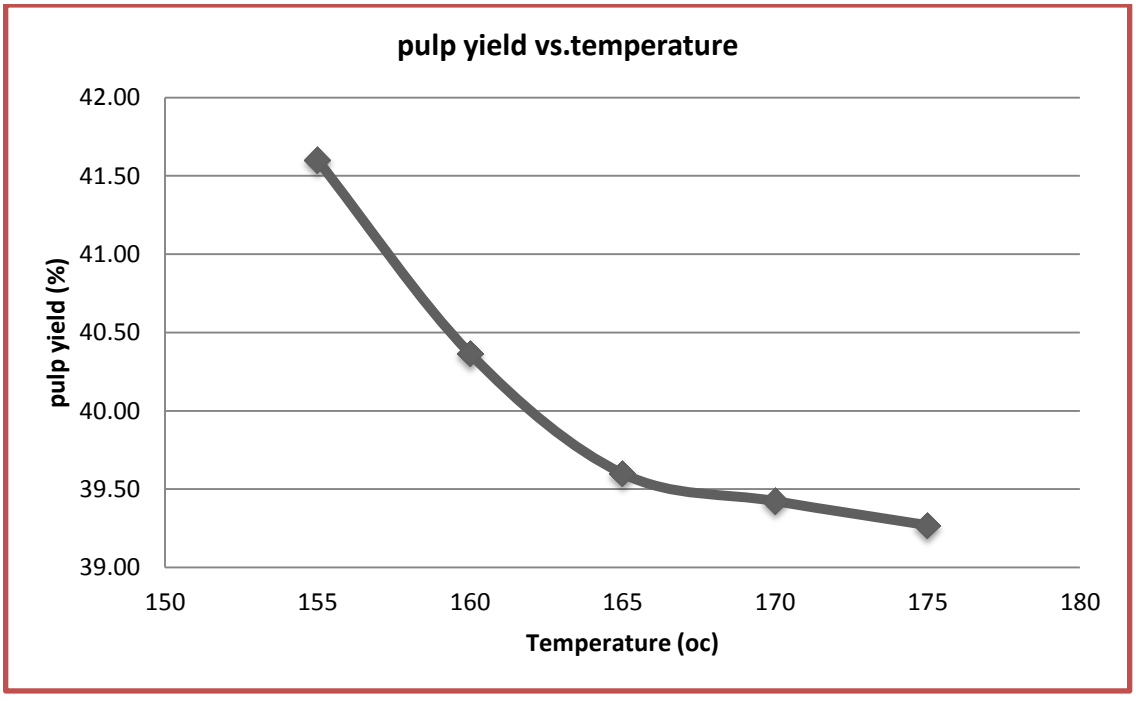


Figure 4.4: Effects of temperature on pulp yield of cotton stalks

Effects of cooking time on pulp yield

Figure 4.5 shows the effect of cooking time on pulp yield of cotton stalks was not much incredible as other three factors. Rather cooking time has less effect on pulp yield. Increasing cooking time from 30 mints to 60 minutes increases pulp yield by 0.076%. But further cooking the cotton stalk was downs the pulp yields again even though it is not significant figure.

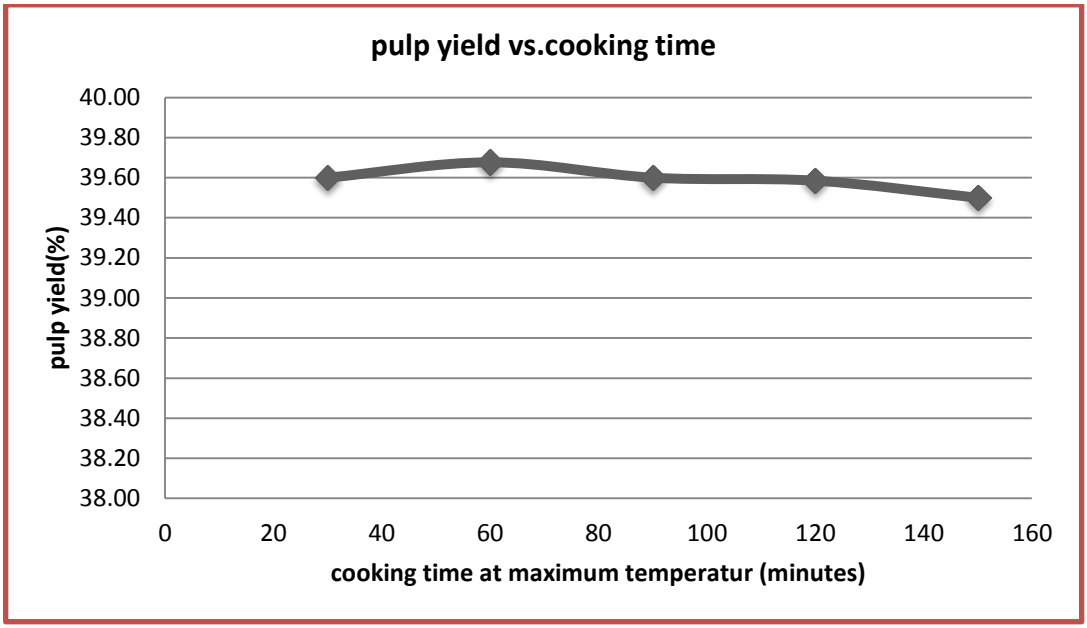


Figure 4.5: Effects of cooking time at maximum temperature on pulp yield of cotton stalks

Analysis of pulp yield using Design Expert9 software

So far the effects of active alkali, sulfidity, temperature and cooking time on quantity of pulp yield of cotton stalks has been discussed. Then here, the resulted data is going to be analyzed to determine the significant factors of the experimental work by using DESIGN-EXPERT 9 software. Pulp yield obtained from laboratory experiments result was an input to the software.

Table 4.7: Analysis of variance (ANOVA) for the response pulp yield of cotton stalks

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	
Model	66.72	14	4.77	1033.60	< 0.0001	Significant
A-Active Alkali	4.77	1	4.77	1034.55	< 0.0001	
B-Sulfidity	0.020	1	0.020	4.43	0.0526	
C-temperature	5.32	1	5.32	1153.83	< 0.0001	
D-Time	0.050	1	0.050	10.93	0.0048	
AB	5.18	1	5.18	1122.42	< 0.0001	
AC	10.73	1	10.73	2326.04	< 0.0001	
AD	0.53	1	0.53	113.99	< 0.0001	
BC	1.89	1	1.89	410.02	< 0.0001	
BD	0.86	1	0.86	185.56	< 0.0001	
CD	0.28	1	0.28	59.77	< 0.0001	
A^2	29.11	1	29.11	6313.17	< 0.0001	
B^2	5.38	1	5.38	1165.82	< 0.0001	
C^2	1.64	1	1.64	356.44	< 0.0001	
D^2	0.025	1	0.025	5.43	0.0342	
Residual	0.069	15	4.611E-003			
Lack of Fit	0.034	10	3.417E-003	0.49	0.8435	not significant
Pure Error	0.035	5	7.000E-003			
Cor Total	66.79	29				

The Model F-value of 1033.60 implies the model is significant. There is only a 0.01% chance that an 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, C, D, AB, AC, AD, BC, BD, CD, A^2, B^2, C^2,

D^2 are significant model terms. Values greater than 0.1000 indicate the model terms are not significant. From this it is possible to conclude that, there is an interaction effect, the only insignificant factor is sulfidity. And the rest of three factors and there interactions with sulfidity are dominating factors. The "Lack of Fit F-value" of 0.49 implies the Lack of Fit is not significant relative to the pure error. There is an 84.35% chance that a "Lack of Fit F-value" this large could occur due to noise. Non-significant lack of fit is good because the model need to be fit.

Table 4.8: R^2 from ANOVA analysis of design expert 9

Std. Dev.	0.068		R-Squared	0.9990
Mean	38.64		Adj R-Squared	0.9980
C.V. %	0.18		Pred R-Squared	0.9963
PRESS	0.25		Adeq Precision	144.396

The "Pred R-Squared" of 0.9963 is in reasonable agreement with the "Adj R-Squared" of 0.9980; i.e. the difference is less than 0.2. "Adeq Precision" measures the signal to noise ratio. A ratio greater than 4 is desirable. The ratio of 144.396 indicates an adequate signal. This model can be used to navigate the design space.

For cotton stalks pulp yield:

Final model equation in terms of Coded Factors:

$$Yield = +39.65 + 0.45A + 0.029B - 0.47C - 0.046D + 0.57AB - 0.82AC - 0.18AD + 0.34BC + 0.23BD - 0.13CD - 1.03A^2 - 0.44B^2 + 0.24C^2 - 0.03D^2 \quad (4.1)$$

Where, A = Active alkali charge,

B = Sulfidity

C = Temperature

D = Time

Final model equation in terms of Actual Factors:

Yield (%) = +252.5+6.49667*Active alkali -1.10583 * Sulfidity -2.96167* temperature
+0.14389 * Time+0.011375 * Active Alkali * Sulfidity -0.03275* Active Alkali
*temperature -1.20833E-003 *Active Alkali * Time +6.87500E-003*
Sulfidity * temperature +7.70833E-004 * Sulfidity * Time -8.75000E-004*
temperature * Time -0.041208*Active Alkali^2 -4.42708E-003 * Sulfidity^2
+9.79167E-003 * temperature^2 - 3.35648E-005* Time^2 (4.2)

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

Model Adequacy Check

The model was tested for adequacy by analysis of variance. The regression model was found to be highly significant with the correlation coefficients of determination of R-Squared, adjusted R-Squared and predicted R-Squared having a value of 0.9999, 0.9980 and 0.9963 respectively.

Table 4.9 and figure 4.6 shows the relation between the actual value of the experiment and the value predicted by the model equation developed by the DESIGN EXPERT9 software.

The quality of the model developed could be evaluated from their coefficients of correlation. The value of R-squared for the developed correlation is 0.9990. It implies that 99.90% of the total variation in the pulp yield is attributed to the experimental variables studied. The results in table 4.9 and figure (4.6) demonstrated that the regression model equation provided a very accurate description of the experimental data, in which all the points are very close to the line of perfect fit. This result indicates that it was successful in capturing the correlation between the four Kraft pulping process variables to the percent pulp yield. Figure 4.6 is the guarantee for the validation of the model equation. The figure shows how the data generated from developed model equation is close to the actual data obtained.

Table 4.9: Difference between the actual (experimental) value and predicted value

Run order	Actual Value	Predicted Value	Residual	Standard Order
1	34.60	34.64	-0.038	17
2	39.60	39.62	-0.021	23
3	36.20	36.22	-0.017	3
4	37.90	37.86	0.037	7
5	39.70	39.65	0.050	26
6	38.30	38.33	-0.033	15
7	39.50	39.55	-0.046	10
8	36.50	36.42	0.079	18
9	38.00	37.94	0.062	20
10	37.80	37.82	-0.021	19
11	39.70	39.65	0.050	30
12	38.70	38.72	-0.017	5
13	40.20	40.25	-0.046	4
14	39.60	39.65	-0.050	27
15	40.20	40.20	0.000	2
16	37.20	37.21	-0.013	11
17	40.50	40.52	-0.017	12
18	39.50	39.44	0.062	24
19	38.30	38.26	0.037	13
20	39.70	39.65	0.050	29
21	38.60	38.62	-0.017	8
22	37.20	37.20	4.167E-003	6
23	41.60	41.57	0.029	21
24	39.50	39.65	-0.15	28
25	38.50	38.45	0.054	1
26	36.00	36.02	-0.017	14
27	38.30	38.36	-0.063	16

28	38.50	38.52	-0.017	9
29	39.70	39.69	0.012	22
30	39.70	39.65	0.050	25

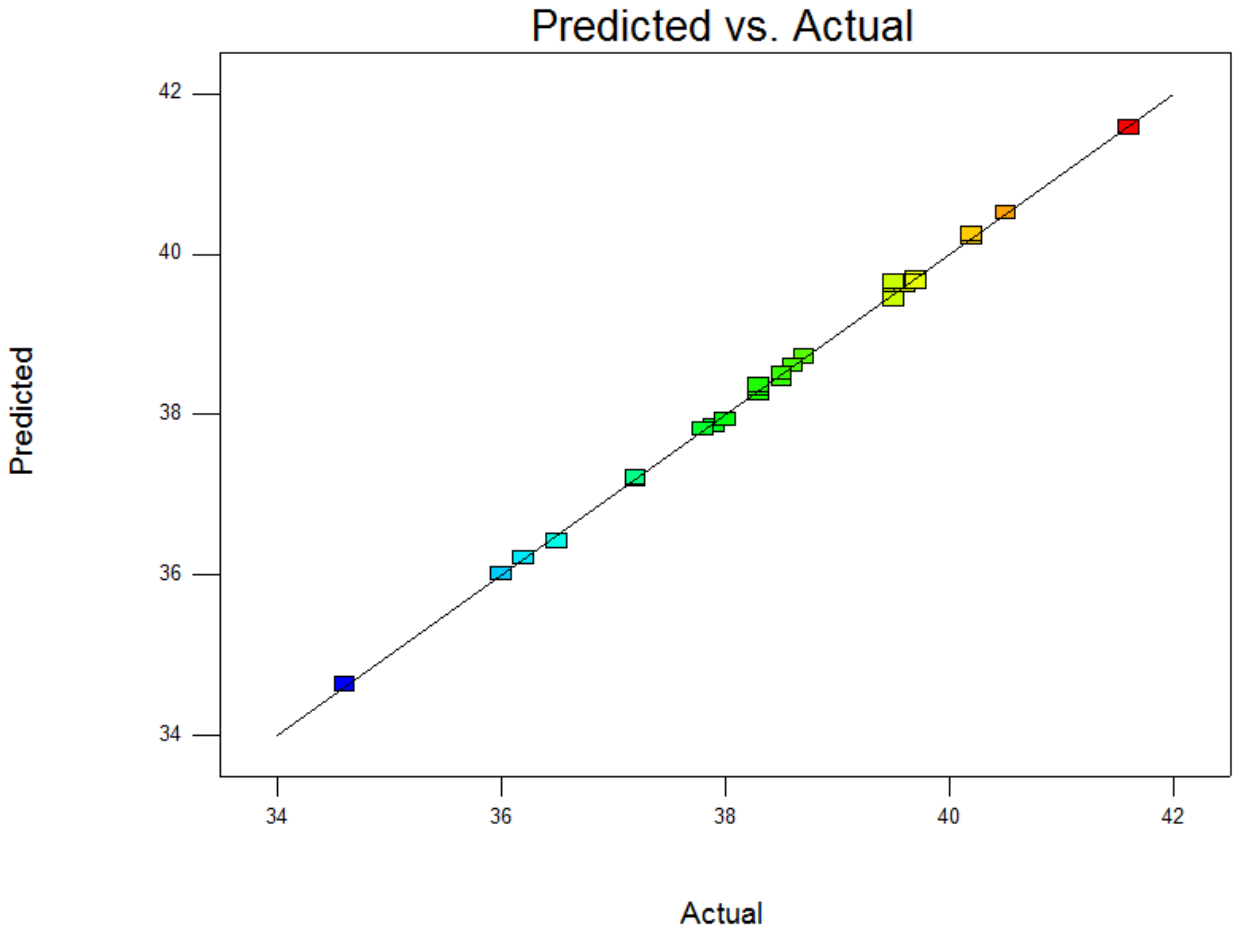


Figure 4.6: predicted Vs actual experimental value for pulp yield of cotton stalks

Interaction Effects

An interaction occurs when the response is different depending on the settings of two factors. Plots make it easy to interpret two factor interactions. They will appear with two non-parallel lines, indicating that the effect of one factor depends on the level of the other. The default "I beam" range symbols on the interaction plots are the result of least significant difference (LSD) calculations. If the plotted points fall outside the range, the differences are unlikely to be caused

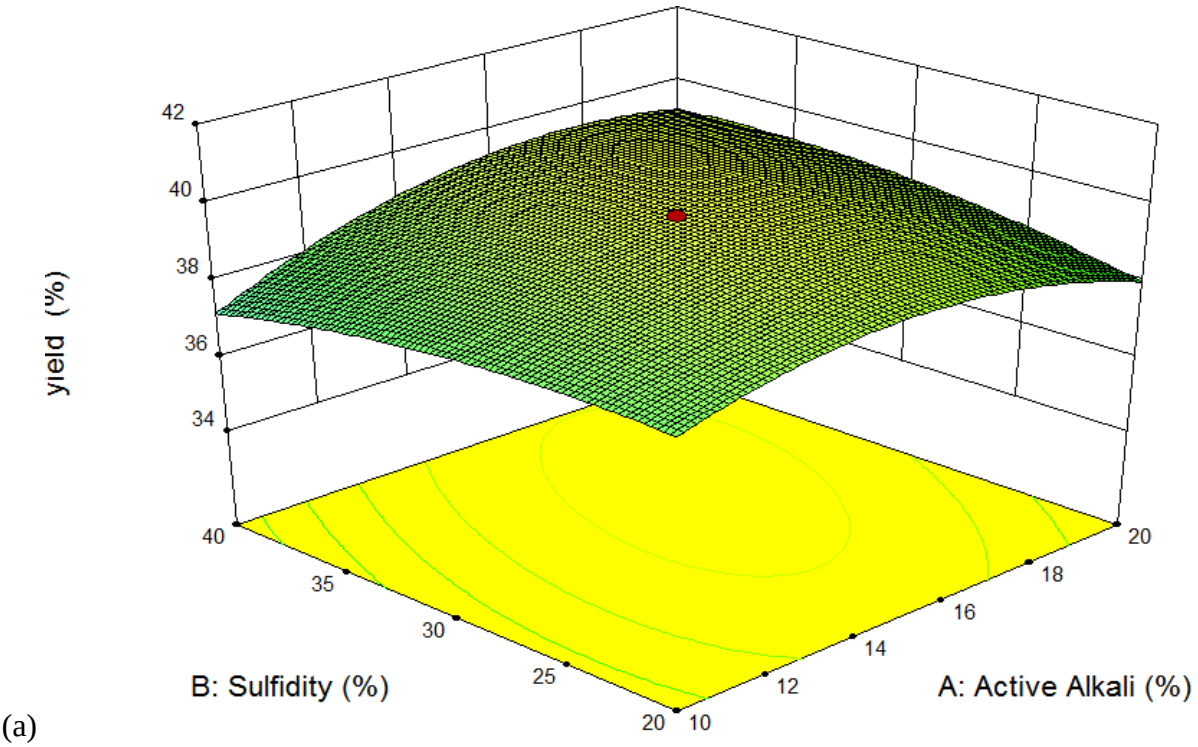
by error alone and can be attributed to the factor effects. If the 'I beams' overlap there is no significant difference (95% confidence is default) between the two points. We can then choose the most economical or convenient level for that factor. As it can be seen from equation (4.1) the interaction factor effects on pulp yield of cotton stalks can be understood easily by the coefficients of interaction factors. There are six interaction factors analyzed by the model equation. These are:

- AB - Active alkali and sulfidity
- AC - Active alkali and Temperature
- AD- Active alkali and Time
- BC - Sulfidity and Temperature
- BD - Sulfidity and Time
- CD - Temperature and Time

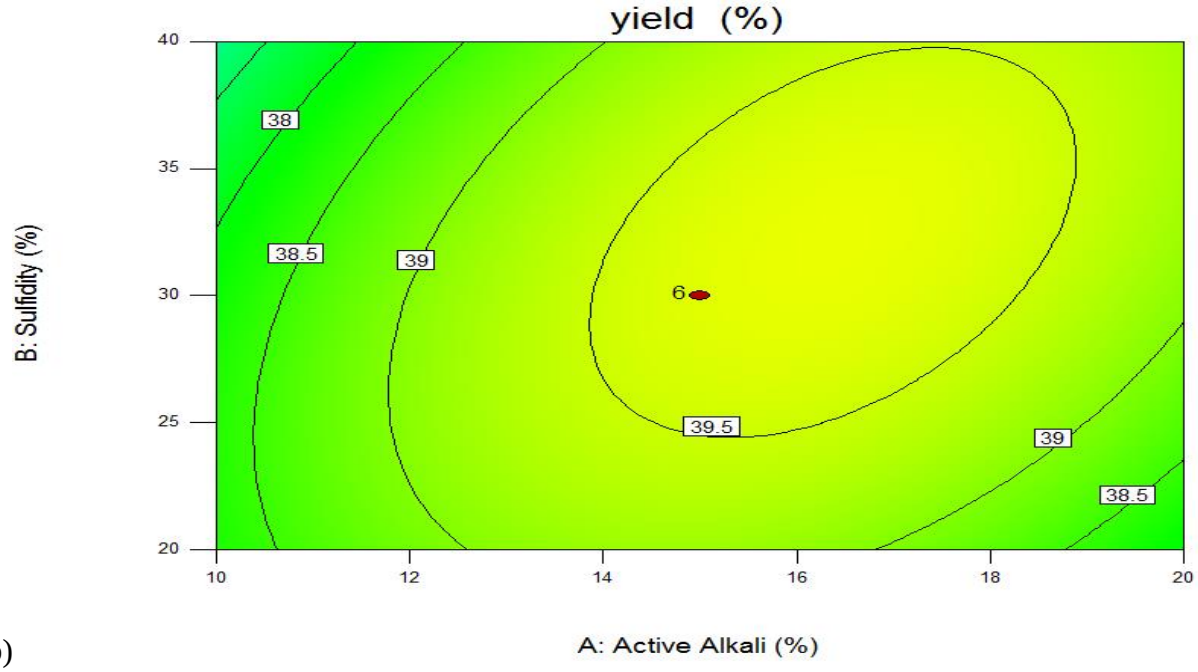
Among these six interaction factors interaction of active alkali and cooking temperature (AC) is the most significant interaction factor for pulp yield as a response, because it is the highest coefficient (0.82) of the rest. The sign of the coefficient of the interaction factor indicates the effect of interaction factor on pulp yield. Therefore, the interaction factors with positive signs have positive effect on pulp yield (as interaction factor increases pulp yield increases). Whereas, interaction factors with negative signs have a negative effect on pulp yield (pulp yield decreases as interaction factor increases). The 3D response surface and contour plots of the effect of interaction of active alkali, sulfidity, temperature and time with the response of pulp yield are discussed below.

Effects of Active Alkali and Sulfidity on pulp yield

The effect of active alkali and sulfidity on pulp yield is shown in the form of 3D plot and contour plots in Figure 4.7. As it can be observed from figure with rising active alkali and sulfidity the pulp yield was increased but it declined when the active alkali and sulfidity increased. The maximum yield was found at the moderate concentrations of both active alkali and sulfidity. This is due to a higher concentration of active alkali is capable to extract more lignin and when sulfidity is more it accelerates lignin more and starts to degrade cellulose.



(a)

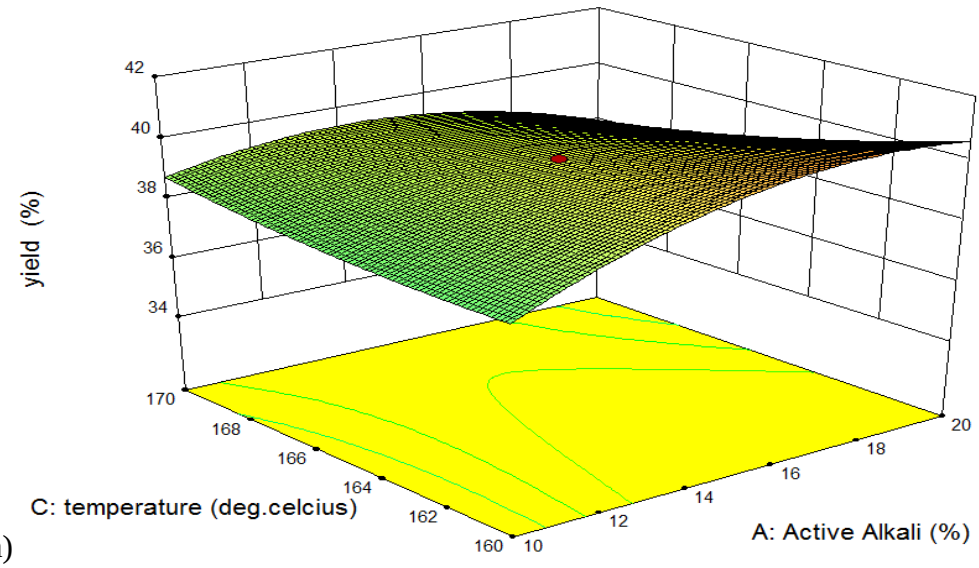


(b)

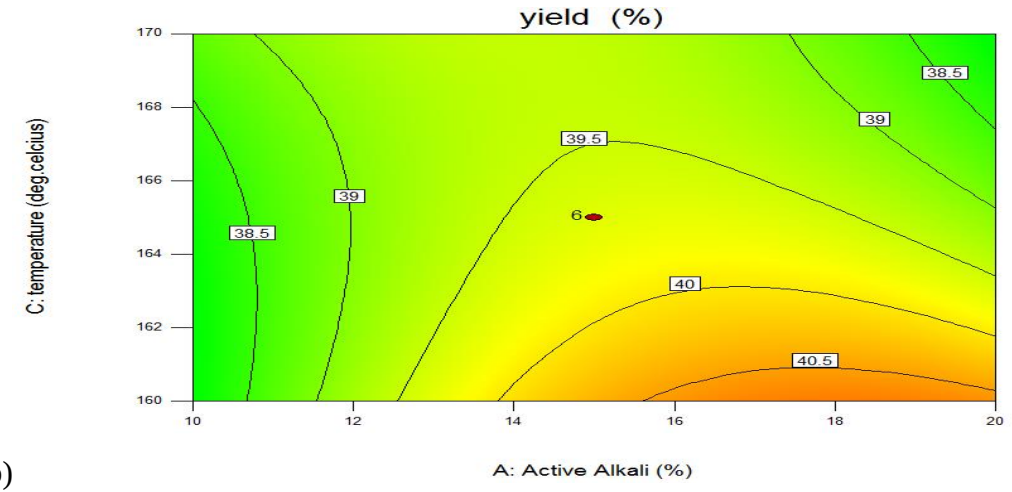
Figure 4.7: 3D plot (a) and contour plot (b) showing the interaction effect of Active alkali and sulfidity versus pulp yield at 165^{o}C pulping temperature and 90 minutes cooking time.

Effects of Active alkali and temperature on pulp yield:

From figure 4.8, it is shown that both active alkali and temperature have strong effect on pulp yield. At higher active alkali concentration and lower temperature pulping conditions there is higher yield. However, further increasing active alkali charge at lower temperatures does not increase pulp yield. On the other hand higher temperature pulping condition decreases pulp yield. In order to get maximum pulp yield the operating temperature and active alkali charge should be set at 160^{o}C and 15% respectively.



(a)

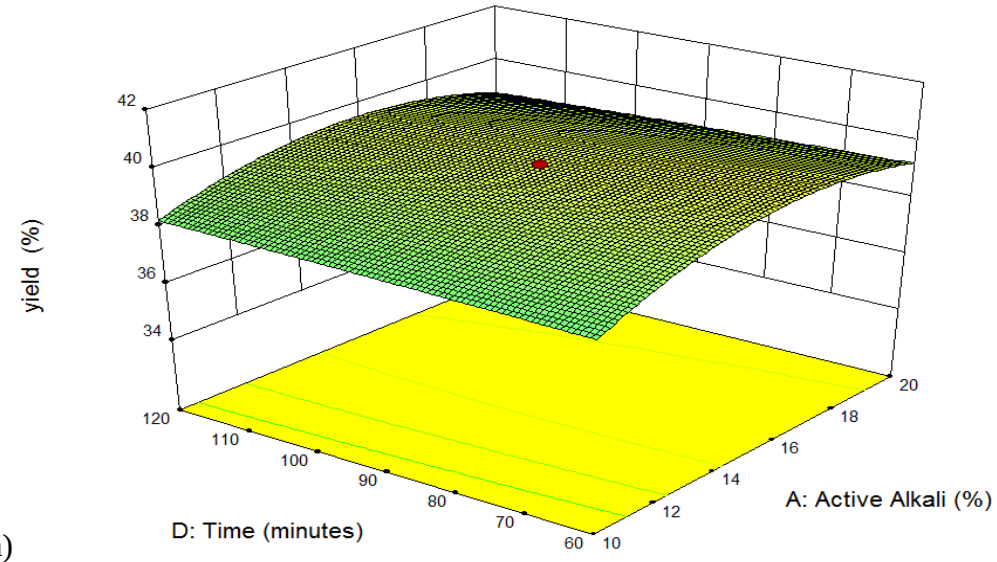


(b)

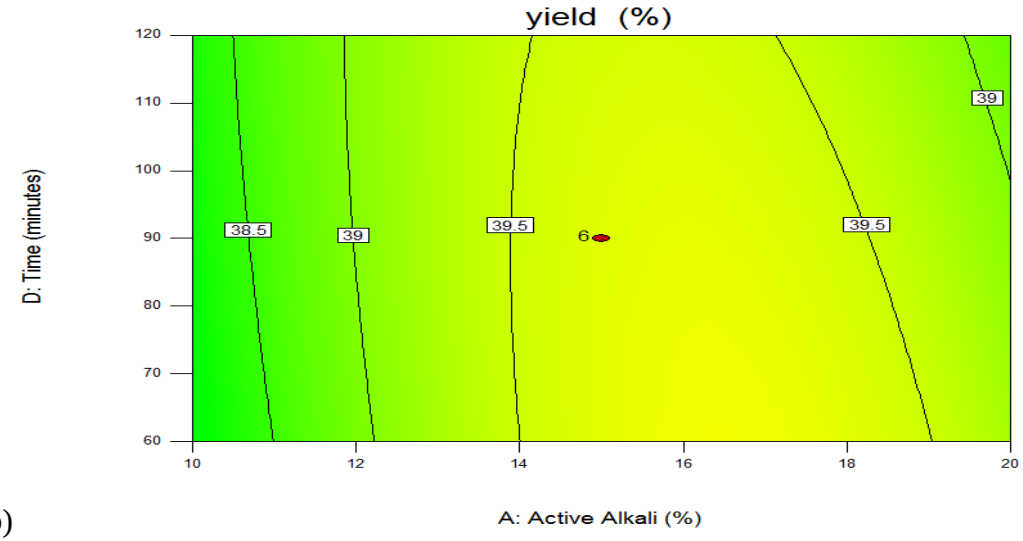
1Figure 4.8: 3D plot (a) and contour plot (b) showing the interaction effect of Active alkali and temperature versus pulp yield at 30% sulfidity and 90 minutes cooking time

Effects of active alkali and cooking time on pulp yield:

Cooking cotton stalks with high concentrations active alkali the kraft process completed in short time and further cooking decreases pulp yield. As it can be seen in figure 4.9, the maximum pulp yield obtained was at moderate concentrations of active alkali and cooking time has no more effect on pulp yield. For these two interaction effects the maximum pulp yield obtained at moderate alkali concentrations and lower cooking time.



(a)



(b)

Figure 4.9: 3D plot (a) and contour plot (b) showing the interaction effect of Active alkali and time versus pulp yield at 30% sulfidity and 165^{o}C cooking temperature

Effect of sulfidity and temperature on pulp yield:

Higher temperature affects pulp yield negatively. Sulfidity accelerates delilignification rate and when it is high concentration pulp yield decreases. This may be due to lignin condensation. Figure 4.10 shows that the maximum pulp yield for temperature and sulfidity is found at moderate sulfidity concentrations and low temperature pulping conditions.

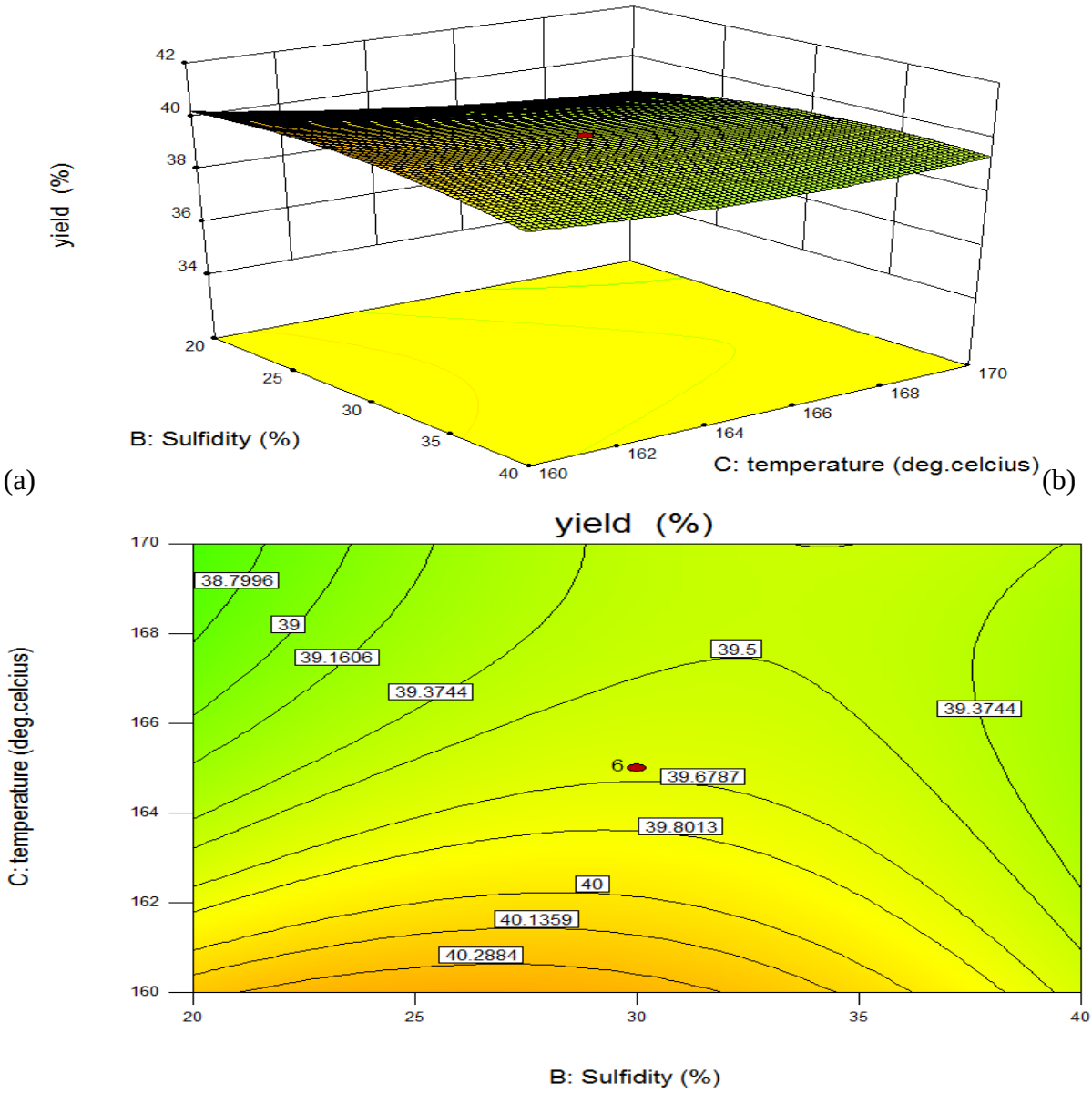
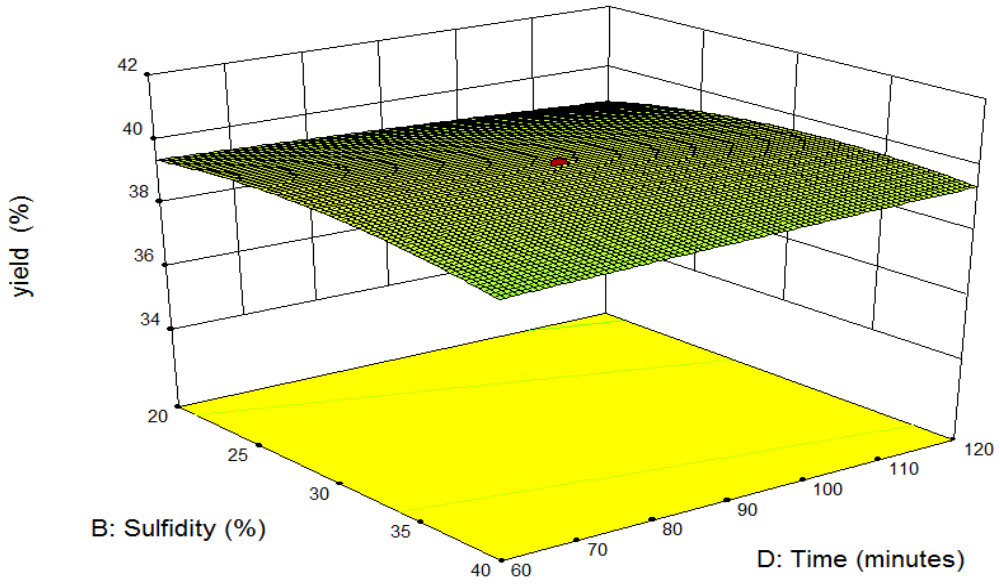


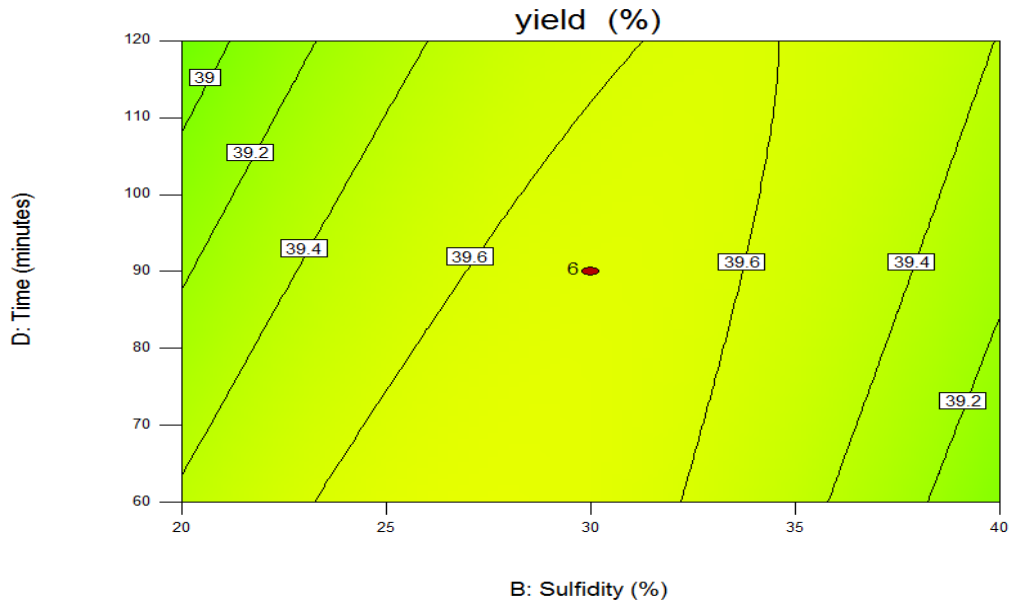
Figure 4.10: 3D plot (a) and contour plot (b) showing the interaction effect of sulfidity and temperature versus pulp yield at 15% active alkali and 90 minutes cooking time

Effects of sulfidity and time on pulp yield:

As it can be observed from Figure 4.11, moderate sulfidity concentration and lower cooking time is the pulping condition that results in maximum pulp yield. Low and high concentrations of sulfidity and high cooking time decreases pulp yield.



(a)

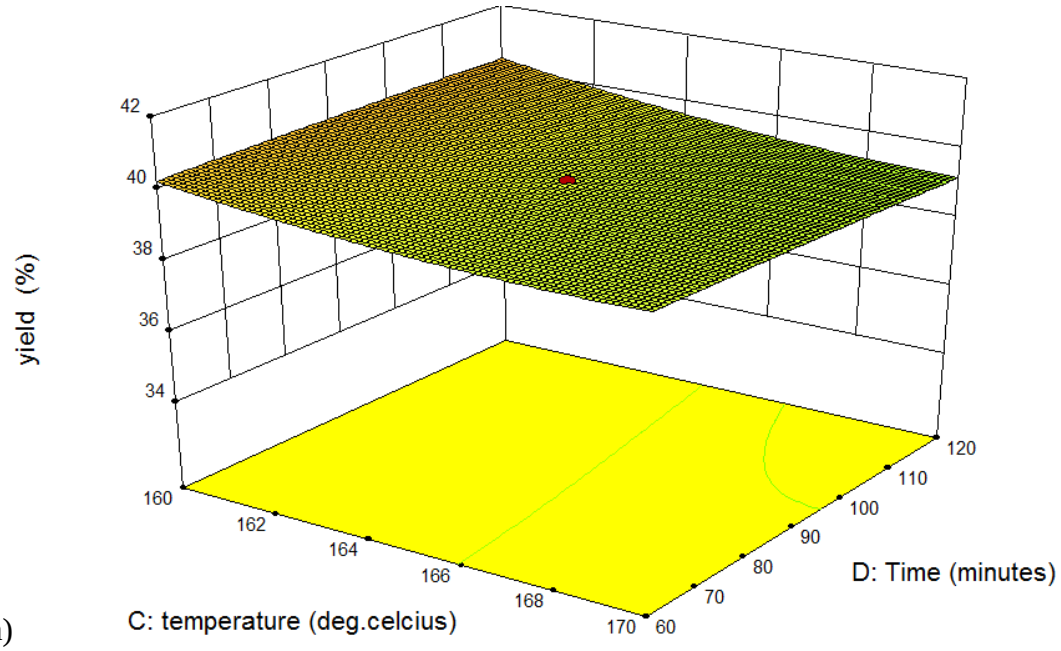


(b)

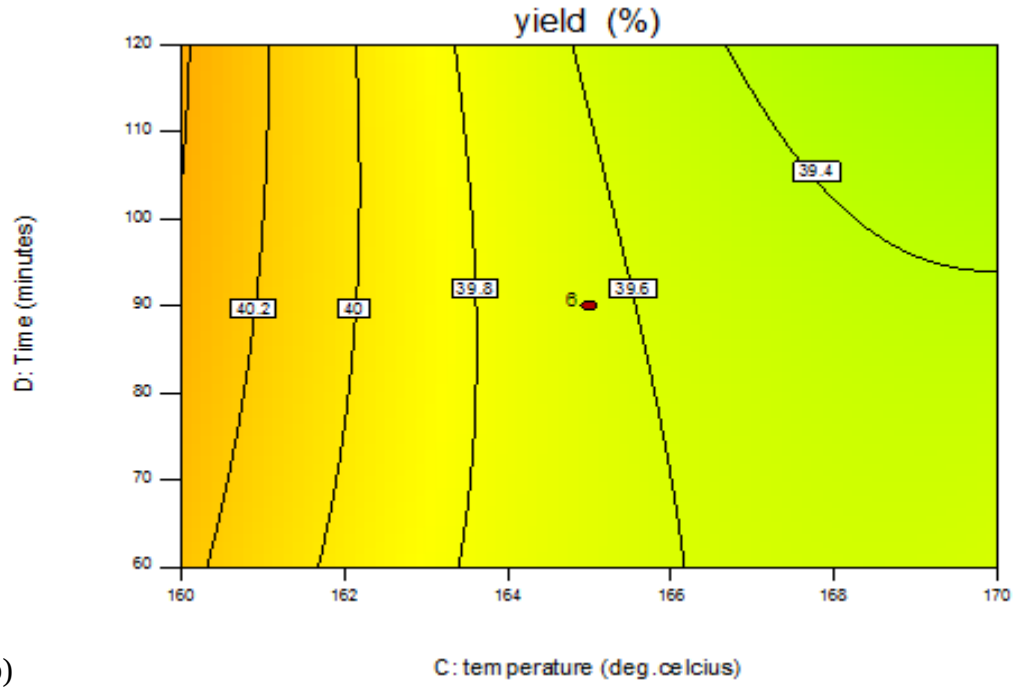
Figure 4.11: 3D plot (a) and contour plot (b) showing the interaction effect of sulfidity and time versus pulp yield at 15% active alkali and 165^{o}C cooking temperature

Effects of temperature and time on pulp yield:

When cooking temperature and cooking time increased total yield had decreased because high temperature and more cooking time helps the cooking liquor to dissolve more lignin and hemicellulose. Therefore low total yield was obtained because better penetration and higher rate of delignification was obtained. Pulp yield also depends on the degradation of carbohydrates and these carbohydrates are degraded by peeling, chain cleavage and the dissolution of short chain carbohydrates. During cooking hemicelluloses which mainly consist of glucomannan and xylan are degraded. Both are degraded at specific conditions and reduce the pulp yield. As shown in the figure 4.12, lower temperatures gives high yield as compared to high temperature. When temperature increases from 160ºC to 170^{o}C pulp yield decreases from 40.2 % to 39.4%. At higher temperature, degradation of both hemicelluloses and celluloses occur which results in reducing the total yield.



(a)



(b)

Figure 4.12: 3D plot (a) and contour plot (b) showing the interaction effect of temperature and time versus pulp yield at 15% active alkali and 30% sulfidity.

4.2.2 Kappa number determination

Table 4.10: Kappa number and pulp yield

		Factors					
Run no.	Code	Active alkali (%)	Sulfiditiy (%)	Max. Pulping temperature (^{o}c)	Time @ max- temp. (minute)	Yield (%)	Kappa n.o
1	-1,-1,-1,-1	10	40	160	60	38.5	33.9
2	1,-1,-1,-1	20	40	160	60	40.2	14.7
3	-1, 1,-1,-1	10	20	170	60	36.2	31.6
4	1, 1,-1,-1	20	20	170	60	40.2	14
5	-1,-1, 1,-1	10	40	170	60	38.7	20.6
6	1,-1, 1,-1	20	40	170	60	37.2	8
7	-1, 1, 1,-1	10	20	170	60	37.9	19.8
8	1, 1, 1,-1	20	20	170	120	38.6	8.6
9	-1,-1,-1, 1	10	40	160	120	38.5	27.9
10	-1,-1,-1, 1	20	40	160	120	39.5	10
11	-1, 1,-1, 1	10	20	160	120	37.2	28.6
12	-1, 1,-1, 1	20	20	160	120	40.5	12.4
13	-1,-1, 1, 1	10	40	170	120	38.3	16.4
14	1,-1, 1, 1	20	40	170	120	36	5.5
15	-1, 1, 1, 1	10	30	170	120	38.3	18.9
16	1, 1, 1, 1	20	30	170	120	38.3	9.2
17	-2, 0, 0, 0	5	10	165	90	34.6	39.6
18	2, 0, 0, 0	25	50	165	90	36.5	10.7
19	0,-2, 0, 0	15	30	165	90	37.8	12.8
20	0, 2, 0, 0	15	30	165	90	38	14.3
21	0, 2, 0, 0	15	30	155	90	41.6	25
22	0, 0, 2, 0	15	30	175	90	39.7	8.6
23	0 ,0, 0,-2	15	30	165	30	39.6	17.3
24	0 ,0, 0, 2	15	30	165	150	39.5	11.8

25	0, 0, 0, 0	15	40	165	90	39.7	15.1
26	0, 0, 0, 0	15	40	165	90	39.7	15.2
27	0, 0, 0, 0	15	30	165	90	39.6	15.0
28	0, 0, 0, 0	15	30	165	90	39.5	15.2
29	0, 0, 0, 0	15	30	165	90	39.7	15.1
30	0, 0, 0, 0	15	30	165	90	39.7	15.1

Kappa number which is an indication of quality of pulp produced was determined by equation (3.14) and the obtained results are reported in the above table 4.10.

Analysis using Design Expert

The effects of four factors on the kappa number of pulp yield were analyzed by the design expert software. The ANOVA table directs to study the main effects of active alkali, sulfidity, temperature and cooking time on the kappa number of cotton stalks pulp and the significance of their interactions.

The Model F-value of 21960.75 implies the model is significant. There is only a 0.01% chance that an 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, D, AB, AC, AD, BC, BD, CD, A^2, B^2, C^2, D^2 are significant model terms. Values greater than 0.1000 indicate the model terms are not significant. The "Lack of Fit F-value" of 1.19 implies the Lack of Fit is not significant relative to the pure error. There is a 44.89% chance that a "Lack of Fit F-value" this large could occur due to noise. Non-significant lack of fit is good because the model need to be fit.

Table 4.11: Analysis of Variance (ANOVA) for responses of kappa number on the main effects and their interactions

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	
Model	1964.27	14	140.30	21960.75	< 0.0001	significant
A-Active Alkali	1248.48	1	1248.48	1.954E+005	< 0.0001	
B-Sulfidity	3.45	1	3.45	540.07	< 0.0001	
C-temperature	407.55	1	407.55	63790.50	< 0.0001	
D-Time	46.20	1	46.20	7231.89	< 0.0001	
AB	2.18	1	2.18	340.53	< 0.0001	
AC	43.89	1	43.89	6869.84	< 0.0001	
AD	2.18	1	2.18	340.53	< 0.0001	
BC	2.18	1	2.18	340.53	< 0.0001	
BD	9.77	1	9.77	1528.53	< 0.0001	
CD	4.31	1	4.31	673.92	< 0.0001	
A^2	172.43	1	172.43	26989.05	< 0.0001	
B^2	4.23	1	4.23	662.09	< 0.0001	
C^2	4.83	1	4.83	756.56	< 0.0001	
D^2	0.56	1	0.56	87.43	< 0.0001	
Residual	0.096	15	6.389E-003			
Lack of Fit	0.067	10	6.750E-003	1.19	0.4489	not significant
Pure Error	0.028	5	5.667E-003			
Cor Total	1964.36	29				

Table 4.12: R^2 for kappa number of cotton stalk pulp

Std. Dev.	0.080		R-Squared	1.0000
Mean	17.03		Adj R-Squared	0.9999
C.V. %	0.47		Pred R-Squared	0.9998
PRESS	0.43		Adeq Precision	603.996

The "Pred R-Squared" of 0.9998 is in reasonable agreement with the "Adj R-Squared" of 0.9999; i.e. the difference is less than 0.2. "Adeq Precision" measures the signal to noise ratio. A ratio greater than 4 is desirable. 603.996 indicate an adequate signal. This model can be used to navigate the design space.

The final model Equation for kappa number in terms of coded factor:

$$Kappa\ number = +15.12 - 7.21A + 0.38B - 4.12C - 1.39D + 0.37AB + 1.66AC + 0.37AD + 0.37BC + 0.78BD + 0.52CD + 2.51A^2 - 0.39B^2 + 0.42C^2 - 0.14D^2 \quad (4.3)$$

The final model equation for kappa number in terms of Actual Factor:

kappa number =+916.16667-15.82500* Active Alkali -1.28833* Sulfidity -7.89167*

temperature-0.70333* Time+7.37500E-003* Active Alkali * Sulfidity

+0.066250* Active Alkali * temperature+2.45833E-003*

Active Alkali * Time +7.37500E-003* Sulfidity * temperature+2.60417E-003

* Sulfidity * Time+3.45833E-003* temperature * Time+0.10029

* Active Alkali^2-3.92708E-003* Sulfidity^2+0.016792* temperature^2

-1.58565E-004* Time^2 (4.4)

Model equations of both Coded and actual factors can be used to make predictions about the response kappa number for given levels of each factor. The coded model equation is useful for identifying the relative impact of the factors by comparing the factor coefficients. Whereas,

equation in terms of actual factors should not be used to determine the relative impact of each factor because the coefficients are scaled to accommodate the units of each factor and the intercept is not at the center of the design space.

Model adequacy check

The model was tested for adequacy by analysis of variance. The regression model was found to be highly significant with the correlation coefficients of determination of R-Squared, adjusted and predicted R-Squared having a value of 1.0, 0.9999 and 0.9998 respectively. The quality of the model developed could be evaluated from their coefficients of correlation. The value of R-squared for the developed correlation is 1.0. It implies that 100% of the total variation in the kappa number is attributed to the experimental variables studied. The graph of the predicted values obtained using the developed correlation versus actual values is shown in Figure (4.8). The results in Figure (4.8) demonstrated that the regression model equation provided a very accurate description of the experimental data, in which all the points are very close to the line of perfect fit. This result indicates that it was successful in capturing the correlation between the four kraft pulping reaction process variables to the kappa number. The adequacy of the model was further checked with analysis of variance (ANOVA) as shown in Table (4.11).The equation in terms of coded factors can be used to make predictions about the response of kappa number for given levels of each factor. The coded equation is useful for identifying the relative impact of the factors by comparing the factor coefficients. The following graph shows the relation between the actual value of the experiment and the value predicted by the model equation developed by the DESIGN EXPERT software.

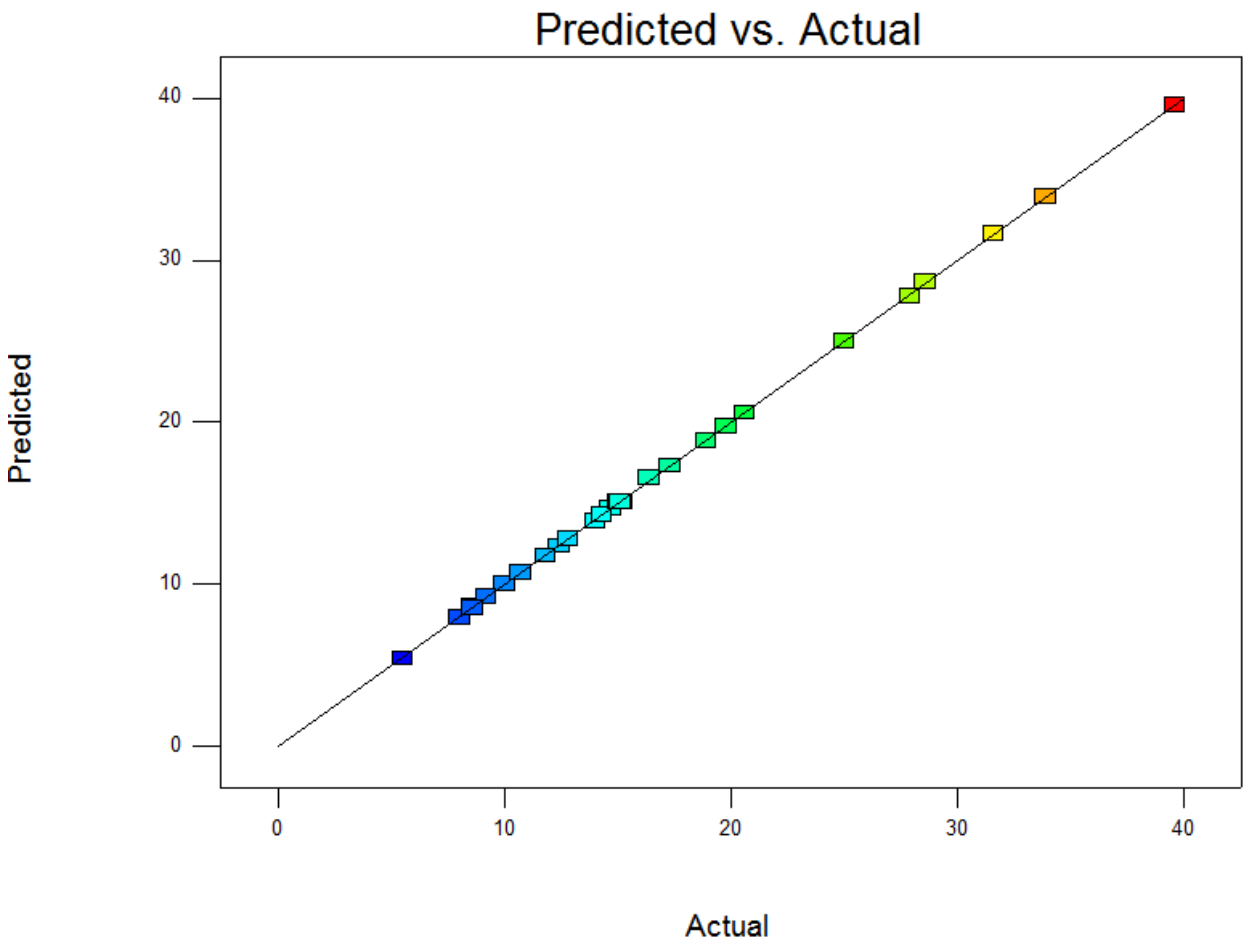


Figure 4.13: Predicted vs actual experimental value for kappa number of cotton stalks pulp

Effects of process variables on kappa number:

The cooking temperature and active alkali charge are two effective parameters that influence the pulp properties more. From the delignification in Kraft pulping, sulfide and hydrosulfide ions facilitate the reaction of lignin removal and sulfur works mainly as a catalyst which is not consumed or transformed much. As it can be seen from Figure 4.9a, c and d; it has been found that the efficiency of lignin removal increases with increasing active alkali, temperature and time. Thus an increase in one of the process variables (Active alkali, temperature and time), by keeping constant the rest of the other three process variables including sulfidity, resulted in a clear reduction in kappa number.

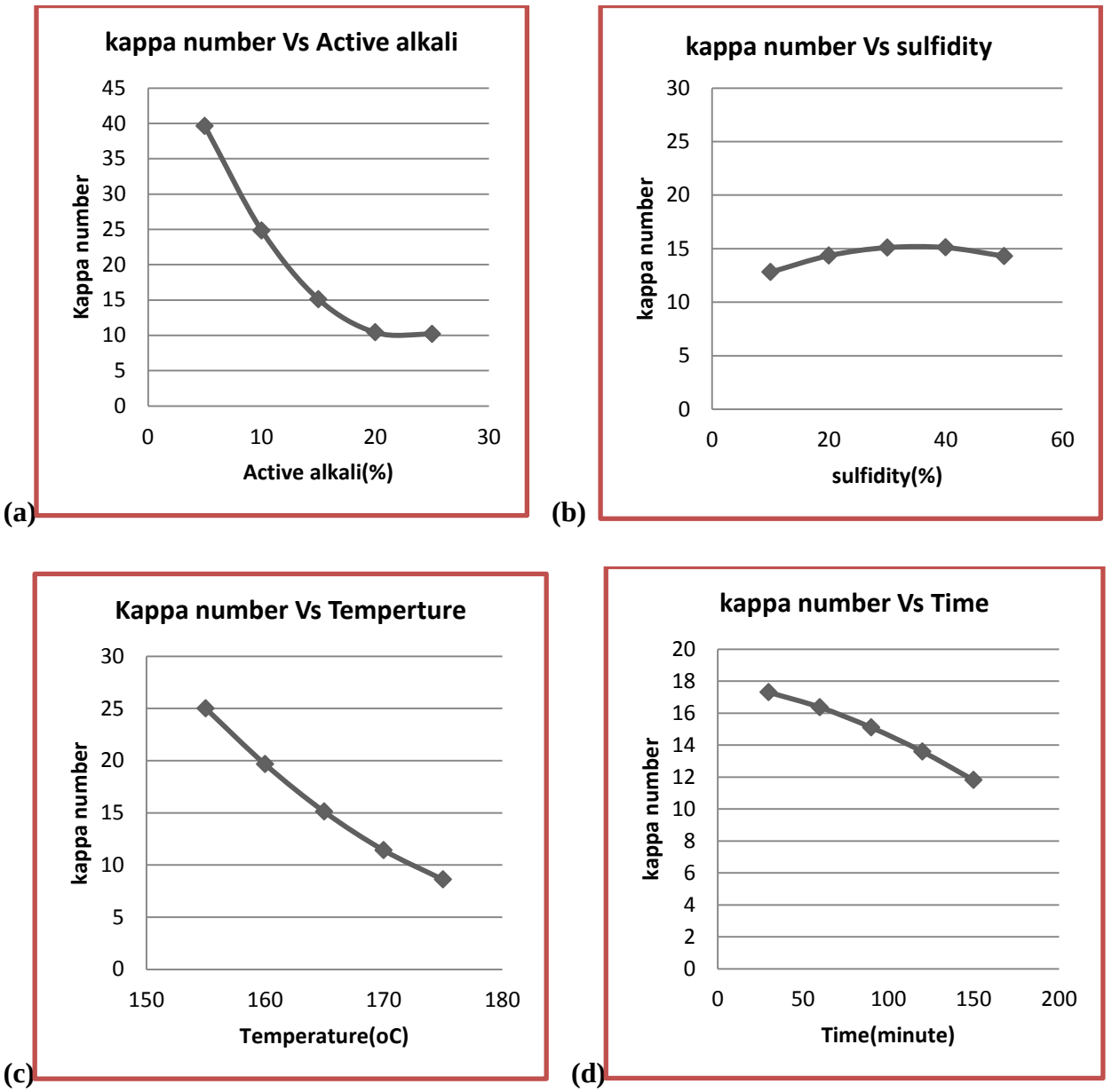


Figure 4.14: The effects of the four pulping variables on kappa number; (a) active alkali, (b) sulfidity, (c) temperature and (d) time

Optimal Kraft pulping condition

To optimize the Kraft pulping condition, it is important to compromise the yield and kappa number of cotton stalks pulp. Pulping condition having high pulp yield and low kappa number is preferable. The main concern need to be considered is the cost of the process. The cost of the Kraft process should be minimal and the pulp yield needs to be high. As it has been discussed in chapter three for hard woods pulp the kappa number should be between 10 and 20 for bleachable grade pulp. From fiber dimension analysis it was observed that cotton stalks have similar characteristics as those of hard woods. Since kappa number is an indication of remaining lignin content of pulp, pulp having high kappa number contains high lignin content. In order to use pulp as raw material of paper the remaining lignin has to be removed by bleaching process. Bleaching of pulp having kappa number greater than 20 is costly and is not recommended. Pulp having kappa numbers less than 10 is also not recommend because it is assumed that fibers will be damaged and result in papers having less strength. Therefore, the desired kappa number is between 10 and 20 for this process. From the conducted experiments (table4.10), those full- fill the kappa number requirement are only 18 runs and are presented in the table below. From these runs the maximum pulp yield obtained after bleaching is calculated by subtracting the lignin content from the yield obtained in laboratory work. Lignin content is calculated by equation (3.15).

Table 4.13: Experimental runs having bleachable grade pulp

		Factor 1	**Factor 2**	**Factor 3**	**Factor 4**	**Response 1**	**Respons 2**	**Response 3**
Std	Run	A:Active Alkali	B:Sulfidity	C:temperature	D:Time	Yield	kappa number	maximum yield after bleaching
		%	%	ºC	min	%	-	%
2	**6**	**20**	**20**	**160**	**60**	**40.2**	**14.7**	**37.995**
4	29	20	40	160	60	40.2	14	38.100
7	10	10	40	170	60	37.9	19.8	34.930
10	27	20	20	160	120	39.5	10	38.000
12	13	20	40	160	120	40.5	13.0	38.550
13	16	10	20	170	120	38.3	16.4	35.840
15	18	10	40	170	120	38.3	18.9	35.465
18	19	25	30	165	90	36.5	10.7	34.895
19	5	15	10	165	90	37.8	12.8	35.880
20	7	15	50	165	90	38	14.3	35.855
23	23	15	30	165	30	39.6	17.3	37.005
24	9	15	30	165	150	39.5	11.8	37.730
25	26	15	30	165	90	39.7	15.1	37.435
26	14	15	30	165	90	39.7	15.2	37.420
27	15	15	30	165	90	39.6	15	37.350
28	8	15	30	165	90	39.5	15.2	37.220
29	2	15	30	165	90	39.7	15.1	37.435
30	17	15	30	165	90	39.7	15.1	37.435

Now, from these remaining runs that has minimum chemical and energy consumption, short time of cooking and high pulp yield after bleaching are selected. The best maximum yield expected after bleaching is 38.55% from run 13 but it consumes large amount of active alkali and sodium sulfide and longer time of cooking. The second best yield 38.1% could be obtained from run 29

but this run uses the same amount of chemical used as run 13. And run 10 that would result 38% yield after bleaching takes longer time. Hence run 6 is the best run that have optimal yield of 37.995% with optimal chemical and energy consumption with short cooking time. Kraft pulping of cotton stalks for bleachable grade pulp is best operated at the condition of 20% active alkali, 20% sulfidity, 160^{o}C and 60 minutes.

Optimization by response surface modeling:

Optimization of pulp yield was carried out by a multiple response method called desirability (D) function to optimize different combinations of process parameters. As indicated on the previous discussion obtaining maximum pulp yield does not mean that giving maximum economic benefit. Based on this ground the optimization was done based on economic benefit.

The goal of optimization was to maximize economic benefit or increasing pulp yield by minimizing process cost. To achieve maximum economic benefit, active alkali, sulfidity, temperature and time were set minimum levels, whereas pulp yield and kappa number were set to maximum levels and in ranges respectively. Based on desirability analysis 30 optimum points via numerical optimization generated (appendix D).

The desirability lies between 0 and 1 and it represents the closeness of a response to its ideal value. If a response falls within the unacceptable intervals, the desirability is 0, and if a response falls within the ideal intervals or the response reaches its ideal value, the desirability is 1. Meanwhile, when a response falls within the tolerance intervals but not the ideal interval, or when it fails to reach its ideal value, the desirability lies between 0 and 1. The more closely the response approaches the ideal intervals or ideal values, the closer the desirability is to 1. Based on the above analysis best local maximum for pulp yield 39.79% with corresponding kappa number 15.6 was found at active alkali 16.65%, sulfidity 20%, temperature 163^{o}C and 60 minutes cooking time and the value of desirability obtained was 0.649.

The model validations have been determined as optimum levels of the process parameters to achieve the pulp yield 39.79%. In order to verify this prediction experiments were conducted and the result showed 40.12% pulp yield was obtained with Kraft pulping (Table 4.14).

Table 4.14: Model validation

Active alkali	Sulfidity	Temperature	Time	Pulp yield		Kappa number	
16.65%	20%	163^{o}C	60 min	Predicted	Experimental	Predicted	Experimental
				39.79%	40.12%	15.6	15.3

Therefore, the numerical optimization can be taken as optimal value because the predicted value is close enough with actual value. The lignin free pulp is estimated by equation (3.15) and for optimal value it is 37.54% yield.

Pulp hand sheet physical tests

After optimization of the cooking condition of Kraft pulping, hand sheets were prepared from the pulp produced at optimized pulping condition as per the method presented in section 3.3. The obtained results are presented in the following table and compared with eucalyptus species used for paper making.

Table 4.15: physical property of cotton stalks pulp at optimized pulp

	Values	
Physical property	Cotton stalk average	Eucalyptus *
Burst index (kpa.m^2/g)	5.5	0.9-10.2
Tensile index (N*m/g)	63	35-120
Tear index (mN*m^2 /g)	8	3.6-12

(* [33])

As it can be seen from the results presented in the above table, it is possible to produce pulp from cotton stalks having acceptable burst, tensile and tear indexes. Hardwood pulps like eucalyptus pulp are used in printing and writing papers contributing to improved printability, sheet bulk, opacity and surface smoothness. Their applications usually comprise fine papers, printing papers and art papers. The physical properties of paper sheets made from cellulosic fibers are

dependent on fiber morphology. The result obtained from morphology of cotton stalks showed that cotton stalks has fiber morphology similar to eucalyptus which is, the most raw material of hard wood pulp. And the results obtained from the physical property of cotton stalks pulp hand sheet lied in the same value range of that of eucalyptus pulp. Therefore, the cotton stalks pulp can be used as eucalyptus pulp like printing and writing papers.

Figure 4.15: cotton stalk pulp hand sheets tested for physical strength indices

5. CONCLUSION AND RECOMMENDATION

5.1 Conclusions

The main objective of this work was to develop a process for the production of pulp from cotton stalks. By present work on the fiber properties, pulping optimization and hand sheet properties. It could be concluded that: (1) from the morphological analysis it was found that cotton stalks have similar fiber dimensions with hard woods. The morphology of cotton stalks cotton stalks fiber have short length, would yield low paper strength. It has narrow diameter and wall thickness but has good derived morphology and due to this the paper produced could collapse easily. (2) For optimization of kraft pulping of cotton stalks it was taken in to consideration high pulp yield, low chemical and energy consumption and short time of cooking. In addition to these chemicals with lower sulfur content is preferable. This method tends to partially prevent water and air pollution and thus, pulp production is more environmentally suitable. Therefore, the chosen experimental combination for Kraft pulping of cotton stalks is at cooking condition of 16.65% Active Alkali, 20% Sulfidity, 163^{o}C and 60 minutes. At this pulping condition we got pulp yield 37.54% which is close to the pulp yield 38.55% found by expense of costs for chemicals and energy used, environmental protection and longtime of cooking. Active Alkali and temperature has great effect on pulp yield. Temperature has negative effect and that of active alkali has increasing and then decreasing effects on pulp yield. Sulfidity at the beginning has increasing effect then decreases pulp yield when it is higher amount. But its general effect is moderate on pulp yield. Holding time at maximum cooking temperature has little effect on pulp yield between 30 and 150 minutes levels. (3) From the 30 experiments conducted, 18 runs lied between 10 and 20 kappa numbers and thus satisfied the bleach ability requirement. The rest 12 experiments are not recommended to bleach because they are either more chemical consumer for kappa numbers above 20 or their fibers are damaged during kraft pulping for kappa numbers below10. Active alkali, temperature and cooking time have negative effects on kappa number. As we increase the value of these factors, we are able to remove more lignin from cotton stalks. But sulfidity has a positive effect on kappa number. So that the presence of sulfidity will sticks the lignin to the fiber and makes pulping difficult. (4) The pulp hand sheet from optimal pulping condition has good tensile and tear indices and somewhat low burst indices. But still the values of these indices are in the same range of eucalyptus species. In a general, the cotton stalks pulp can be used for

production of papers that are applicable for stationary paper (i.e. printing and writing), news print, and paper card. Because its fiber morphology and hand sheet strength indices are similar to eucalyptus which is the most source of hard wood pulp.

5.2 Recommendations

- Experiments performed on kraft puling of cotton stalks, showed that bleachable grade pulp can be produced from our cotton farm by product. But before implemented further studies on process design and feasibility studies need to be done. It is also possible to find pulping methods other than kraft pulping if they give better results. To do this chemical characterization of the raw material may be use full to choose cooking chemicals for pulping. Whatever the process is cotton stalks could be a promising raw material for paper productions.
- Black liquor which is rich in kraft chemicals, lignin and other extracts are a valuable by product from pulping process. Therefore, for the recovery of original kraft chemicals and to use organic extracts of cotton stalks for fuel as tall oil further investigations should be worked out.
- Even though it is recommend total chlorine free bleaching system for environment case, Bleaching process is complicated by itself and further research would be governor idea to select bleaching process.
- One can also do investigate the effects of the size of cotton stalks used and solid to liquor ratio during pulping as other factors on a pulp yield.
- Cotton stalks pulps can be used in combination with other fibers for the production of specialty papers and when there is shortage of soft wood pulps. But investigation will tell us how to do this.
- Harvesting and storage techniques of cotton stalks could be another research in field work.

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APPENDICES

Appendix A: Glossary

White liquor:

The main active chemical agents in the kraft process are hydroxide and hydrosulfide anions which are present in the kraft cooking liquor, an aqueous solution of caustic sodium hydroxide and sodium sulfide, denoted as white liquor.

Black liquor:

It is white liquor enriched with degraded wood components with a residual hydroxide ion concentration of ca. 0.25 mol L^{-1}. Black liquor is removed from a pulp after countercurrent washing of pulp.

Green liquor:

The remaining smelt on the bottom of the boiler is again dissolved in water and normally stored in a tank. The now forming solution of sodium carbonate and sodium sulfide is known as green liquor.

Tall oil:

The tall oil originates from the nonvolatile fraction of the wood extractives mainly lignin, is removed during evaporation of the black liquor by skimming and used for energy production.

Nucleophile:

In chemistry, an atom or molecule that in chemical reaction seeks a positive center, such as the nucleus of an atom, because the nucleophile contains an electron pair available for bonding. Examples of nucleophiles are the halogen anions (I^-, Cl^-, Br^-), the hydroxide ion (OH^-), the cyanide ion etc**.**

Kraft liner and Kraft Paper:

Paper made from wood using the kraft or sulphate chemical pulping process. It may be bleached or unbleached and produces a strong paper which is used for wrapping and packaging. Kraft liner is used specifically in the production of cardboard boxes (called Packaging Containers in this work), acting as the liners (outer layers). When recovered paper is used this paper is called test

liner. The rippled material or corrugating acting as filler between the two liners is called fluting.
Kraft Pulp:

A wood pulp produced by chemical pulping of the wood, also called the sulphate process. This removes the lignin from the wood, leaving cellulose fiber used in high quality paper manufacture. The removed lignin, called black liquor, is used for energy production.
Mechanical Pulp:

Pulp produced by the physical (as opposed to chemical) treatment of the wood to produce papermaking fiber. The process can be purely through the action of grinding the wood (ground wood), to pretreatments of heat (thermo mechanical, TMP) and chemical (chemo thermo mechanical pulp, CTMP). The remaining presence of lignin in the pulp causes yellowing through reaction with light. Papers made from this pulp include newsprint and magazines, are termed mechanical papers.

Mechanical Paper:
Paper, the furnish of which contains a substantial proportion of mechanical pulp. These papers can be coated (coated mechanical) with a thin coating to improve printability, and called lightweight coated papers (LWC), used in magazine papers. Uncoated mechanical paper includes those where the surface is smoothed and prepared across large rollers, called calendars, again to improve printability, termed super calendared papers (SC). These are used in flyers, inserts and magazines.

Newsprint:

Paper intended for the printing of newspapers, mainly produced from recovered paper (through the recycling process) and also mechanical pulp.

Printing and Writing Paper (P&W):

Paper grades which are used for books, commercial printing, copying, business forms, stationary and laser and digital printing. These are often categorized as coated wood free and uncoated wood free. Wood free is a term which refers to papers using chemical pulps – where wood free means the lignin is removed. In uncoated form these can be copying paper and letterhead.

Coatings refer to surface treatments and additives which enhance printability. These papers are found in advertising, commercial printing.

Specialty Papers:

A diverse group of products that are sold on their performance, technical or appearance attributes. Examples include: filtration products; security and banknotes; decorative papers; abrasives (e.g. sand paper); letterhead; tracing and greaseproof papers.

Test liner:

The liner (outer layers) for corrugated container board (cardboard boxes) made principally from recycled fiber furnish. It can be used for bleached and unbleached. The virgin fiber alternative, Kraft liner, has uses where contact is important, such as food packaging, and purity/cleanliness of the fiber furnish is necessary. Test liner and Kraft liner can be bleached and coated for better printability and presentation.

Appendix B: Some Laboratory work pictures

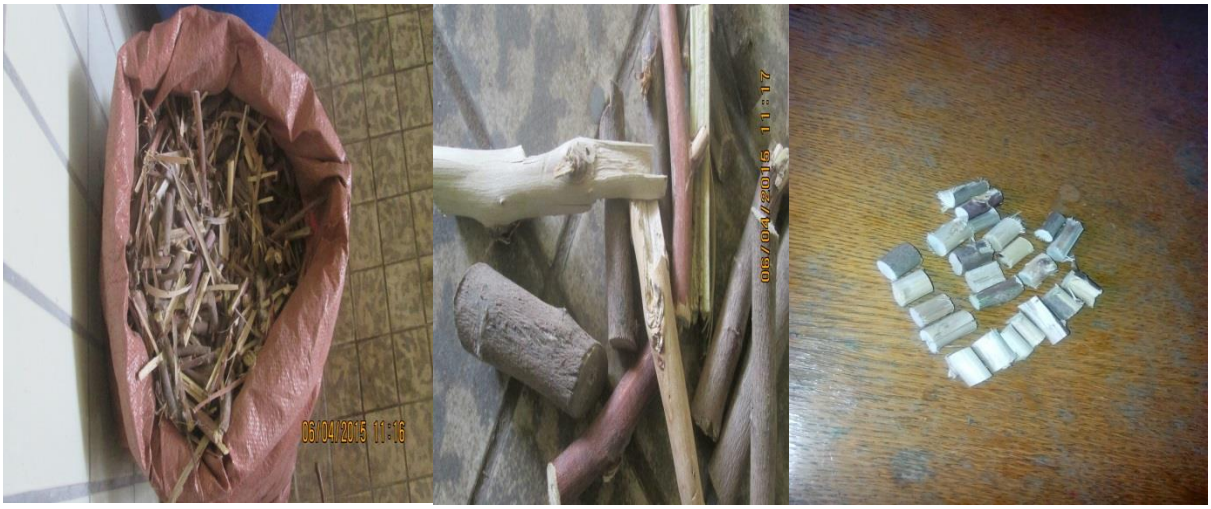


Figure B1: Collected Cotton Stalks

(a) **(b)**

Figure B2: Slicer (a) and motic electron microscope (b) used for fiber dimension measurement

(a) (b) (c)

Figure B3: laboratory autoclave (a) pulp before washing (b) and pulp after drying (d)

(a) **(b)** **(c)**

Figure B4: Magnetic stirrer (a) funnel filter (b) prepared samples for kappa number measurement using spectrometry.

Appendix C: Pictures taken from motic electron microscope and used for fiber dimension measurement

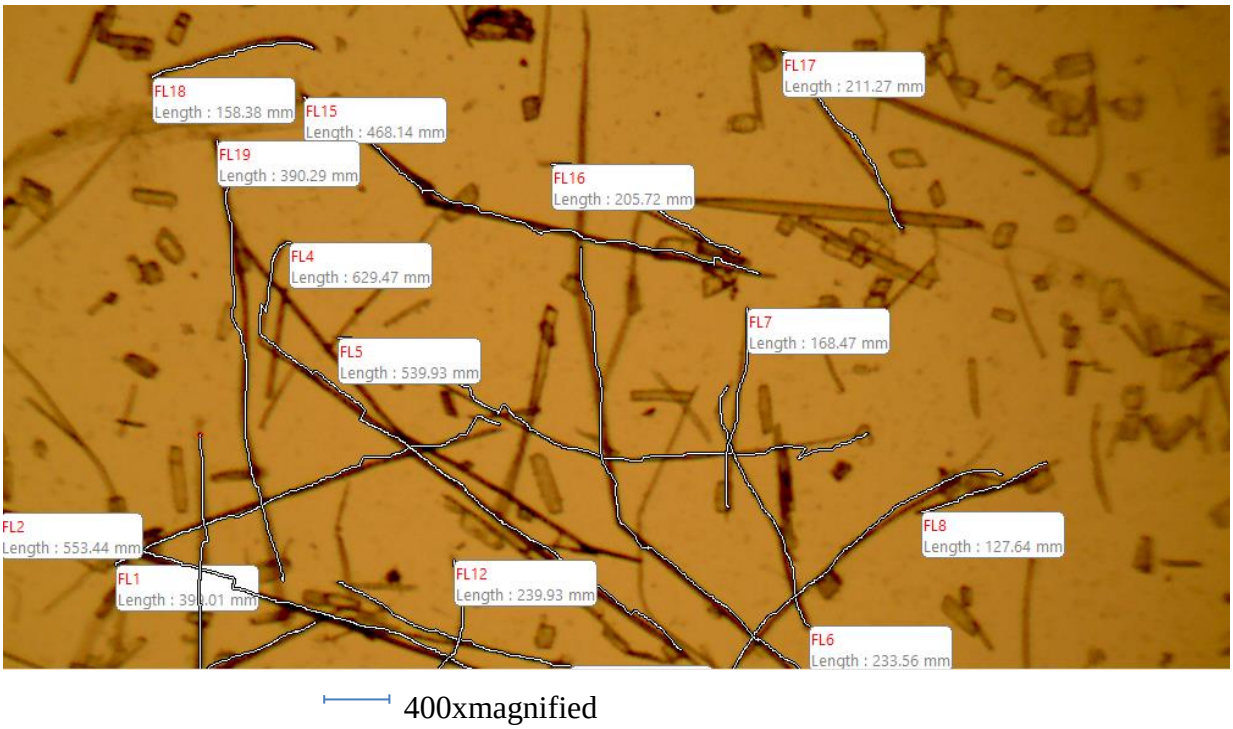


Figure D1: Pictures taken from motic electron microscope for fiber length measurement

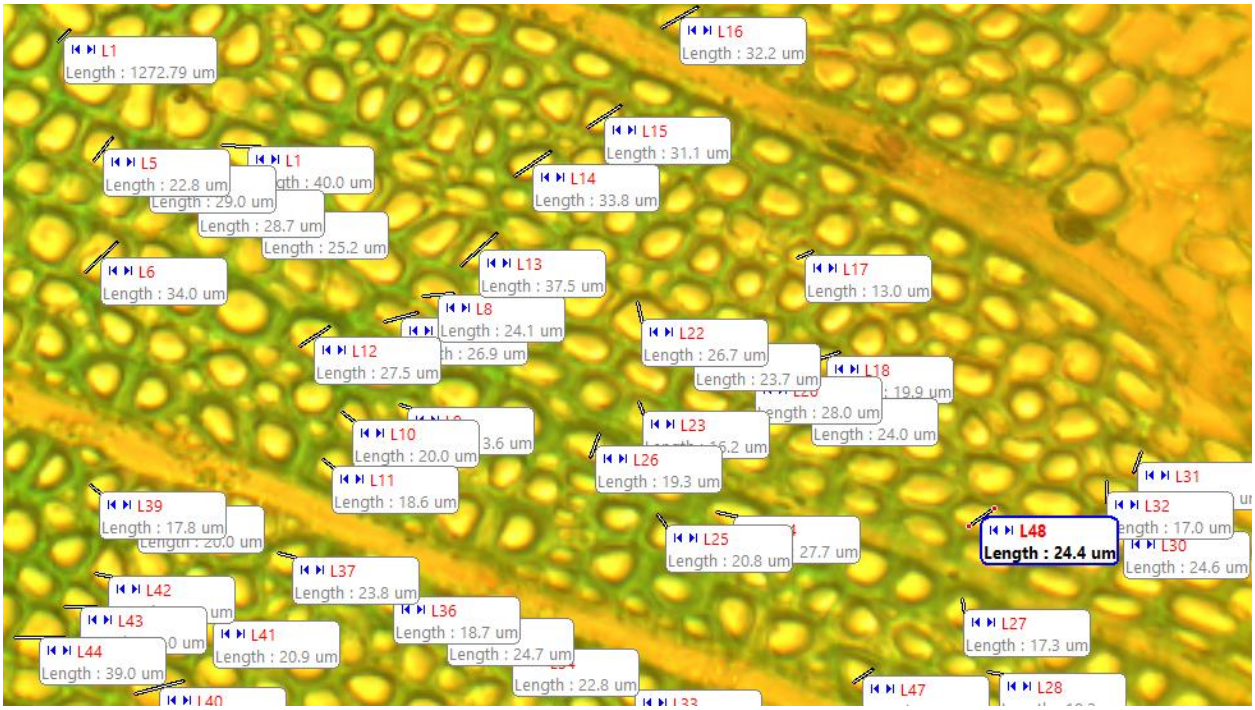


Figure C 2: pictures taken from motic electron microscope for fiber diameter, lumen width, cell wall thickness measurement

Appendix D: Numerical optimization solutions for pulp yield

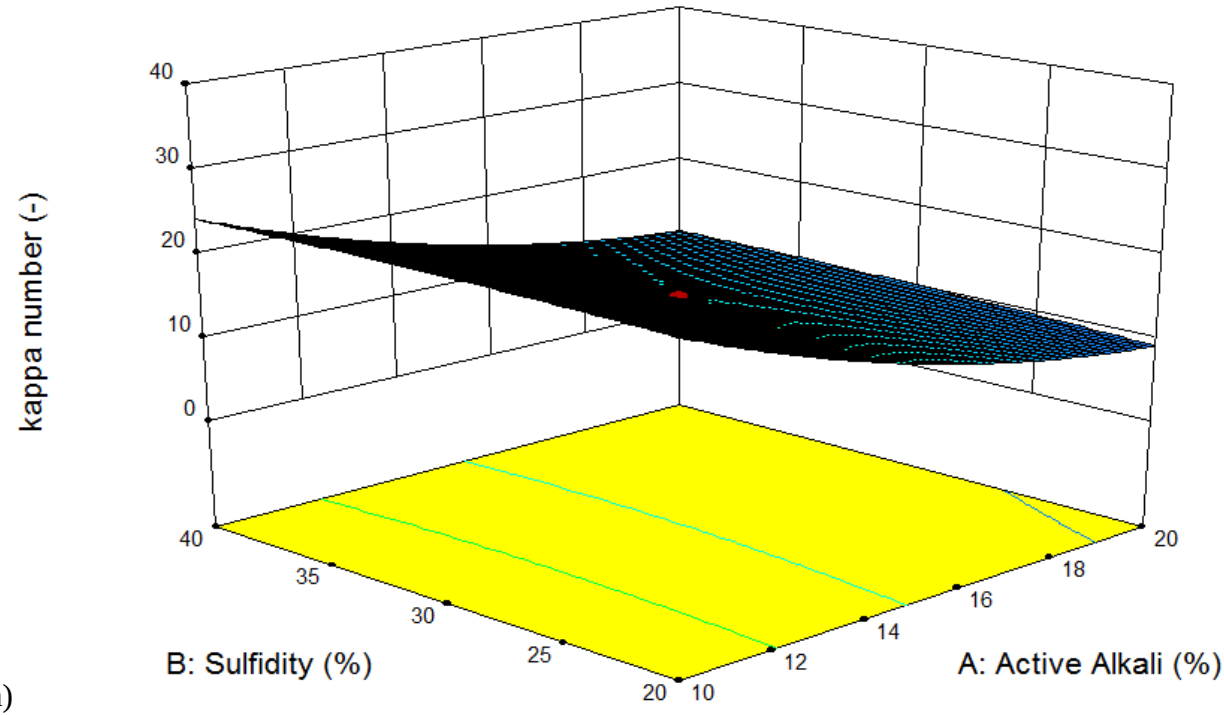
Table D1: Numerical optimization and solutions for pulp yield

		Constraints	
Name	**Goal**	**Lower Limit**	**Upper Limit**
A:Active Alkali	minimize	10	20
B:Sulfidity	minimize	20	40
C:temperature	minimize	160	170
D:Time	minimize	60	120
yield	maximize	34.6	41.6
kappa number	minimize	10	20

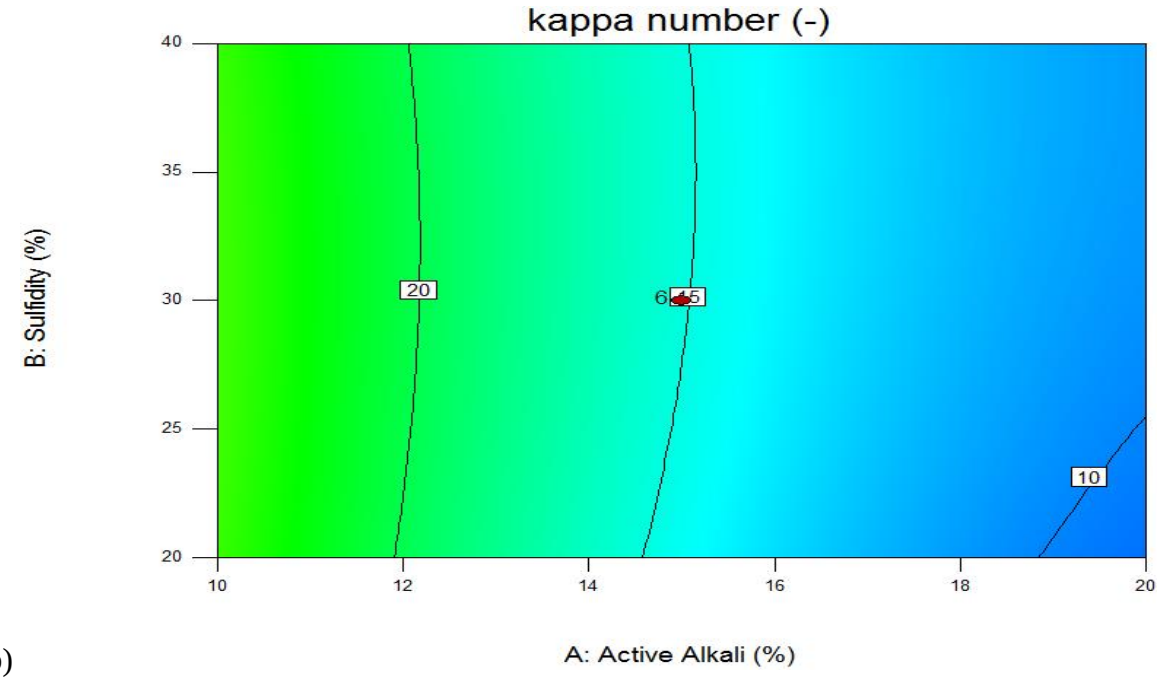
Solutions

Number	Activ Alkali	Sulfidty	Temp.	Time	yield	Kappa #.	Desirability
1	16.544	20.000	163.529	60.000	39.641	15.514	0.649
2	16.556	20.000	163.483	60.000	39.651	15.542	0.649
3	16.519	20.000	163.588	60.002	39.630	15.492	0.649
4	16.507	20.000	163.545	60.001	39.640	15.550	0.649
5	16.573	20.000	163.401	60.002	39.667	15.595	0.649
6	16.621	20.000	163.413	60.001	39.662	15.519	0.649
7	16.462	20.000	163.658	60.001	39.619	15.505	0.649
8	16.619	20.000	163.497	60.001	39.643	15.441	0.649
9	16.549	20.000	163.440	60.138	39.659	15.583	0.649
10	16.536	20.000	163.553	60.238	39.635	15.487	0.649
11	16.498	20.000	163.768	60.022	39.594	15.350	0.649
12	16.419	20.000	163.540	60.001	39.647	15.678	0.649
13	16.704	20.000	163.288	60.006	39.683	15.523	0.649
14	16.469	20.000	163.417	60.000	39.670	15.725	0.649
15	16.650	20.000	163.192	60.001	39.709	15.688	0.649
16	16.436	20.000	163.874	60.001	39.576	15.336	0.649
17	16.562	20.000	163.239	60.006	39.704	15.766	0.649
18	16.743	20.000	163.277	60.000	39.683	15.481	0.649
19	16.357	20.000	163.887	60.005	39.579	15.433	0.649
20	16.398	20.000	163.480	60.001	39.661	15.764	0.649
21	16.398	20.000	163.926	60.019	39.568	15.339	0.649
22	16.555	20.087	163.590	60.001	39.634	15.445	0.649
23	16.747	20.001	163.427	60.001	39.649	15.335	0.649
24	16.554	20.000	163.331	60.619	39.679	15.649	0.649
25	16.495	20.000	163.593	60.787	39.625	15.471	0.649
26	16.363	20.051	163.645	60.001	39.632	15.658	0.649
27	16.468	20.133	163.511	60.001	39.660	15.642	0.648
28	16.524	20.185	163.505	60.002	39.662	15.572	0.648
29	16.570	20.000	163.349	61.699	39.666	15.539	0.648
30	16.349	20.000	163.726	61.276	39.602	15.517	0.648

Appendix E: Figures taken from design expert software for process variables interaction effect on kappa number

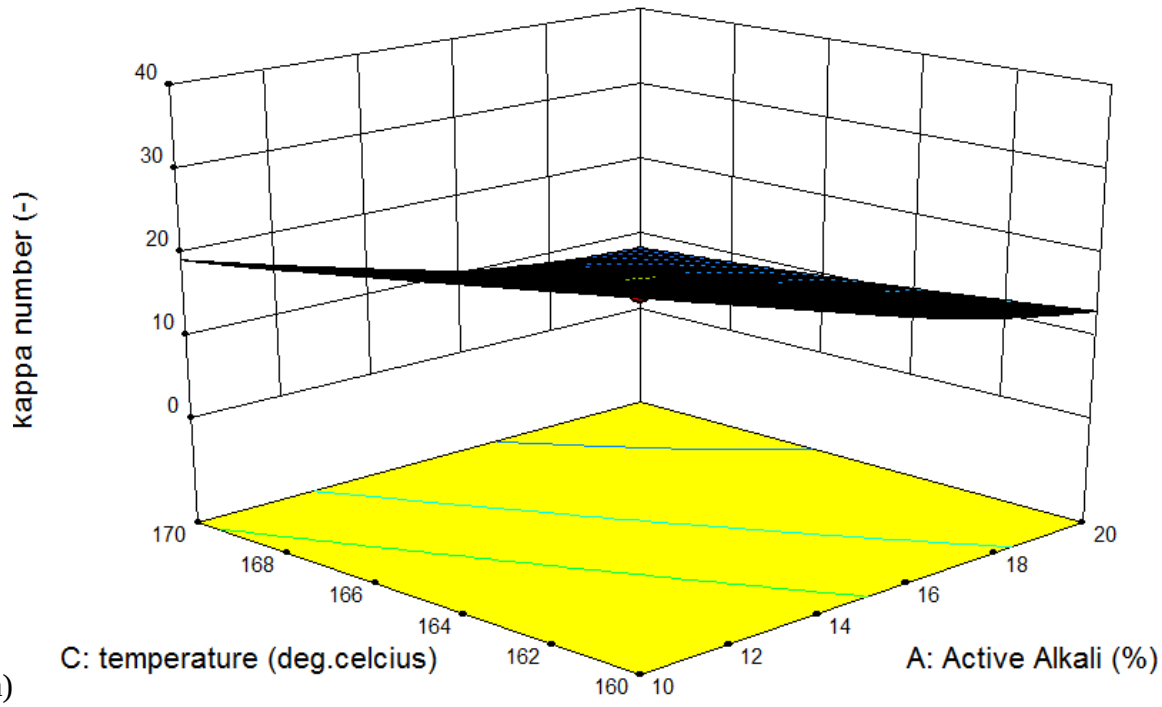


(a)

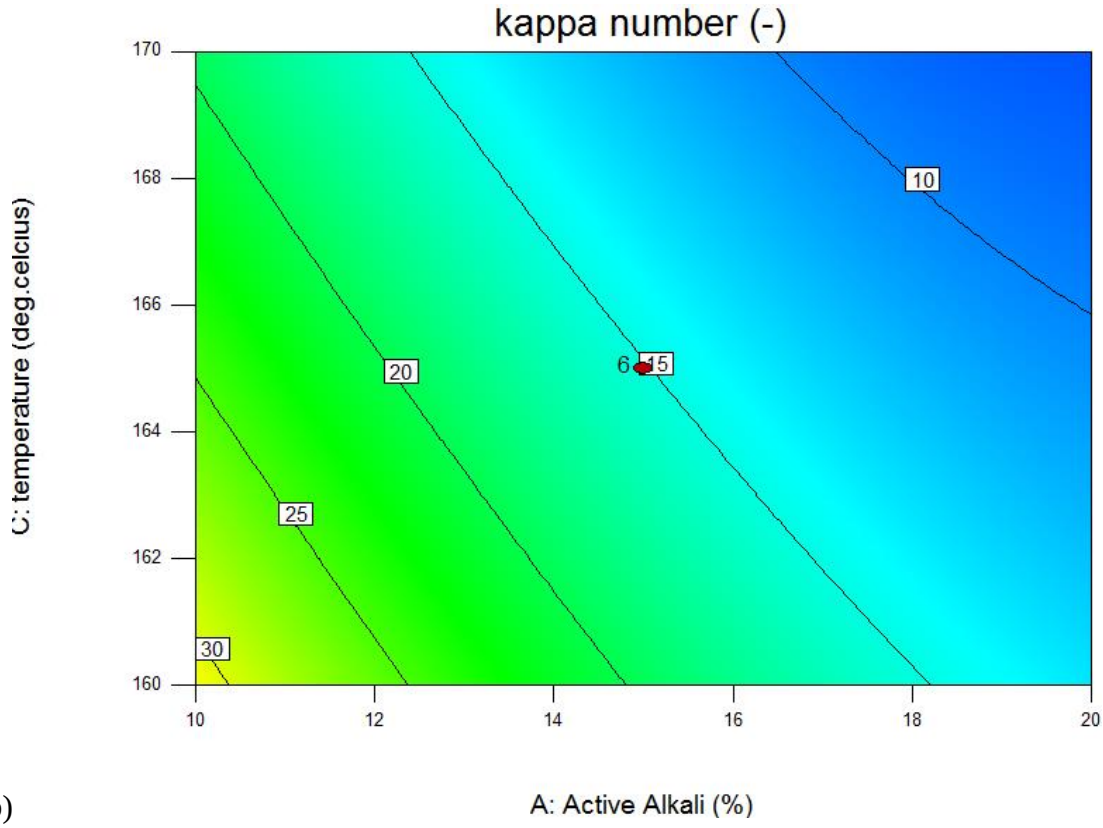


(b)

Figure E1: 3Dplot (a) and contour plot (b) for the interaction effects of Active alkali and sulfidity on Kappa number

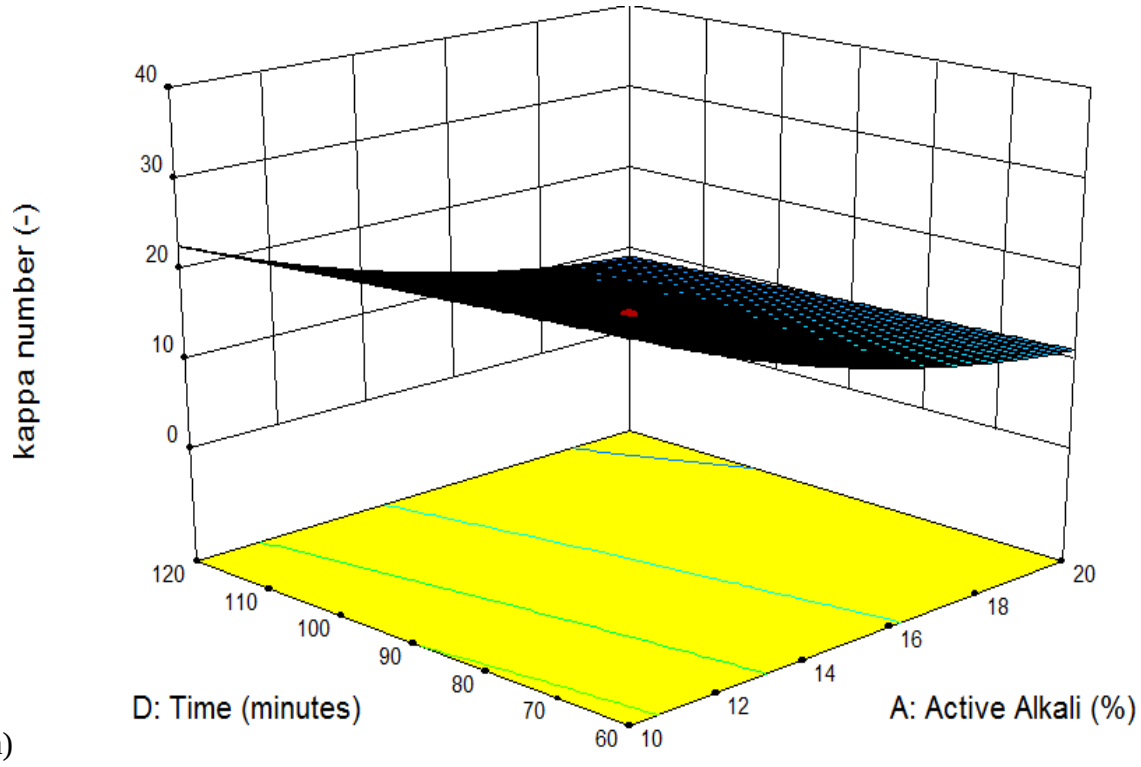


(a)

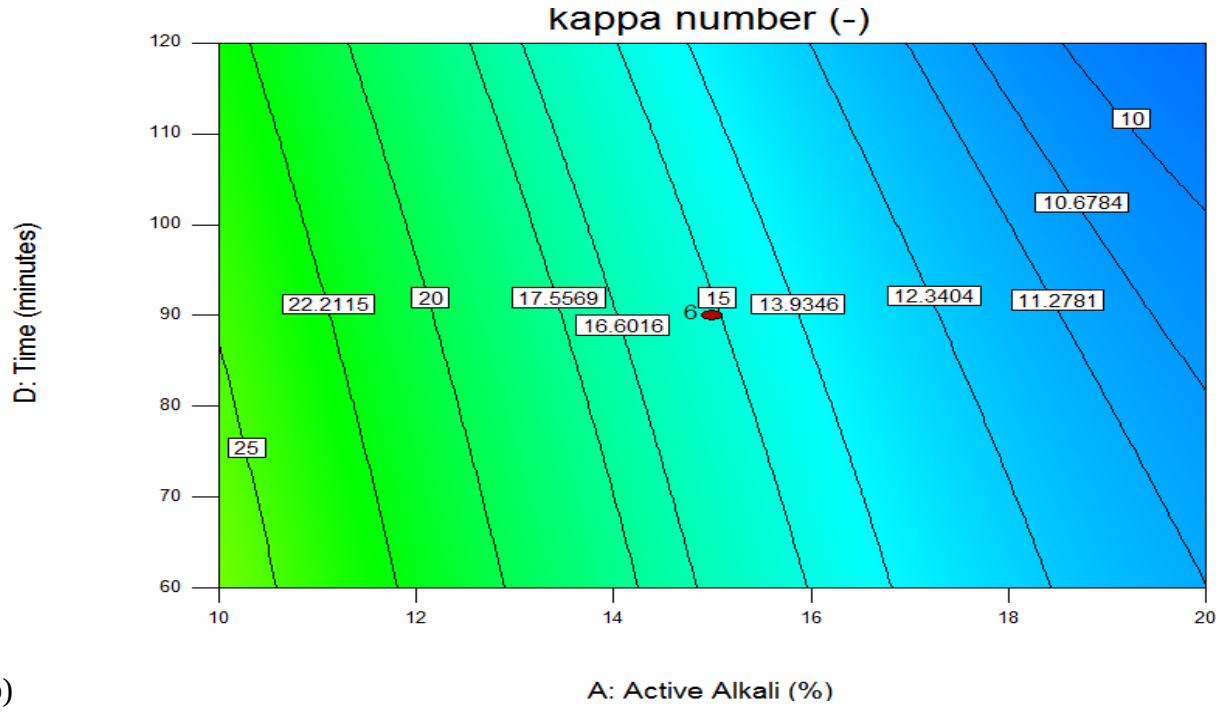


(b)

Figure E2: 3D plot (a) and contour plot (b) for interaction effects of Active alkali and temperature on kappa number

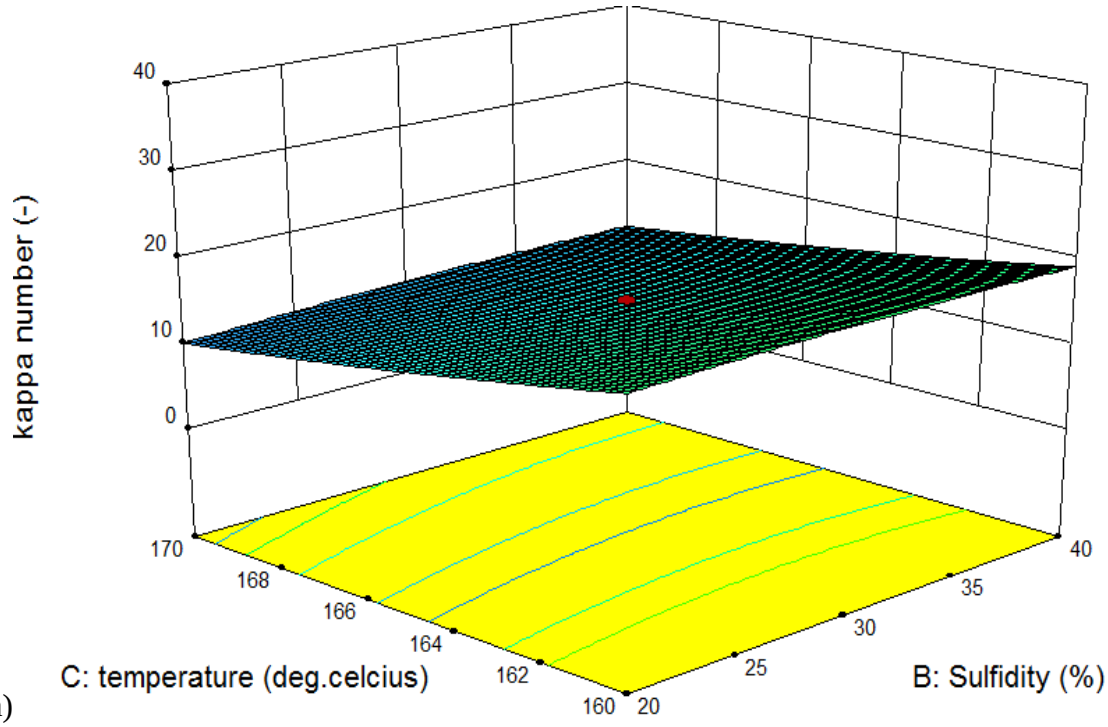


(a)

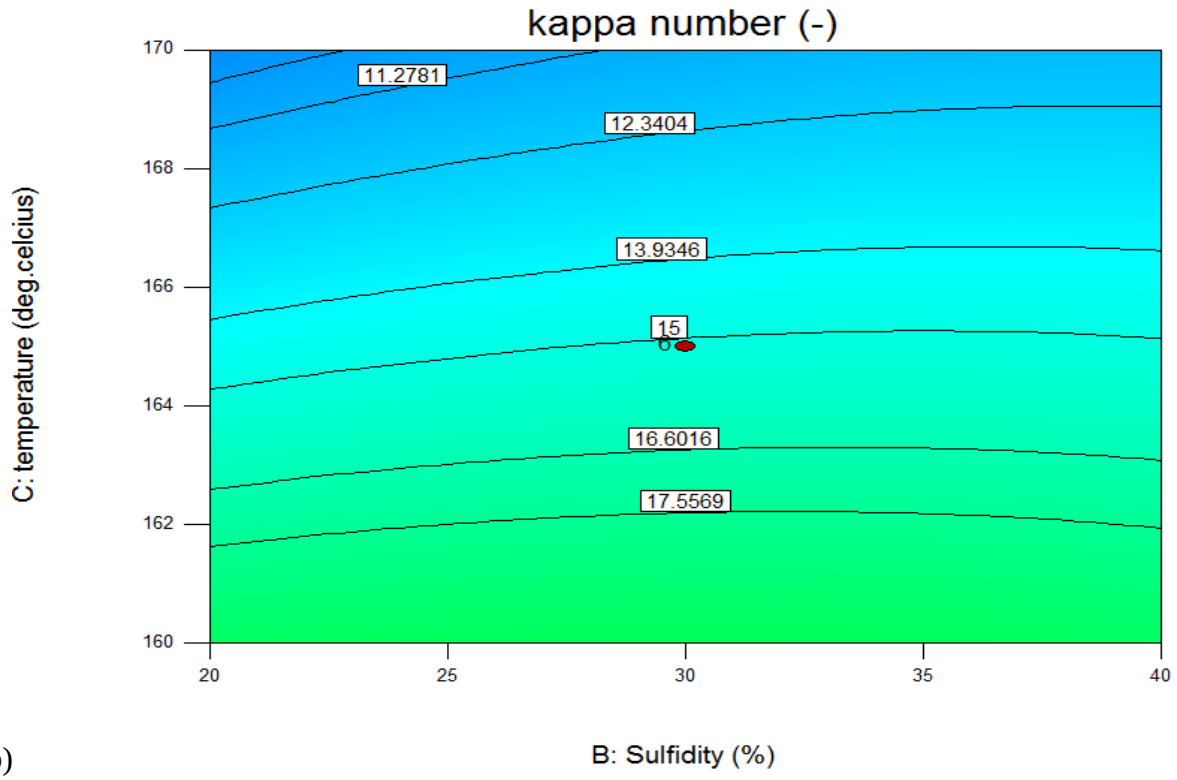


(b)

Figure E3: 3D plot (a) and contour plot (b) for interaction effects of active alkali and time on kappa number

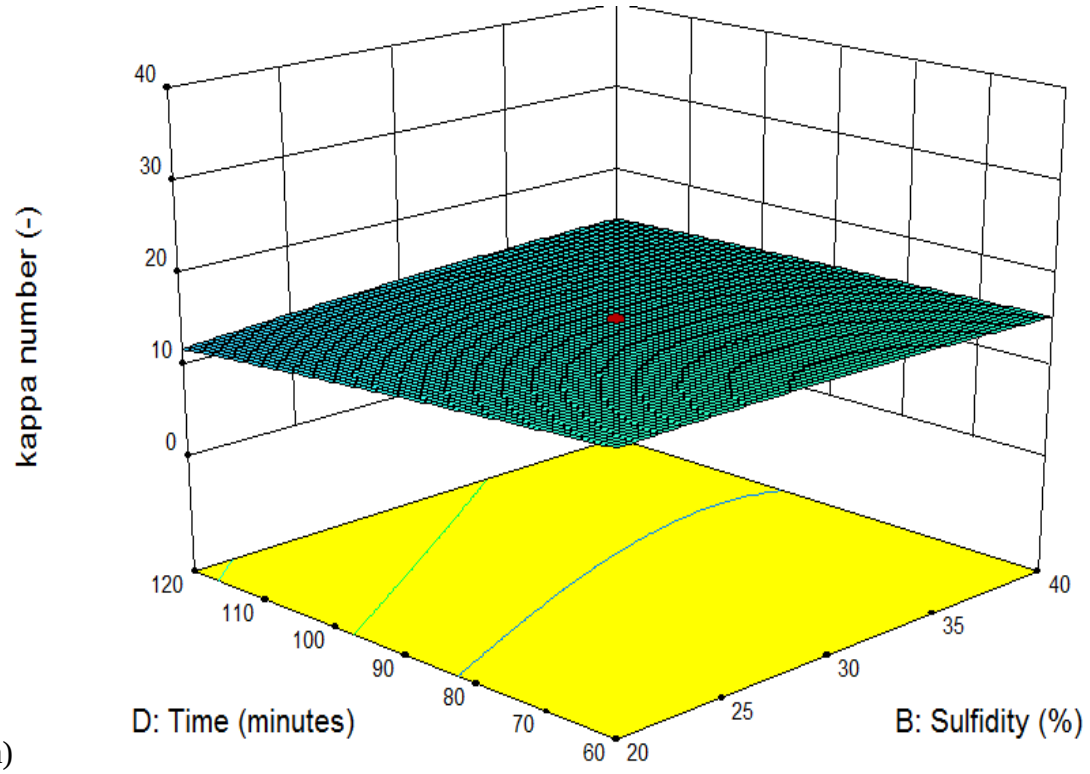


(a)

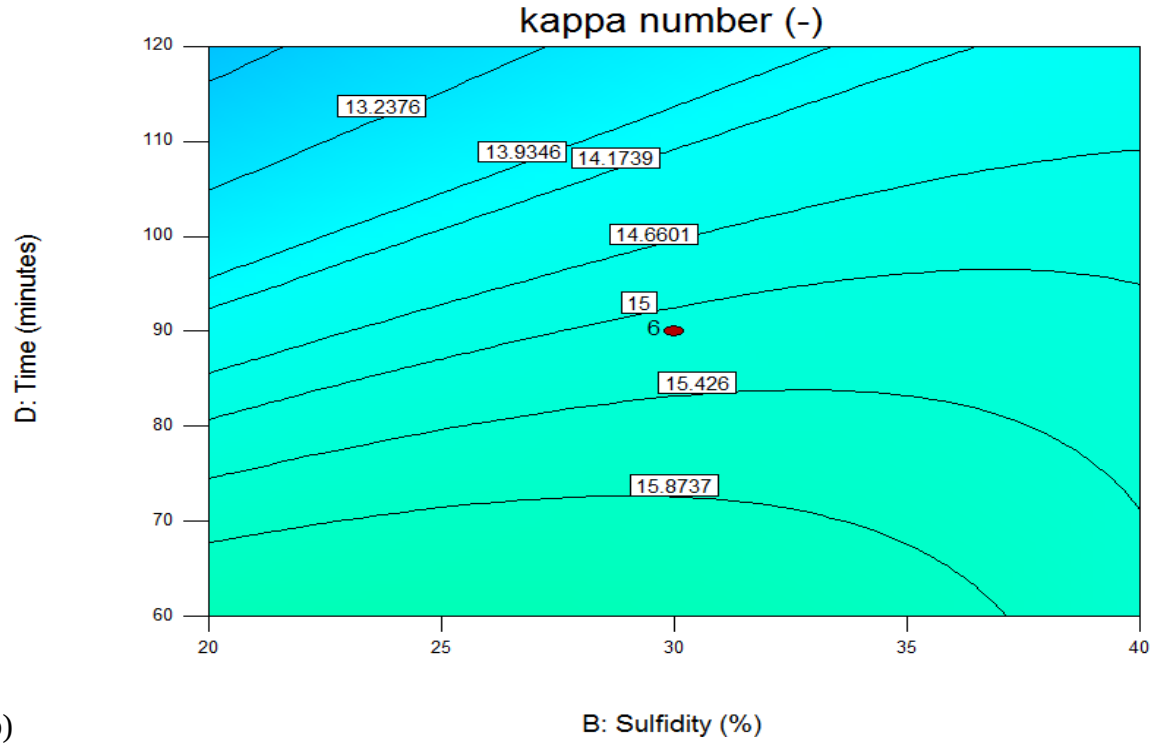


(b)

Figure E4: 3D plot (a) contour plot (b) for interaction effects of sulfidity and temperature on kappa number

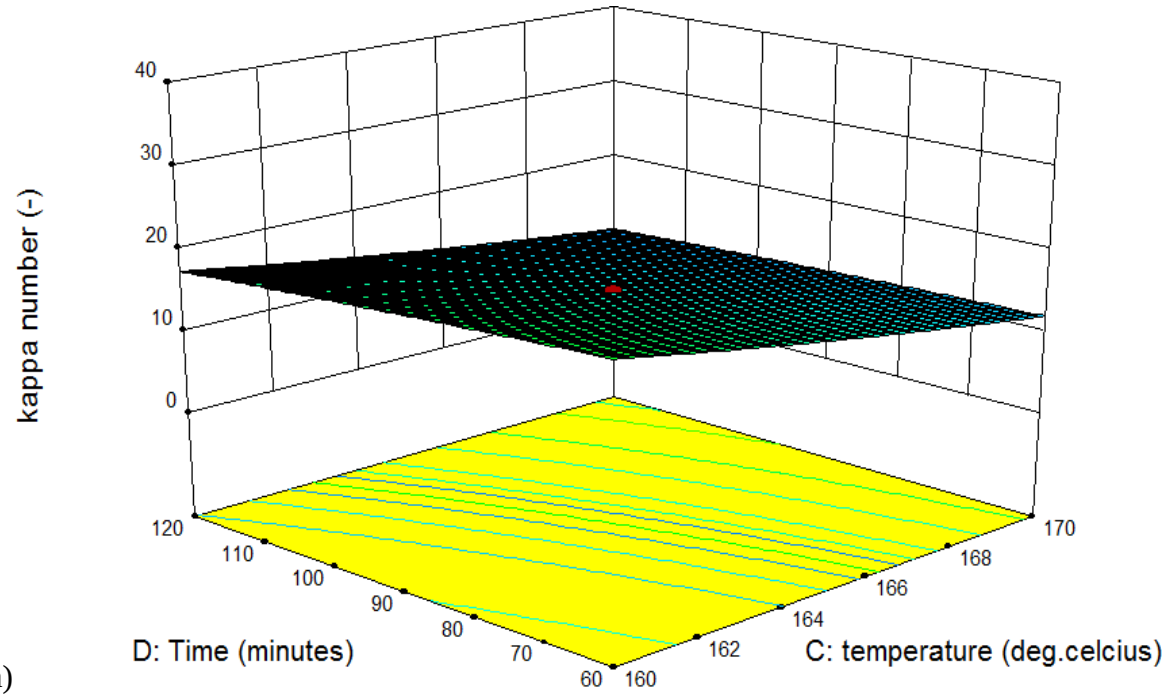


(a)

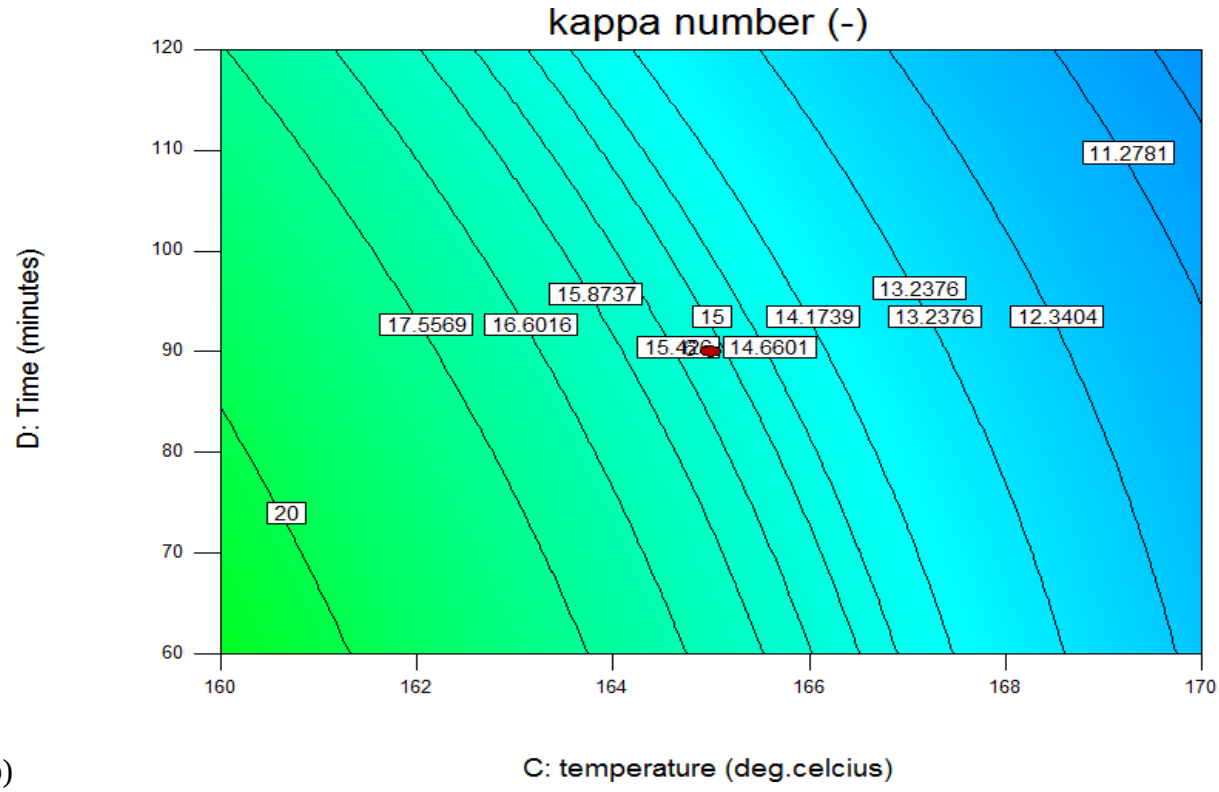


(b)

Figure E7: 3Dplot (a) and contour plot (b) interaction effects of sulfidity and time on kappa number



(a)



(b)

Figure E5: 3D plot (a) and contour plot (b) for interaction effect of temperature and time on kappa number