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Pulp Production from Agricultural Residues

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July, 2015

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A Thesis Submitted in Partial Fulfillment of the Requirements for the Award of a Master's Degree in Chemical Engineering under Environmental Engineering

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ACRONYMS

AAiT	Addis Ababa Institute of Technology
ANOVA	Analysis of Variance
AQ	Antraquinone
ASTM	American Society of Testing Materials
CCD	Central Composite Design
DF	Degree of Freedom
RSM	Response Surface Method
TAPPI	Technical Association of the Pulp and Paper Industry

ABSTRACT

Growth in pulp and paper production entails massive felling of trees, which in turn leads to deforestation. Increasing competition for wood supplies coupled with gradually rising costs of wood have generated renewed interest in the use of non-wood plant fibers for papermaking in the highly industrialized countries.

The utilization of agricultural residues for the production of value-added products presents an innovative opportunity for sustainable resource management, provides additional income for farmers and contributes to the development of rural economies.

In this study pulping of wheat straw was carried out by conventional soda-antraquinone (AQ) pulping under different conditions. The influence of soda concentration (10, 12 and 14% on the basis of dried wheat straw), cooking temperature (155,160 and 165^0C) and cooking time (20, 35 and 50 min) on pulp properties were studied. Results indicated that soda concentration and cooking time had a significant influence on yield and kappa number.

However the best result with respect to yield and kappa number was obtained with 10% soda concentration with 20 min cooking time.

Physical tests of hand sheets made from wheat straw soda-AQ pulps were carried out at Ethiopian Pulp and Paper Factory located at Wonji. At the optimum operating conditions tensile, tear and burst index were determined to be 67.9 Nm/g, 7.5 mNm^2/g and 7.3 kN/g respectively.

1. BACKGROUND

The use of agricultural residues as a source of cellulose in the paper industry is supported by many institutions, due in part to increasing environmental pressures (Camarero et al., 2004). Non-wood plants represent an important alternative fiber source for the pulp and paper industry. The role of agro-fiber biomass is particularly prominent in countries with limited wood resources. In some regions of Asia, Africa and Latin America, this is the only source of industrial papermaking fibers. Recently, there has been a growing interest in using non-wood fibers for the production of cellulose for paper and other industrial applications (Rezayati-Charani et al., 2011).With an increasing demand for cellulose pulp and decreasing supply of wood, many countries all over the world are using various types of agricultural residues, reeds and other plants to produce pulp. All these materials, collectively known as non-wood plant fibers, can be used for the same purposes as wood, especially for the manufacture of pulp, paperboards and news print. The economic use of these important renewable resources has been neglected by most countries in the past (Kennedy et al., 2010). Being an agriculture-dependent country with limited forest resources, Ethiopia is still far from utilizing the current potential of agricultural residues in the cellulose industry.

Regions like Asia and also some countries in the Middle East concentrated on the utilization of non-woods as raw material. Even though it seems unrealistic, but it is believed that the non-wood pulp production will take the momentum at the annual rate between 12-15%. In this expansion path, the share of underdeveloped countries, which are facing limitations of wood fiber supply, will be greater than that of fiber-rich countries. Since 1970, globally, the non-wood plant fiber pulping capacities increased two to three times faster than the wood pulping capacity. It has been estimated that the pulp production from wheat straw in China will reach almost 13 million tons in 2020 (Ahmad et al., 2014).

The global interest in non-wood and nonconventional fiber pulping has attracted attention worldwide and various groups and organizations started research, development, improvement and implementation of non-wood pulping (Ahmad et al., 2014).

1.1 Statement of the Problem

The demand for paper in Ethiopia is both met through import and local production. However most of the supply is from import. The demand for paper is ever increasing due to increasing economic and social activities. As the per capita consumption of paper is directly related to the economic growth of the country, the demand for paper and paper products will grow proportionally as the economy of the country grows. Ethiopia as a developing country has a strong vision to become a middle income country. The educational sector in the past few years has been increasing tremendously and as a result the demand for paper required for the manufacturing of exercise books and for printing of various types of educational materials has grown substantially. Therefore in order to satisfy these demands, building pulp and paper factories in different parts of the country is economical. Most of the pulp and paper industries use woods as a raw material but this activity has a problem of deforestation and other environmental issues. However using agricultural residues like wheat straw may have economic and environmental advantages and utilization of wheat straw could provide partial replacement of the wood fiber shortfall expected in the upcoming years.

Growth in pulp and paper production entails massive felling of trees, which in turn leads to deforestation. Increasing competition for wood supplies coupled with gradually rising costs of wood have generated renewed interest in the use of non-wood plant fibers for papermaking in the highly industrialized countries. The use of agricultural-residues in pulping and papermaking might be desirable because it averts the need for disposal, which currently increases farming costs and causes environmental deterioration through pollution, fires, and pests (Chandra, 1998).

Already, a number of non-wood fibers are commonly used in many countries for papermaking. Straws are by far the largest source of non-wood fibers followed by bagasse and bamboo (Chandra, 1998).

The present research aims at studying the possibility of producing pulp from wheat straw, one of the most abundantly found agricultural residues, by using chemical pulping method.

1.2 Objectives

1.2.1 General Objective

The general objective of this study is to produce pulp from agricultural residues using chemical pulping method.

1.2.2 Specific Objectives

The specific objectives of this study are:

- To prepare pulp from wheat straw using Soda-AQ pulping method.
- To characterize the physico-chemical properties of the hand sheets made from the pulp produced.
- To investigate the interaction effect of the three parameters (soda concentration, temperature and time) on yield and kappa number.
- To find the optimum operating conditions to prepare pulp.

1.3 Significance of the Study

The significance of the production of pulp from agricultural residues is that, first with respect to the economic development of the country especially in areas of industrialization, Ethiopia will be able to fulfill its demand of pulp and also to partially substitute its raw material demand with low cost for pulp and paper industries. The utilization of agricultural residues for the production of value-added products presents an innovative opportunity for sustainable resource management, provides additional income for farmers and contributes to the development of rural economies.

The other significance of this study is to reduce deforestation level and to protect the environment. Since paper is going to be produced from agricultural residues, this study will be considered as one away of transforming a solid waste into useful material.

2. LITERATURE REVIEW

2.1 Pulp and Papermaking Process

Pulp consists of wood or other lignocellulosic materials that have been broken down physically and/or chemically such that (more or less) discrete fibers are liberated and can be dispersed in water and reformed into a web (Biermann, 1996). Paper is a finished product of the pulping process whereas pulp is an intermediate product obtained during paper manufacture.

Pulp and paper are manufactured from raw materials containing cellulose fibers, generally wood, recycled paper, and agricultural residues. In developing countries, about 60% of cellulose fibers originate from non-wood raw materials such as bagasse, cereal straw, bamboo, reeds, esparto grass, jute, flax, and sisal (Gullichsen, 2000).

2.1.1 Pulp Making Process

Pulp consists of fibers, usually acquired from wood. The pulping processes aim first and foremost to liberate the fibers from the wood matrix. In principal, this can be achieved in two ways, either mechanically or chemically (Monica, 2009).

In the case of mechanical pulp, the wood is processed into fiber form by grinding it against a quickly rotating stone under addition of water. The yield of this pulp amounts to approximately 95%. The result is called wood pulp or MP – mechanical pulp. The disadvantage of this type of pulp is that the fiber is strongly damaged and that there are all sorts of impurities in the pulp mass. Mechanical wood pulp yields a high opacity, but it is not very strong. It has a yellowish color and low light resistance (Monica, 2009).

Chemical pulping is used on most papers produced commercially in the world today (Smook, 1992b; Biermann, 1996b). Chemical pulps are made by cooking (digesting) the raw materials, using the kraft (sulfate), sulfite and soda processes. The kraft (sulfate) process is the most dominating chemical pulping process worldwide. The term “sulfate” is derived from the makeup chemical sodium sulfate, which is added in the recovery cycle to compensate for chemical losses. In the kraft pulp process the active cooking chemicals (white liquor) are

sodium hydroxide (NaOH) and sodium sulfide (Na_2S). Kraft process is applicable to all types of wood species but its chemistry carries with it an inherent potential problem of malodorous compounds. Kraft pulp possesses superior pulp strength properties in comparison to sulphite pulp. Kraft processes produce a variety of pulps used mainly for packaging and high-strength papers and board.

Sulfite process uses different chemicals to attack and remove lignin. The sulphite process is characterized by its high flexibility compared to the kraft process, which is a very uniform method, which can be carried out only with highly alkaline cooking liquor. In principle, the entire pH range can be used for sulphite pulping by changing the dosage and composition of the chemicals (Smook, 1992b; Biermann, 1996b). Thus, the use of sulphite pulping permits the production of many different types and qualities of pulps for a broad range of applications. The sulphite process can be distinguished according to the pH adjusted into different types of pulping. The main sulphite pulping processes are Acid (bi)sulphite, Bisulphite (Magnefite), Neutral sulphite (NSSC), and Alkaline sulphite.

The soda process, using aqueous sodium hydroxide solution as cooking liquor, is used primarily for the pulping of annual plants and, in combination with small amounts of anthraquinone (ca. 0.05% on wood), also for the pulping of hardwoods (Sixta, 2006).

Pulps prepared by most pulping processes are too dark in colour to be used for many paper products without some form of bleaching. This is particularly true of pulps derived from alkaline processes, which are brown. Unbleached pulps from these processes are used mainly for packaging grades. Pulps from mechanical and sulphite processes are lighter in colour and can be used in products such as newsprint. The sulphite process produces chemical pulps with the lightest color (Bajpai, 2005).

Unbleached pulps for the production of unbleached papers and boards require no screening or cleaning, if fiberizing refiners are included in the system. Because of dark particles from the nodes of plant stalks, and shive and epidermal material in the case of bast and leaf fiber, screening and very thorough centri-cleaning are required for the production of bleached pulp (Hurter, 1988).

Almost all of the non-wood chemical and semi chemical pulps are easy to bleach. A single hypochlorite stage or three-stage bleaching - chlorination, caustic extraction, and hypochlorite – is sufficient for paper pulps produced in integrated pulp and paper mills. Even dissolving pulp from cotton linters does not require more than chlorination, caustic extraction and hypochlorite. Market pulp mills may require an additional peroxide or chlorine dioxide super bleaching stage to reach the brightness demanded of market pulps today (Hurter,1988).

The "mechanical" pulps produced from bagasse are also easy to bleach with peroxide if the bagasse is fresh. However, if the harvesting season is short and bagasse must be stored for a long time, the bagasse brightness may be so low that it is not readily possible to attain an acceptable brightness (Hurter, 1988).

Bleaching of pulp is done to achieve a number of objectives. The most important of these is to increase the brightness of the pulp so that it can be used in paper products, such as printing grades and tissue papers. For chemical pulps an important benefit is the reduction of fiber bundles and shives as well as the removal of bark fragments. This improves the cleanliness of the pulp. Bleaching also eliminates the problem of yellowing of paper in light, as it removes the residual lignin in the unbleached pulp. Resin and other extractives present in unbleached chemical pulps are also removed during bleaching, and this improves the absorbency, which is an important property for tissue paper grades. In the manufacture of pulp for reconstituted cellulose, such as rayon and for cellulose derivatives, such as cellulose acetate, all wood components other than cellulose must be removed. In this situation, bleaching is an effective purification process for removing hemicelluloses and wood extractives as well as lignin (Bajpai, 2005).

Removal of the residual lignin in the pulp increases fiber flexibility and strength. On the other hand, a lowered hemicellulose content results in a lower swelling potential of the fibers and a reduced bonding ability of the fiber surfaces. If bleaching conditions are too severe there will be fiber damage, leading to a lower strength of the paper. The purpose of bleaching is to dissolve and remove the lignin from wood to bring the pulp to a desired brightness level (Bajpai, 2005).

Table 2.1-Chemicals Used in Bleaching Processes (Bajpai, 2005).

Symbol	Chemical	Symbol	Chemical
C	Chlorine	Z	Ozone
D	Chlorine dioxide	E	Sodium hydroxide
H	Hypochlorite	X	Enzymes
O	Oxygen	Q	Chelating agents
P	Hydrogen peroxide	A	Acid

2.1.2 Paper Making Process

Before pulp can be made into paper, it must undergo several steps called stock preparation (Smook, 1992d; Biermann, 1996e). Stock preparation is conducted to convert raw stock into finished stock (furnish) for the paper machine. The quality of the finished stock essentially determines the properties of the paper produced. Stock preparation consists of several process steps that are adapted to one another as fiber disintegration, cleaning, fiber modification, and storage and mixing. After stock preparation, the next step is to form the slurry into the desired type of paper at the wet end of the paper machine.

The pulp is pumped into the head box of the paper machine at this point (Smook, 1992e; Biermann, 1996f). The slurry consists of approximately 99.5% water and approximately 0.5% pulp fiber. The exit point for the slurry is the "slice" or head box opening. The fibrous mixture pours onto a traveling wire mesh in the Fourdrinier process, or onto a rotating cylinder in the cylinder machine (Biermann, 1996f). As the wire moves along the machine path, water drains through the mesh. Fibers align in the direction of the wire travel and interlace to improve the sheet formation. After the web forms on the wire, the task of the remaining portion of the paper machine is to remove additional water. Vacuum boxes located under the wire aid in this drainage. The next stop for the paper is the pressing and drying section where additional dewatering occurs (Smook, 1992e; Biermann, 1996f). The newly created web enters the press section and then the dryers. As the paper enters the press section, it undergoes compression between two rotating rolls to squeeze out more water. The extent of water removal from the

forming and press sections depends greatly on the design of the machine and the running speed. When the paper leaves the press section, the sheet usually has about 65% moisture content. The paper web continues to thread its way through the steam heated dryers losing moisture each step of the way. The process evaporates many tons of water. Paper will sometimes undergo a sizing or coating process. The web in these cases continues into a second drying operation before entering the calendaring stacks that are part of the finishing operation. Moisture content should be about 4–6% as predetermined by the mill. If the paper is too dry, it may become too brittle (Bajpai, 2010).

About 90% of the cost of removing water from the sheet occurs during the pressing and drying operations. Most of the cost is for the energy required for drying (Bajpai, 2010).

At the end of the paper machine, paper continues onto a reel for winding to the desired roll diameter. The machine tender cuts the paper at this diameter and immediately starts a new reel with the additional paper falling as an endless web (Bajpai, 2010).

For grades of paper used in the manufacture of corrugated paperboard, the process is now complete. For those papers used for other purposes, finishing and converting operations will now occur, typically off line from the paper machine. These operations can include coating, calendaring, or super calendaring and winding (Bajpai, 2010).

2.2 Properties of Non-Wood Plants as Raw Material for Paper Making

Analysis of fiber morphology and chemical composition of plant material has been useful in searching for candidate fiber crops. The properties of the fiber depend on the type of cells from which fiber is derived, as the chemical and physical properties are based on the cell wall characteristics. Anatomically, plant fibers are composed of narrow, elongated sclerenchyma cells. Mature fibers have well-developed, usually lignified walls and their principal function is to support, and sometimes to protect the plant (McDougall et al., 1993).

2.2.1 Fiber Morphology in Non-Wood Plants Used in Paper Making

Morphological characteristics, such as fiber length and width, are important in estimating pulp quality of fibers. Fiber length and width of non-woody species vary depending on plant species and the plant part from which the fiber is derived. The average fiber length ranges from 1 mm to 30 mm, being shortest in grasses and longest in cotton. The average ratios of fiber length to diameter range from 50:1 to 1500:1 in non-wood species. Lumen size and cell wall thickness affect the rigidity and strength of the papers made from the fibers (Hurter, 1988; McDougall et al., 1993).

Table 2.2-Dimensions of Fibers Obtained from Some Non-Wood Species (Hurter, 1988).

Source of fibers		Average fiber length μm (L)	Average fiber diameter μm (D)	L:D-ratio
Cereals	-rice	1410	8	175:1
	-wheat, rye, oats, barley, mixed	1480	13	110:1
Grasses	-esparto	1100	9	120:1
	-sabai	2080	9	230:1
Reeds	-papyrus	1500	12	125:1
	-common reed	1500	20	75:1
	-bamboo	1360-4030	8-30	135-175:1
	-bagasse	1700	20	85:1

Non-wood plant fibers can be divided into several groups depending on the location of the fibers in the plant. Ilvessalo-Pfäffli (1995) has described for fiber types: grass fibers, bast fibers, leaf fibers and fruit fibers. Grass fibers are also termed stalk or culm fibers.

Wheat (*Triticum aestivum* L.) is the monocotyledon that is used most in commercial pulping. However, fibers from rye (*Secale cereal* L.), barley (*Hordeum vulgare* L.) and oat (*Avena sativa* L.) are similar to those of wheat (Ilvessalo-Pfäffli, 1995) and they could also be used in papermaking.

2.2.2 Chemical Composition

Table 2.3-Content of Alpha-Cellulose, Lignin, Pentosan, Ash and Silica (% of Dry Matter) in Selected Fiber Plants. Adapted from Hurter (1988).

Plant species		Alpha-cellulose %	Lignin %	Pentosans %	Ash %	SiO_2 %
Stalk fibers (grass fibers)						
Cereals	-rice	28-36	12-16	23-28	15-20	9-14
	-wheat	29-35	16-21	26-32	4-9	3-7
	-oat	31-37	16-19	27-38	6-8	4-7
	-barley	31-34	14-15	24-29	5-7	3-6
	-rye	33-35	16-19	27-30	2-5	0.5-4
Grasses	-esparto	33-38	17-19	27-32	6-8	2-3
	-sabai	-	17-22	18-24	5-7	3-4
Reeds	-common reed	45	22	20	3	1.5-3
	-bamboo	26-43	21-31	15-26	1.7-5	0.7-3
	-bagasse	32-44	19-24	27-32	1.5-5	
Wood fibers						
Coniferous trees		40-45	26-34	7-14	1	<1
Leaf trees		38-49	23-30	19-26	1	<1

Chemical composition of the candidate plant gives an idea of how feasible the plant is as raw material for papermaking. The fibrous constituent is the most important part of the plant. Since plant fibers consist of cell walls, the composition and amount of fibers is reflected in the

properties of cell walls. Cellulose is the principal component in cell walls and in fibers. The non-cellulose components of the cell wall include hemicelluloses, pectins, lignin and proteins, and in the epidermal cells also certain minerals. The amount and composition of the cell wall compounds differ among plant species and even among plant parts and they affect the pulping properties of the plant material (McDougall et al., 1993).

2.3 Commercial and Potential Methods for Pulping Non-Woody Plants

Table 2.4-Commercial and Potential Pulping Methods for Non-Woody Plants. Adapted from Katri (2001).

Process	Major pulping chemical	Commonness
Soda	NaOH	Commonly used
Kraft	NaOH + Na_2S	Commonly used for wood
Sulphite	$NaHSO_3$ and/or Na_2SO_3	Commonly used
Phosphate	Na_3PO_4	Potential method
Milox	Formic acid	Potential method
IDE	NaOH, sodium carbonate, ethanol-water blend	Potential method
Alcell	Ethanol-water blend	Potential method

Pulping for papermaking is a process of delignification, where by lignin is chemically dissolved permitting the separation of fibers in the raw material. “Paper pulp” is actually an aggregation of the cellulosic fibers that are liberated from the plant material (Biermann, 1993). It has been estimated that there are about 40 different processes suitable for pulping non-woody plants, but only a few of them have been used commercially (Katri, 2001).

The most used methods include alkaline processes such as sulphate (Kraft) - and soda (NaOH) - methods and also sulphite methods. The most commonly used commercial method in pulping non-woody species in countries producing non-wood pulp is still the soda method (Sadawarte, 1995). The soda process is a common method for producing non-wood or straw pulp (Katri, 2001). In the soda process the cooking chemical is mainly sodium hydroxide. This process leaves more insoluble carbohydrates in pulp and gives a better pulp yield than Kraft method. However, the strength properties and lignin content are similar in pulps produced with the soda and the Kraft processes (Katri, 2001). The soda process was the basis for the development of the straw pulping industry in Europe (Katri, 2001). Various modifications to the kraft and soda processes have been devised in order to attempt to overcome low pulp yields and environmental problems. These generally involve the addition of chemicals to the digest liquor. The most important of these is anthraquinone (AQ). The benefits of AQ pulping include increased delignification rates together with reduced alkali charges and improved pulp properties (Bajpai, 2005).

2.4 Applications and Uses of Non-Wood Pulps

The fiber length, the length to diameter ratio, the fiber length distribution and the chemical composition of the non-wood pulps vary over a wide range. As might be expected, the papermaking characteristics of the non-wood pulps also vary greatly-much more so than those of wood pulps (Hurter, 1988).

In some cases, non-wood pulps are substituted for wood pulp, in papers normally produced from wood pulp when wood is available. In other cases, the non-wood pulps are used to produce specialty papers that cannot be produced readily from wood pulps; in yet other cases, non-wood pulps are used as additives to impart some special characteristic that cannot be obtained by using wood pulp alone (Hurter, 1988).

As pulps from plant stalks are generally short fibered, it is not possible to produce papers of substantial strength from pulps based on plant stalks alone because of the short fiber length. Bamboo pulp is an exception because of the high fiber length to diameter ratio which gives it characteristics closer to those of softwoods. However, short fiber pulps can be readily used for

the production of writing and printing papers as strength is not an important factor. In fact, pulps from stalk fibers will form very uniform sheets free of the cloudy and wild formation that can occur when using long fiber pulps (Hurter, 1988).

Since stalk fiber pulps have high hemicellulose content, they are easy beating pulps and very little power is required for stock preparation. This allows the production of greaseproof and glassine papers with very low power consumption. The high hemicellulose content makes stalk fibers ideally suited for the production of corrugating medium. Cereal straws, and especially bagasse, produce corrugating medium equal to the best produced from wood. Short fiber pulps are also suitable for the production of multi-ply boards though some long fiber pulp is required for the top layer to provide the necessary resistance to bending (Hurter, 1988).

2.5 Cereal Straw as a Source of Pulp

Straw, the above-ground part of the cereal plant that remains after the nutrient grain or seed has been removed, comprises about half the total dry weight of the crop. For many centuries, straw was valued as the most useful by-product of cereal production, and it has been used for feeding livestock, bedding, growing mushroom, and so on (Staniforth, 1979). Agricultural crop residues, such as straws of wheat, barley, rice, maize, oats, rye, and cotton, as well as sugarcane bagasse and other residues, represent an enormous underutilized energy resource, which has a great potential as feed for ruminants and also as raw materials for paper, chemicals, and other technical products (Theander, 1985).

Generally, for every ton of cereal production worldwide, about 1.5 tons of straw is obtained as a by-product. World production of cereals exceeds 1000 million tons per annum, which means about 1500 million tons of cereal straw is produced each year, in which china produce more than 700 million tons cereal straws per year (Stacey, 1976). Straw and other fibrous by-products from cereals available in the world amount to approximately 3000 million tons per year (Kossila, 1984). Because of the enormous quantity of straw, utilization of straw to the utmost extent is now demanding attention in the major cereal-growing areas of the world.

One of the most traditional utilizations of straw is as feed for livestock. Unfortunately, we notice that even though straw contains enough cellulose, which makes it an excellent source of energy for ruminants, it is a poor-quality feed in its natural state. The limited use of straw as feed is due to its low rate of degradation in the rumen, low digestibility, and low voluntary intake (Ørskov, 1985; Jackson, 1977). This is caused by the chemical structure of the straw, which limits the digestion of cellulose and hemicelluloses. The chemical factors include lignification, silicification, crystallinity of cellulose, and other factors (Han et al., 1974). The problem of straw being used for livestock feeding is discussed in detail by Han et al. and Morrison.

The demand for paper has increased significantly in recent years. The current annual production of pulp cannot meet the increasing demand, which continues to grow at a dramatic rate. This steady increase in the demand of paper is gradually leading to a worldwide shortage of wood fiber supplies. The virgin forests from which most of the pulp for paper has been obtained for the past 100 years are shrinking. In addition, environmental and population growth pressures are contributing to long-range changes in forest-land management practices, which reduce the harvest of wood for wood products and for pulp and paper manufacture. One possible solution to this problem lies in the use of annual and non-wood plants (Run-Cang, 2010).

A number of non-wood fibers are in use all over the world for making paper and other products. Straw materials are by far the largest source of non-wood fibers, followed by bagasse and bamboo. Straw was used for the first time as a raw material for paper in 1800, and in 1827, the first commercial pulp mill began operations in the United State using straw. In many countries, straw has been used for paper and board production, and interest in this field continues to grow. This is particularly important in these countries where the pulp wood availability is extremely limited. Wheat and rye straws are used in some European countries, such as Bulgaria, Denmark, Greece, Holland, Hungary, Italy, Rumania, Spain, and Yugoslavia, where pulpwood supplies are limited, and the purchase of wood pulp from outside sources is too expensive to support local paper production. The growing utilization of cereal straws has received the attention of many developing countries, particularly Algeria, Argentina, China, Egypt, India, Indonesia, Mexico, Pakistan, Sri Lanka, Syria, and Turkey. In

these countries, corrugating medium, board, and packaging paper are produced from high-yield unbleached straw pulps; bleached straw pulp is used as a major furnish for fine-quality writing, printing, and other paper grades. The greatest part of this increase is attributed to the developing market economies, especially in Asia. Most of the world's increased use of non-wood plant fibers has been attributed to the tremendous increase in non-wood pulping capacities in China. At present, China produces more than two-thirds of non-wood pulp produced worldwide. Major agriculture residues used in China's pulp and paper industry include wheat straw and bagasse. Straw is a major source of fiber for the paper industry in China, which is mainly due to its ready availability (Run-Cang, 2010).

The main drawbacks that are considered to limit the use of non-wood fibers are the difficulties in collection, transportation, and storage. Besides, straw contains significant amounts of silica, ranging approximately from 3 to 13.3%, which creates potential problems in conventional chemical recovery systems. Despite these drawbacks, the use of straw shows potential as a means of addressing the shortage of raw materials for paper manufacture (Run-Cang, 2010). Furthermore, the production of pulp from non-wood resources has many advantages such as easy pulping capability, excellent fibers for the special types of paper, and high-quality bleached pulp. Finally, we should note that the analysis of fiber morphology and chemical composition of plant material has been useful in searching for candidate fiber crops. This has provided an indication of the papermaking potential of various species. Morphological characteristics, such as fiber length and width, are important in evaluating the pulp quality of fibers, and the chemical composition of the candidate plant gives an idea of the feasibility of using the plant as a raw material for papermaking (Run-Cang, 2010).

2.6 Challenges in Non-Wood Processing

The main problems associated with using industrially non-wood materials are the logistics of the bulky raw material and its typically short harvesting time. Thus, the raw material must be stored between harvest seasons. If the raw material is stored outside under prevailing climate conditions, moisture and biological activity easily cause the material to decay. In addition, non-wood plants usually have high silica content and the silicates dissolve in alkaline cooking liquor which makes alkaline recovery difficult and in many cases places an excessive burden

on the local environment. Finally, the poor drainage of produced non-wood pulp results in low production rates (Anja, 2011).

Typically the processes are adapted from wood processing which benefit from the larger mill size. However, concerns associated with the local availability of non-wood raw material force pulp mills to remain small and thus lead to the need for processes to be as simple as possible in order to be competitive unless very valuable by-products can also be extracted. The benefits of utilizing agro-fibers are their generally lower lignin content compared with woods (Anja, 2011).

Generally, non-woods are easier to pulp and thus are cooked at low temperatures with lower chemical charge. From a farming and agro industrial point of view, non-food applications can generate additional income alongside income from food crops or cattle production. In addition, paper production from non-wood fibers could help in reducing the need to procure pulpwood from natural forests and the requirement for large-scale plantations. To conclude, annual plants are a potential raw-material source for the chemical pulping industry (Anja, 2011).

Table 2.5-The Advantages and Disadvantages of Straw as a Fiber Source (Biermann, 1993).

Advantages	*Disadvantages*
By product from agriculture	Transportation and storage problems
Often cheaper than wood	Straws are bulky and contain silica
Large annual crop - 1 to 10 tons per acre per year	Short harvest time of 1 to 2 months; thus heavy drain on capital
Needs little refining	Degrades very quickly - high losses
Makes excellent filler, good printing and smoothness	Low freeness (drainage) rates and thus low production rates

3. MATERIALS AND EXPERIMENTAL WORK

3.1 Materials and Equipments

3.1.1 Major Equipments

The major equipments used are an electrically heated Autoclave, furnace (Box-type Resistance Furnace, Model SX-2f.12), Borosilicate glass (1000 ml beaker), 500μm sieve, Oven, Agitator, Water bath, balance and burette.

3.1.2 Chemicals and Reagents

The major chemicals used for pulp production from wheat straw are analytical grade sodium hydroxide (98%) and Antraquinone (AQ). Hydrogen peroxide is used for bleaching. The reagents used are potassium permanganate solution, sodium thiosulfate solution, potassium iodide solution, sulfuric acid, starch indicator solution and distilled water.

3.2 Experimental

3.2.1 Raw Material

The sun-dried wheat straw was collected from local wheat field around Addis Ababa. Before pulping, the raw material was cleaned, cut and sample pieces of approximately 2 cm to 4 cm in length were selected. The chemical composition of wheat straw was determined as follows: 42.7% cellulose, 19.4 % lignin, 6.9 % ash and the moisture content was 7.9 %.

3.2.2 Characterization of Wheat straw

3.2.2.1 Proximate Analysis

The proximate analysis of a substance is a simple means of determining the distribution of products obtained when the sample is heated under specified conditions. As defined by (ASTM 2010), proximate analysis separates the products into four groups: (1) moisture, (2) volatile matter, consisting of gases and vapors driven off during pyrolysis, (3) fixed carbon, the nonvolatile fraction of sample, and (4) ash, the inorganic residue remaining after

combustion. Proximate analysis is the most often used analysis for characterizing a material in connection with their utilization.

Ash content:

Sample was measured (1 gram) taken and weighted in a crucible (W_1). It was then heated to 650 ^{0}C for 3 hr. During this test, the crucible was left open. After heating to the required temperature and time, the crucible was cooled in desiccator and then reweighed (W_2).

The ash content was determined by following the formula:

$$\% \, ash \, content = \frac{W_2}{W_1} * 100 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 3.1$$

Where:

W_1 = weight of dry sample before heating (gram).

W_2 = weight of ash (gram).

Moisture content:

1gram of sample was measured and taken in a crucible. It was spread nicely on the crucible and weighed (W_1). It is heated then to 105 ^{0}C for 6 hrs. The crucible was left open during the heating process. After heating sample was removed, cooled in desiccators and then weighed until constant weight is obtained (W_2).

The moisture content was determined by following the formula:

$$\% \, moisture = \frac{W_1 - W_2}{W_1} * 100 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 3.2$$

Where:

W_1 = weight of sample and crucible before drying (gram).

W_2 = weight of sample and crucible after drying (gram).

3.2.2.2 Lignocellulosic Composition

Cellulose

Amount of cellulose were determined based on standard procedures given in (Pereira, 1988) as follows.

An acid solution was prepared by mixing H_2SO_4 and CH_3COOH. A weighed sample of oven dried wheat straw was then put in the vessel containing this solution. The mixture was kept in a water bath that was maintained at 40 ^{O}C for 35 minutes. After allowing it to settle for few minutes, the heated mixture was transferred on to glass crucible where it was filtered and simultaneously washed by CH_3OH. The crucible was dried in an oven and percentage composition of cellulose was determined as seen below.

$$\%\ cellulose = \left(\frac{M_{dried\ crucible} - M_{empty\ crucible}}{M_{initial\ straw\ sample}}\right) * 100 \quad \text{.....3.3}$$

Lignin

Lignin composition was determined following standard procedures given in ASTM D 1106 – 96 as follows.

Wheat straw sample was dissolved in 72% H_2SO_4 solution and left to stand for 2 hours after it was continuously stirred for about 1 min. The acid concentration was brought down to 3% by adding 560 ml of distilled water and the resulting solution was boiled in the water bath for 4 hours before being washed by distilled water during filtration. After oven drying the crucibles for 24 hours at 105 ^{0}C, the lignin contents were calculated as follows.

$$\%\ lignin = \left(\frac{M_{dried\ crucible} - M_{empty\ crucible}}{M_{initial\ straw\ sample}}\right) * 100 \quad \text{.....3.4}$$

3.2.3 Pulping of Wheat Straw

The pulp was obtained by using an electrically heated Autoclave, with the required instruments for measurement and control of the pressure and temperature, which is found at the process engineering laboratory of School of Chemical and Bio-Engineering. In each experiment 60g of wheat straw was used. The soda concentrations, temperatures and times used were 10–14% (on dried raw material), 155–165 ^{0}C and 30–50 min, respectively. All tests were performed at the same anthraquinone concentration (1% on dried raw material) and the solid/liquor ratio was fixed to 1/10.

The raw material was cooked in the Autoclave. Next, the cooked material was washed with water on 500μm sieve.

The kappa number of the pulp was determined according to ISO standards. Pulp yield was determined by weighing the oven dried pulp.

3.2.3.1 Bleaching Process

Pulps prepared by most pulping processes are too dark in color to be used for many paper products without some form of bleaching. Bleaching of pulp is done to achieve a number of objectives. The most important of these is to increase the brightness of the pulp so that it can be used in paper products, such as printing grades and tissue papers. For chemical pulps an important benefit is the reduction of fiber bundles and shives as well as the removal of bark fragments. This improves the cleanliness of the pulp. Bleaching also eliminates the problem of yellowing of paper in light, as it removes the residual lignin in the unbleached pulp (Bajpai, 2005).

Bleaching experiments were carried out in 1000ml beakers by using alkaline-H_2O_2. The pH was first adjusted between 10 and 11 with NaOH. Then 4 percent H_2O_2 was added in one stage. The bleaching time was 1hour at 80 ^{0}C.

3.2.4 Analysis and Characterization of the Product

The products from each experiment were collected and measured for different parameters as follows.

Yield

Percentage yield of the pulp from each experiment was calculated as:

$$\%\ yield\ of\ pulp = \left(\frac{M_{\ after\ cooking(washed\ \&\ dried)}}{M_{\ before\ cooking\ (feed)}}\right) * 100 \quad \text{.....3.5}$$

Kappa number

The kappa number of pulp is an important parameter in pulp manufacturing. It is used for indirectly indicating lignin content, relative hardness, and bleachability of pulp. Once the kappa number is known, the amount of bleaching agent needed for achieving desired pulp brightness can then be ascertained. The pulp kappa number can be determined by the volume of 0.02 mole/liter (0.1N) potassium permanganate ($KMnO_4$) solution consumed through an oxidation reaction by 1 gram of moisture-free or oven dry (O.D) pulp in an acidic medium, where potassium permanganate, also referred to herein simply as permanganate, is a strong oxidation agent.

Presently, the titration method is a universally known and commonly used method for measuring the kappa number of various pulps. This titration method is described in Tappi Test Methods—T236 cm-85, Tappi Press, 1996.

Using the titration method, the pulp kappa number is calculated using the difference between the initial volume of potassium permanganate blank solution and the final volume of potassium permanganate remaining after the oxidation of lignin in the pulp-permanganate solution. It is known in the art that potassium permanganate blank solution is simply potassium permanganate solution without pulp. The final volume is determined by titration to determine how much unconsumed potassium permanganate remains after a predetermined time period. In accordance with the method, the final volume is measured after ten minutes, thereby presuming that the oxidation of lignin in a fiber or pulp sample is complete after that

time. Also, the titration method is performed wherein the pulp-permanganate solution temperature is maintained at 25°C. and under an initial H+ concentration of 0.4 mol/L, or pH of about 0.4, acidic conditions (Tappi Press, 1996).

The kappa number is the volume (in milliliters) of 0.1N potassium permanganate solution consumed by one gram of moisture-free pulp under the conditions specified in this method. The results are corrected to 50% consumption of the permanganate added.

The kappa number of the pulps from each experiment was determined according to the Tappi-T236 om-99 test method as follows:

- Small amount of pulp specimen was weighed and stirred in 500ml distilled water until free of fiber clots and undispersed fiber bundles.
- The test specimen was transferred to 2000 ml reaction beaker and enough distilled water added up to the total volume of 795 ml.
- The beaker was placed in the water bath adjusted to 25 ^{0}C during the entire reaction and continuously stirred.
- 100 ml of potassium permanganate solution and 100 ml of the sulfuric acid solution was pipetted into a 250-ml beaker. The mixture was brought to 25 ^{0}C quickly and added to test specimen immediately, simultaneously a stopwatch was started. The beaker was rinsed with distilled water not more than 5ml.
- At the end of exactly 10.0 min, the reaction was stopped by adding 20 mL of the potassium iodide solution from a graduated cylinder.
- Immediately after mixing, but without filtering out the fibers, the free iodine was titrated with the sodium thiosulfate solution, adding a few drops of the starch indicator toward the end of the reaction.
- A blank determination was carried out using exactly the same method as above but omitting the pulp.

The kappa number is calculated using the following formula,

$$K = \frac{p*f}{w} \text{ and } p = \frac{(b-a)N}{0.1} \quad \text{.....3.6}$$

Where:

K = kappa number

f = factor for correction to a 50% permanganate consumption, dependent on the value of p (see Table 3.1 below)

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

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

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

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

N = normality of the thiosulfate

Table 3.1-Factors *f* to Correct for Different Percentages of Permanganate Used.

P	**+ 0**	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**
30	0.958	0.960	0.962	0.964	0.966	0.968	0.970	0.973	0.975	0.977
40	0.979	0.981	0.983	0.985	0.987	0.989	0.991	0.994	0.996	0.998
50	1.000	1.002	1.004	1.006	1.009	1.011	1.013	1.015	1.017	1.019
60	1.022	1.024	1.026	1.028	1.030	1.033	1.035	1.037	1.039	1.042
70	1.044									

Factors in Table 3.1 are based on the equation: $\log K = \log p/w + 0.00093\ (p\text{-}50)$.

3.2.4.1 Hand Sheet Paper Properties

Laboratory sheets were made for physical tests at Ethiopian Pulp and Paper Factory located at Wonji. Tensile index, tear index and burst index were determined as follows:

Tensile strength

Tensile strength is the maximum tensile force per unit width that a test piece of paper or board will withstand before breaking in a tensile test.

Tensile index is tensile strength divided by grammage.

If M is the mass and A is the area of test specimen in the units of measurements, then the grammage per square meter (gm/m^2) may be calculated by the formula:

$$G = K * \frac{M}{A} \quad \text{.....3.7}$$

Where:-

$K = 10^4$

M = mass of test specimen, gm

A = area of test specimen, m^2

Schopper type tensile strength tester was used for tensile test according to the following procedure:

From specimens of undamaged paper 15 mm wide and 230 mm long test pieces were cut.

The test piece was placed in the clamps making sure that any slack is eliminated.

All readings were recorded except for test pieces that break with in 2 mm of clamming line.

Calculation:

Tensile strength

$$X_1 = \frac{a}{b} \quad \text{.....3.8}$$

Where:-

X_1 = tensile strength (kN/m)

a = maximum tensile force (N)

= instrument reading = kg

= to change into (N):- ($kg * 9.807$)

b = initial width of the sample in (mm)

Tensile index

$$X_2 = 1000 * \frac{X_1}{G} \quad \text{.....3.9}$$

Where:-

X_2 = tensile index (Nm/gm)

X_1 = tensile strength (KN/m)

G = grammage (gm/m^2)

Tearing resistance

The tearing resistance is the force required to continue the tearing of an initial cut in a single sheet of paper.

Tear index is the tearing resistance of a paper (board) divided by its grammage. The result is expressed in millinewton square meters per gram (mNm^2/gm).

Principle of tear measurement

A test piece of superimposed sheets (normally four), with a specified pre-cut slit, is torn through a fixed distance using pendulum, which applies the tearing force by moving in a plane perpendicular to the initial plane of the test piece. The work done in tearing the test piece is measured by the loss in potential energy of the pendulum.

The average tearing force (work done divided by the total distance torn) is indicated by a scale on the pendulum or a digital display.

The tearing resistance of the paper is determined from the average tearing force and the number of sheets comprising the test piece.

$$X = \frac{a}{G} \quad \text{.....3.10}$$

Where:-

X = the tear index (Nm^2/kg)

G = grammage (gm/m^2)

a = tearing resistance (mN)

Bursting strength, burst factor and index

The bursting of paper is the maximum uniformly distributed pressure, applied at the right angle to its surface that a test piece will stand under standardize conditions.

The burst index is the bursting strength divided by basis weight (grammage).

Motor driven Mullen (burst) tester was used to determine burst index according to the following procedure:

- The test specimen used for the test was 2.5 by 2.5 inches.
- The test piece was clamped in the tester tightly.
- The maximum reading pointer was set to zero position.
- The pump motor was started and the pumping system was engaged and then the test piece was waited to burst.
- Finally the maximum reading pointer was read.

Instrument reading was in kg/cm^2 and to change to SI unit of bursting strength it was multiplied by 98.07.

Burst factor (Tappi Standard T 205M)

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

$$Burst\ factor = \frac{Bursting\ Strength\ (kg/cm^2)}{Basis\ weight\ (gm/m^2)} * 1000 \quad \ldots\ldots\ldots\ldots\ldots\ldots 3.11$$

Burst index: - Bursting strength divided by basis weight.

$$X = \frac{a}{W} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 3.12$$

Where:-

X = Burst index (Kpa m^2/Kg)

a = Burst strength in Kpa

W = Basis weight (gm/m^2)

3.3 Experimental Design

3.3.1 Studied Factors

The experimental factors studied in the production of wheat straw pulp were selected based on the significance of the influence on pulp yield.

Effects of the following experimental factors were thus studied:

i. Soda concentration in the cooking liquor – C (%)
ii. Cooking temperature – T (^{0}C); and
iii. Cooking time – t (min)

A total of 20 runs were required to complete the experiment. Each of the three factors had three levels as shown in the table 3.2. The mass of wheat straw, the solid to liquor ratio, and the percentage of antraquinone were fixed to be 60gm, 1/10, 1% respectively. The soda concentration was based on the mass of dried wheat straw.

Table 3.2-Experimental Factors and Corresponding Levels.
Source: *Tappsa Journal March 2009* Page 36.

Factors	Units	Low (-1) level	Intermediate (0) level	High (+1) level
Soda concentration	%	10	12	14
Cooking temperature	^{0}C	155	160	165
Cooking time	minute	20	35	50

3.3.2 Selected Type of Experimental Design and Analysis

The production of pulp was studied using a standard Response Surface Methodology design called a central composite design (CCD). This method can optimize the effective parameters (operating condition for preparation of the samples) with a minimum number of experiments. It also helps to analyze the interaction effect between those parameters. Generally, the CCD consists of a 2k factorial runs with 2k axial or star runs and n_c center runs (6 replicates) [Montgomery, 1997], where k is the number of parameters.

Figure 3.1 shows the layout provided by CCD for experiments needed to study a 3-parameter (P_1, P_2 and P_3) process. The factorial portion is represented by the points forming a box and the blue points (axial points) are located outside the cube passing through the center point.

The axial points are located at (± α, 0, 0), (0, ±α, 0), (0, 0, ±α) where α is the distance of the axial point from center, for this research face centered type is selected (i.e. α = 1). Center runs include 6 replications which are performed by setting all factors at their midpoints to estimate the residual error (Montgomery, 2009).

Six replications were performed at the center point, eight runs were performed at the axial points and additional six runs were done at the face center of the cube. Therefore, the total number of experiments (N) required is determined as;

$$N = 2^k + 2k + n_c = 2^3 + 2*3 + 6 = 20 \quad \text{……..3.13}$$

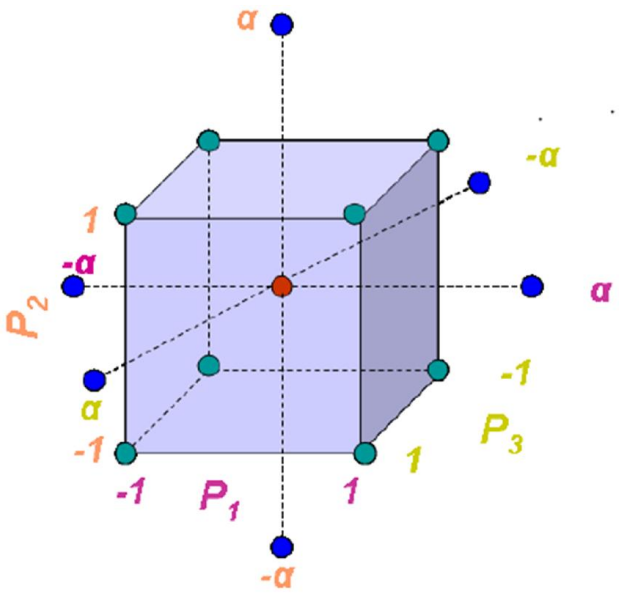

Figure 3.1: Central Composite Design for Three Factors.

According to the range of each variable, the independent variables are coded to the (-1, 0, +1) interval, these are low, intermediate and high levels respectively.

Therefore, response surface methodology using center composite design method was used to optimize the maximum yield as well as the low kappa number.

RSM approach enabled the analyses of influences from factors' interaction in addition to main effects (Montgomery, 2009). Not only that but it also helped to further quantify the relationships between one or more measured responses and the vital input factors (Stat-Ease, Inc., 2007).

The experimental design and analysis of data, as well as the regression computations to statistically fit the response and factors' into a model made use of the software package Design-Expert® 7.1.

The effects of soda concentration in the feed, cooking temperature, and cooking time on the percentage yield from the experiment runs were thus studied.

Table 3.3-Samples Prepared under Different Operating Conditions.

St	Run	Block	Factor 1 Soda Conc.	Factor 2 T (^{0}C)	Factor 3 t (min)	Response 1 Yield (%)	Response 2 Kappa Number
3	1	Block 1	10	165	20		
19	2	Block 1	12	160	35		
12	3	Block 1	12	165	35		
8	4	Block 1	14	165	50		
5	5	Block 1	10	155	50		
4	6	Block1	14	165	20		
15	7	Block 1	12	160	35		
20	8	Block 1	12	160	35		
18	9	Block 1	12	160	35		
10	10	Block 1	14	160	35		
13	11	Block 1	12	160	20		
7	12	Block 1	10	165	50		
11	13	Block 1	12	155	35		
17	14	Block 1	12	160	35		
14	15	Block 1	12	160	50		
2	16	Block 1	14	155	20		
9	17	Block 1	10	160	35		
1	18	Block 1	10	155	20		
16	19	Block 1	12	160	35		
6	20	Block 1	14	155	50		

4. RESULTS AND DISCUSSION

4.1 Characterization of Wheat Straw

The results obtained from analyses that were used to characterize wheat straw are the following.

4.1.1 Proximate Analysis

The proximate analysis (composition) of wheat straw was done, before pulping process or cooking, in order to know the moisture content, and ash content. The proximate analysis was carried out using Box-type furnace found in our school. The proximate analysis was done using (ASTM; D1762-84 (Reapproved 2001)) and the result obtained is shown in table below.

Table 4.1-Proximate Analysis of Wheat Straw

Moisture (%)	Ash (%)
7.9	6.9

The above result shows that the ash content of the raw material (wheat straw) is found to be relatively higher when compared to some other non-wood plants in the literature like common reed, bamboo, bagasse, and rye straw which are used for pulp production but it is lower when it is compared to rice straw.

4.1.2 Lignocellulosic Composition

The lignin and cellulose composition of wheat straw was determined and the result is given in the table below.

Table 4.2-Lignin and Cellulose Content of Wheat Straw

Lignin (%)	Cellulose (%)
19.4	42.7

These results were compared with corresponding values given in literatures for woody and non-woody plants. It was thus shown that wheat straw had low lignin content especially when it is compared to woody plants. Lower lignin content needs lower chemicals during cooking and bleaching stages. The wheat straw cellulose content was found to be around the average.

4.2 Pulping Results

Yield

The amount of pulp produced at different operating conditions is provided in the table below. The experiments were done with two replications and the result is given as mean percent yield with the corresponding variance.

Table 4.3-Mean Percentage Yield of the Pulp Produced (dry weight basis).

Run	Experimental Factors			Mean Yield of Pulp (%)	Variance
	Soda Conc. (%)	T (^{0}C)	t (min)		
1	10	165	20	44.8	3.92
2	12	160	35	35	4.5
3	12	165	35	34.5	1.28
4	14	165	50	30	2.42
5	10	155	50	33.7	1.62
6	14	165	20	33.3	7.22
7	12	160	35	32.8	3.38
8	12	160	35	35.8	5.78
9	12	160	35	34.8	8
10	14	160	35	29.3	3.92

Run	Experimental Factors			Mean Yield of Pulp (%)	Variance
	Soda Conc. (%)	T (^{0}C	t (min)		
11	12	160	20	37.5	5.12
12	10	165	50	35.8	2.88
13	12	155	35	31.8	3.92
14	12	160	35	33.8	2.42
15	12	160	50	34	1.62
16	14	155	20	34.2	2
17	10	160	35	42.8	1.28
18	10	155	20	43.5	1.62
19	12	160	35	34.3	3.92
20	14	155	50	33.5	1.62

The maximum pulp yield (44.8%) was obtained when 10% soda concentration was used at 165^{0}C and at 20 minutes (Run #1). The second maximum pulp yield (43.5%) was obtained when 10% soda concentration was used at 155^{0}C and 20 minutes (Run #18). On the other hand, the minimum pulp yield (29.3%) was obtained when 14% soda concentration was used at 160^{0}C and 35 minutes (Run #10).

Kappa Number

The residual lignin present in the pulp is expressed in terms of the kappa number. The kappa number of wheat straw soda-AQ pulp was determined and given in table 4.4 below.

Table 4.4-Mean Percent Yield and Corresponding Kappa Number.

Run	Experimental Factors			Mean Pulp Yield (%)	Kappa Number
	Soda Conc. (%)	T (^{0}C)	t (min)		
1	10	165	20	44.8	22.2
2	12	160	35	35	12.4
3	12	165	35	34.5	12.1
4	14	165	50	30	9.3
6	14	165	20	33.3	10.7
5	10	155	50	33.7	22.8
7	12	160	35	32.8	12.3
8	12	160	35	35.8	12.5
9	12	160	35	34.8	12.4
10	14	160	35	29.3	10
11	12	160	20	37.5	16
12	10	165	50	35.8	22.3
13	12	155	35	31.8	12.5
14	12	160	35	33.8	12.3
15	12	160	50	34	12
16	14	155	20	34.2	11
17	10	160	35	42.8	22.9
18	10	155	20	43.5	23.4
19	12	160	35	34.3	12.4
20	14	155	50	33.5	9.6

According to results, the pulp from run #18 had the highest kappa number. In contrast, the pulp from run #4 had the lowest kappa number.

The kappa number of the maximum pulp yield was determined to be 22.2 (run #1) and this result is acceptable since it is easily bleachable. Therefore, for this study the optimum condition was selected to be 10% soda concentration, 165^0C and 20 min.

4.3 Effect of Processing Conditions on the Pulp Yield

Soda concentration and cooking time significantly influenced the pulp yields both separately (main effects) and interacting (interaction effects). Cooking temperature, however, had the minimal effect on the pulp yield.

4.3.1 Effect of Soda Concentration on Pulp Yield

Yield is important from economic point of view. These properties may vary owing to the cooking liquor composition. Figure 4.1 displays the effect of cooking liquor composition on yield of the pulp. It is evident from the figure 4.1 that the yield of pulp decreased with increase in the soda concentration.

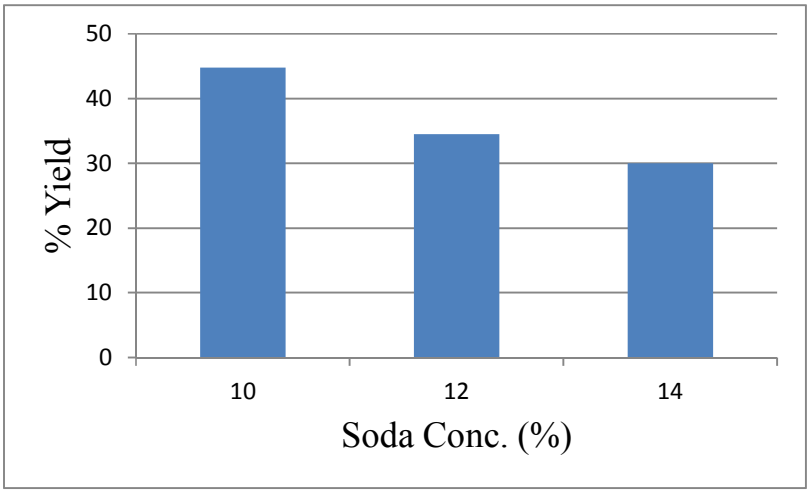

Figure 4.1: Effect of Soda Concentration on Pulp Yield

4.3.2 Effect of Temperature on the Pulp Yield

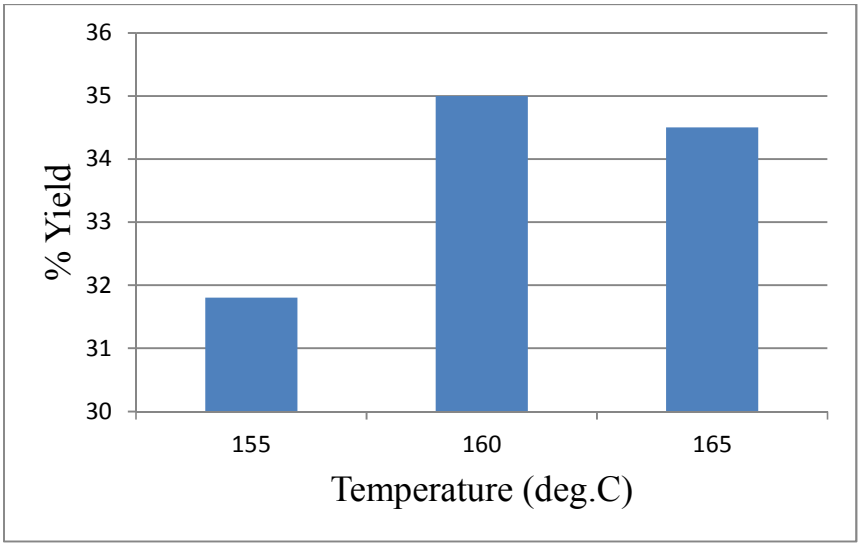

Figure 4.2: Effect of Temperature on the Pulp Yield

Figure 4.2 compares the effect of cooking temperature with the percent yield of wheat straw pulp. The graph does not show a continuous increasing or decreasing of pulp yield at a constant soda concentration and cooking time of 12% and 35 minutes respectively.

4.3.3 Effect of Cooking Time on the Pulp Yield

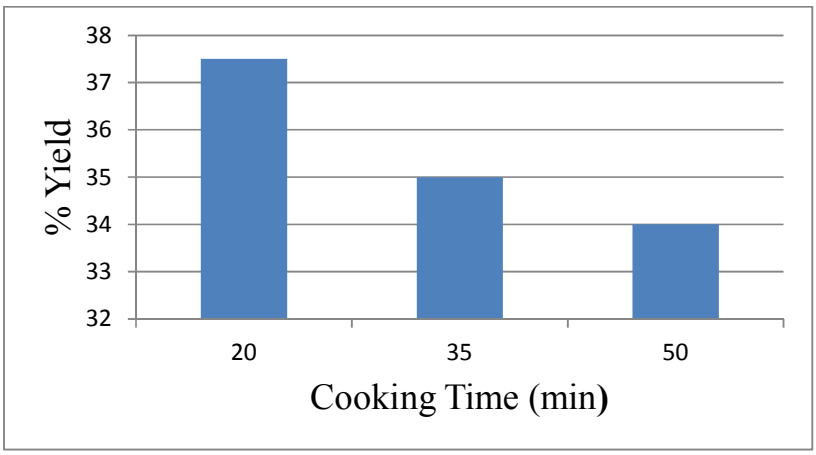

Figure 4.3: Effect of Cooking Time on the Pulp Yield

Figure 4.3 shows the effect of cooking time on the percent yield of wheat straw pulp at a constant soda concentration and temperature of 12% and 160^0C. As cooking time increases percent yield of the pulp decreases.

4.4 Effect of Processing Conditions on Kappa Number of the Pulp

4.4.1 Effect of Soda Concentration on Kappa Number

Figure 4.4 shows the effects of soda concentration on kappa number during the soda –AQ pulping of wheat straw.

It can be seen that soda concentration had a significant influence on kappa number. An increase in soda concentration at constant temperature and time resulted in a clear reduction in kappa number.

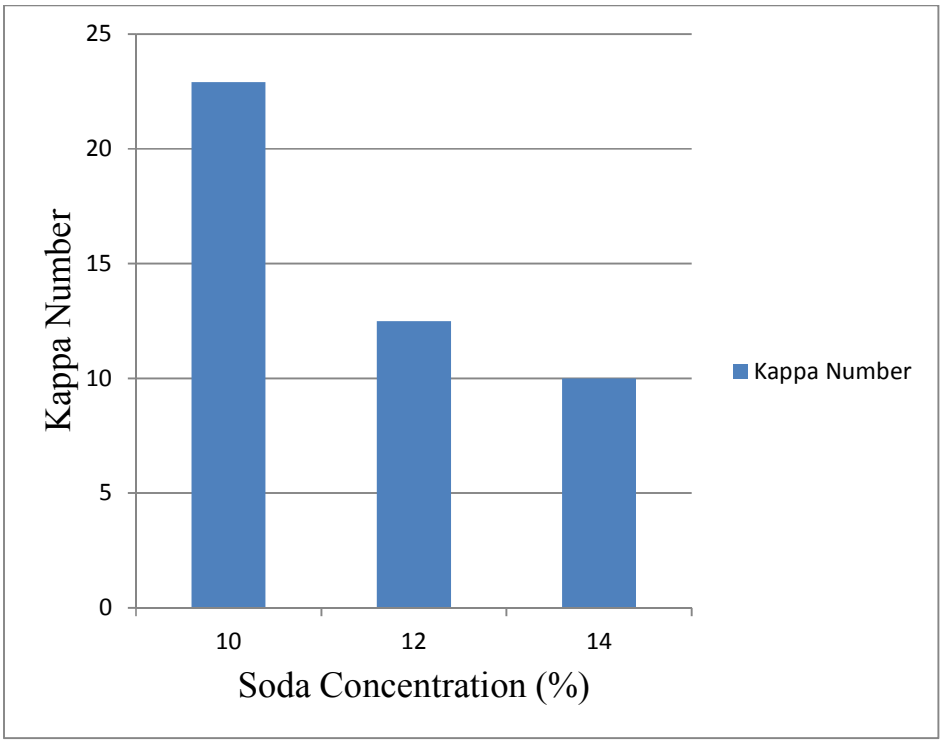

Figure 4.4: Effect of Soda Concentration on Kappa Number

4.4.2 Effect of Cooking Time on Kappa Number

From figure 4.5 it can be seen that cooking time had a minimal effect on kappa number when it is compared to the effect of soda concentration on kappa number.

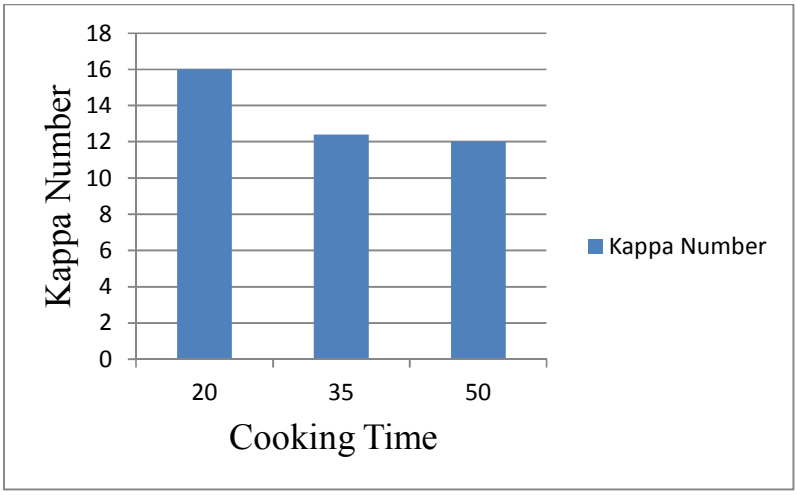

Figure 4.5: Effect of Cooking Time on Kappa Number

4.4.3 Effect of Temperature on kappa Number

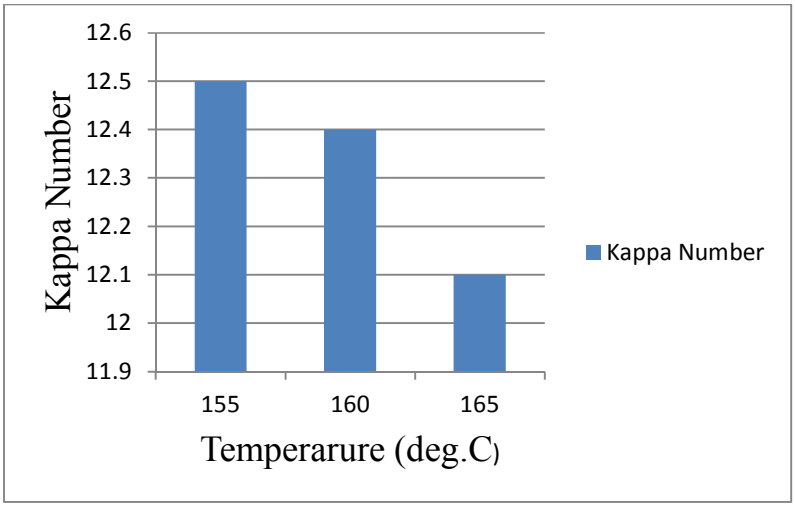

Figure 4.6: Effect of Temperature on Kappa Number.

It can be seen from figure 4.6 that cooking temperature had a minimal effect on kappa number. The graph shows the kappa number at 155^0C, 160^0C and 165^0C with constant soda concentration and cooking time.

4.4.4 Interaction Effect of Parameters

The interaction effect of the three operating conditions, namely: soda concentration, cooking temperature and cooking time are studied and the results obtained are best described using Design expert software. Therefore, the interaction effects of the parameters on the pulp yield and the kappa number was discussed.

4.4.4.1 Interaction Effect on Pulp Yield

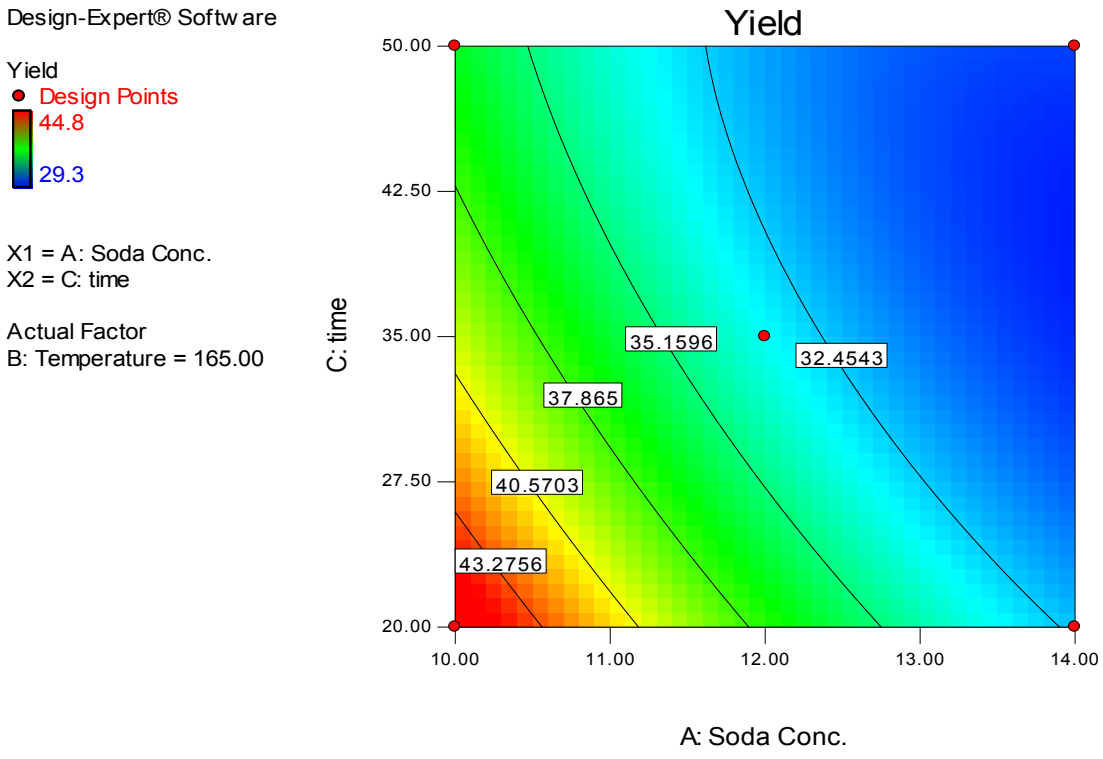

Figure 4.7: The Interaction Effect of Parameters on the Pulp Yield.

The interaction effects of the three parameters on the yield of the product can be explained using the graph (figure 4.7) shown above. The graph shows the interaction effect of the two most significant parameters (soda concentration and cooking time) keeping the cooking temperature at 165^0C. From the graph it can be seen that, as both soda concentration and cooking time decreases the pulp yield increases.

4.4.4.2 The Interaction Effect of Parameters on Kappa Number

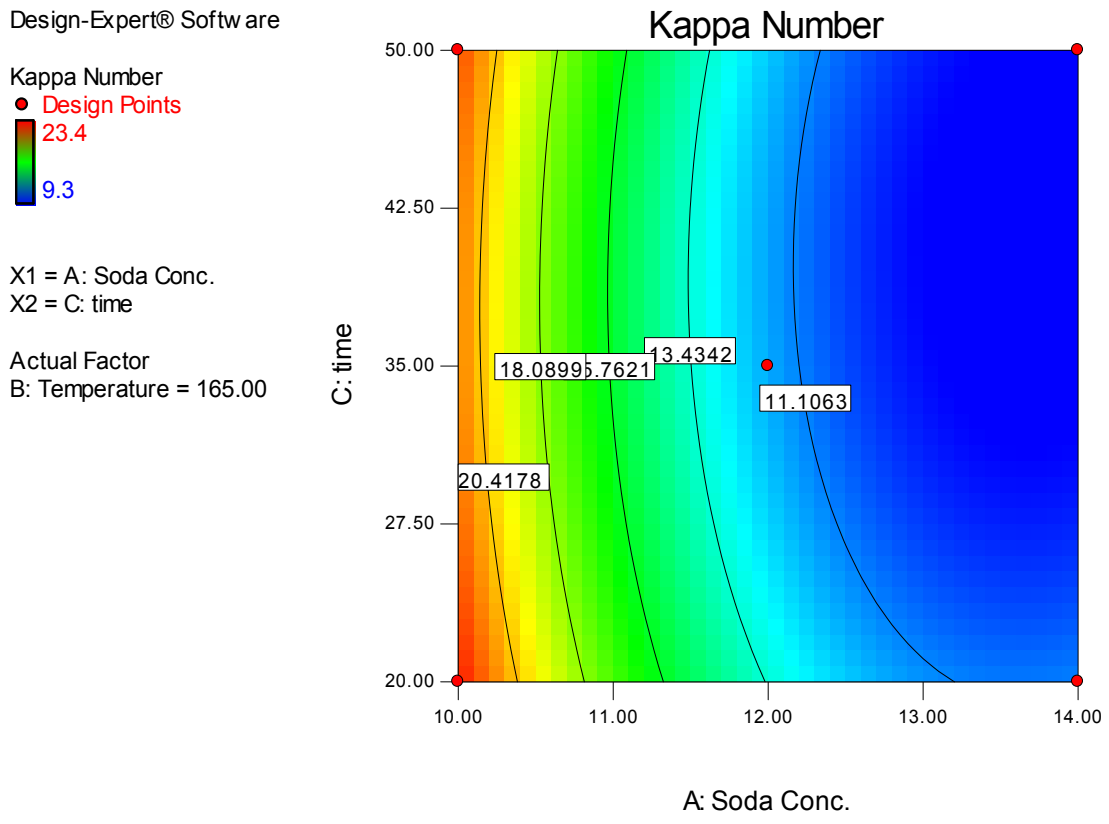

Figure 4.8: Interaction Effect of Parameters on Kappa Number.

Figure 4.8 shows, the interaction effect of soda concentration and cooking time on the kappa number of the pulp. Here also the cooking temperature is taken as 165^0C. As shown in the figure, the effect of soda concentration is more significant than cooking time on the kappa number of the pulp. The kappa number is needed to be low. The kappa number decreases as soda concentration and cooking time increases.

4.5 Physical Properties of the Hand Sheets

The physical test results of tensile index, tear index, and burst index of the hand sheets made from wheat straw soda-AQ pulp are given in table 4.5 below.

Table 4.5-The Physical Test Results of Hand Sheets

Run	Soda Conc. (%)	T (^{0}C)	t (min)	Pulp Yield (%)	Kappa Number	Tensile Index (Nm/g)	Tear Index (mNm^2/g)	Burst Index (kN/g)
1	10	165	20	44.8	22.2	67.9	7.5	7.3
2	12	160	35	35	12.4	68	7.7	7.2
3	12	165	35	34.5	12.1	68	7.6	7.2
4	14	165	50	30	9.3	67.4	8.3	7.4
5	10	155	50	33.7	22.8	67.7	7.6	7.2
6	14	165	20	33.3	10.7	67.5	7.8	7.5
7	12	160	35	32.8	12.3	69	7.6	7.3
8	12	160	35	35.8	12.5	69	7.6	7.3
9	12	160	35	34.8	12.4	69	7.6	7.3
10	14	160	35	29.3	10	68	8	7.4
11	12	160	20	37.5	16	68.2	7.5	7.2
12	10	165	50	35.8	22.3	67.8	7.6	7.4
13	12	155	35	31.8	12.5	68.1	7.4	7.2
14	12	160	35	33.8	12.3	69	7.5	7.2
15	12	160	50	34	12	68.7	7.7	7.3
16	14	155	20	34.2	11	67.6	8.1	7.3
17	10	160	35	42.8	22.9	67.8	7.4	7.4
18	10	155	20	43.5	23.4	67.5	7.3	7.2
19	12	160	35	34.3	12.4	69	7.6	7.3
20	14	155	50	33.5	9.6	67.8	7.9	7.4

The effects of soda concentration and cooking time on the physical properties of the hand sheets made from wheat straw soda-AQ pulp were studied. The study of the physical specifications of the hand sheets produced showed that their physical properties are not considerably improved with increasing the soda concentration and cooking time. Consequently, for pulping wheat straw with soda-AQ method, a relatively short cooking time (around 20 min) is recommended, as well as soda concentration of around 10% to 12%.

4.6 Statistical Analysis

4.6.1 Yield

Response 1 Yield

ANOVA for Response Surface Quadratic Model

Analysis of variance table [Partial sum of squares - Type III]

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	
Model	287.80	9	31.98	10.39	0.0005	significant
A-Soda Conc.	*162.41*	*1*	*162.41*	*52.79*	*< 0.0001*	
B-Temperature	*0.29*	*1*	*0.29*	*0.094*	*0.7655*	
C-time	*69.17*	*1*	*69.17*	*22.48*	*0.0008*	
AB	*7.60*	*1*	*7.60*	*2.47*	*0.1470*	
AC	*27.38*	*1*	*27.38*	*8.90*	*0.0137*	
BC	*0.40*	*1*	*0.40*	*0.13*	*0.7243*	
A^2	*7.28*	*1*	*7.28*	*2.37*	*0.1550*	
B^2	*4.45*	*1*	*4.45*	*1.45*	*0.2566*	
C^2	*4.84*	*1*	*4.84*	*1.57*	*0.2381*	
Residual	30.77	10	3.08			
Lack of Fit	*25.36*	*5*	*5.07*	*4.69*	*0.0576*	*not significant*
Pure Error	*5.41*	*5*	*1.08*			
Cor Total	318.57	19				

Figure 4.9: Analysis of Variance Table for Pulp Yield.

Results from the statistical analysis of experimental data showed that soda concentration had the strongest effect on pulp yield whereas cooking time had less influence.

Quadratic model was selected according to analysis results which showed significance of the model (P-value = 0.0005 for α = 0.05). F-Distribution Test for significance of model and factor effects dictated that the null hypothesis must be rejected if $F_0 > F_{\alpha,v_1,v_2}$; where ν_1 and ν_2 are the numerator and denominator degrees of freedom, respectively (Montgomery, 2009). Calculated F-Value for the model was F_0 = 10.39 whereas from table we had $F_{0.05,9,10}$ = 3.02 which confirmed the rejection of the null hypothesis. Software-generated ANOVA results showing respective F-values and other parameters are given in Figure 4-9 (see below). Other complementary information for statistical analysis of the experimental data that used quadratic model is given in the appendix.

The Model F-value of 10.39 implies the model is significant. There is only a 0.05% (α) chance that a "Model F-Value" this large could occur due to noise.

Values of "Prob > F" less than 0.0500 indicate model terms are significant. In this case A, C, AC are significant model terms.

Values greater than 0.1000 indicate the model terms are not significant.

The "Lack of Fit F-value" of 4.69 implies there is a 5.76% chance that a "Lack of Fit F-value" this large could occur due to noise.

4.6.2 Kappa Number

Results from the statistical analysis of experimental data showed that soda concentration and cooking time had significant effect on the pulp kappa number.

Quadratic model was selected according to analysis results which showed significance of the model (P-value = 0.0001 for α = 0.01). F-Distribution Test for significance of model and factor effects dictated that the null hypothesis must be rejected if $F_0 > F_{\alpha,v_1,v_2}$; where ν_1 and ν_2 are the numerator and denominator degrees of freedom, respectively (Montgomery, 2009). Calculated F-Value for the model was F_0 = 100.55 whereas from table we had $F_{0.01,9,10}$ = 4.94 which confirmed the rejection of the null hypothesis. Software-generated ANOVA results showing respective F-values and other parameters are given in Figure 4.10 (see above). Other

complementary information for statistical analysis of the experimental data that used quadratic model is given in the appendix.

Response 2 Kappa Number

ANOVA for Response Surface Quadratic Model

Analysis of variance table [Partial sum of squares - Type III]

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	
Model	476.62	9	52.96	100.55	< 0.0001	significant
A-Soda Conc.	*396.90*	*1*	*396.90*	*753.55*	*< 0.0001*	
B-Temperature	*0.73*	*1*	*0.73*	*1.38*	*0.2667*	
C-time	*5.33*	*1*	*5.33*	*10.12*	*0.0098*	
AB	*0.15*	*1*	*0.15*	*0.29*	*0.6038*	
AC	*0.66*	*1*	*0.66*	*1.26*	*0.2887*	
BC	*0.061*	*1*	*0.061*	*0.12*	*0.7402*	
A^2	*33.60*	*1*	*33.60*	*63.79*	*< 0.0001*	
B^2	*1.18*	*1*	*1.18*	*2.24*	*0.1656*	
C^2	*3.01*	*1*	*3.01*	*5.71*	*0.0380*	
Residual	5.27	10	0.53			
Lack of Fit	*5.24*	*5*	*1.05*	*184.90*	*< 0.0001*	*significant*
Pure Error	*0.028*	*5*	*5.667E-003*			
Cor Total	481.89	19				

Figure 4.10: Analysis of Variance Table for Kappa Number.

The Model F-value of 100.55 implies the model is significant. There is only a 0.01% chance that a "Model F-Value" this large could occur due to noise.

Values of "Prob > F" less than 0.0500 indicate model terms are significant.

In this case A, C, A^2, C^2 are significant model terms.

Values greater than 0.1000 indicate the model terms are not significant.

The "Lack of Fit F-value" of 184.90 implies the Lack of Fit is significant. There is only a 0.01% chance that a "Lack of Fit F-value" this large could occur due to noise.

5. CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

The demand of pulp is growing dramatically in Ethiopia. Deforestation has resulted from excessive use of wood for different activities. Therefore, the use of alternative, non-wood materials is of particular interest. In the recent past, much attention of the world agricultural research was focused on non-wood materials with perspective for environmental industrial utilization. Agricultural wastes constitute one of the main alternative raw materials for the pulp and paper industry. Production of pulp from non-wood resources has many advantages such as easy pulping capability, excellent fibers for the special types of paper and high-quality bleached pulp. It can be used as an effective substitute forever decreasing forest wood resources.

From the results of this work, it can be concluded that wheat straw can be used as a raw material for pulp and paper production. Wheat straw can be successfully pulped with soda-AQ process in different conditions. Wheat straw pulps 29.3-44.8% yield could be prepared with soda concentration (10-14% on dry basis). The operating pressure was not easily controllable and due to this the result of pulp yield might be varied slightly with pressure variation.

In any case, the maximum pulp yield was determined to be 44.8% at 10% soda concentration, 165 ^{0}C and 20 min pulping conditions.

Kappa number is the indication of residual lignin in the pulp and it was determined at different conditions. From the results of the experiment, it can be seen that as the soda concentration increases the kappa number decreases. At the maximum yield the kappa number was determined to be 22.2.

The study of the physical specifications of the hand sheets produced showed that their physical properties are not considerably improved with increasing the soda concentration and cooking time.

5.2 Recommendations

Annual production of wheat in Ethiopia is increasing from year to year. After the crop is collected high amount of residue remains on the ground. Using this residue for the production of pulp is economically advantageous.

Pulping of wheat straw with alkaline (soda and Kraft) pulping processes removes the silica from fibers. The silica appears in the black liquor as sodium silicate and/or other complex siliceous compounds. High silica content may lead to scaling in the evaporator and recovery boiler tubes, thus interfering with the chemical recovery process. Therefore, future researches should include the investigation of solving the problem of silica.

The effect of operating pressure on the quality of wheat straw soda-AQ pulp is not studied here. Considering the effect of operating pressure may help to produce a better quality of pulp.

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APPENDIX

A.1. Experimental Design and Analysis Data

A.1.1. ANOVA Table

Table A.1 ANOVA Table for % Yield

ANOVA for Response Surface Quadratic Model

Analysis of variance table [Partial sum of squares - Type III]

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	
Model	287.80	9	31.98	10.39	0.0005	significant
A-Soda Conc.	*162.41*	*1*	*162.41*	*52.79*	*< 0.0001*	
B-Temperature	*0.29*	*1*	*0.29*	*0.094*	*0.7655*	
C-time	*69.17*	*1*	*69.17*	*22.48*	*0.0008*	
AB	*7.60*	*1*	*7.60*	*2.47*	*0.1470*	
AC	*27.38*	*1*	*27.38*	*8.90*	*0.0137*	
BC	*0.40*	*1*	*0.40*	*0.13*	*0.7243*	
A^2	*7.28*	*1*	*7.28*	*2.37*	*0.1550*	
B^2	*4.45*	*1*	*4.45*	*1.45*	*0.2566*	
C^2	*4.84*	*1*	*4.84*	*1.57*	*0.2381*	
Residual	30.77	10	3.08			
Lack of Fit	*25.36*	*5*	*5.07*	*4.69*	*0.0576*	*not significant*
Pure Error	*5.41*	*5*	*1.08*			
Cor Total	318.57	19				

The Model F-value of 10.39 implies the model is significant. There is only a 0.05% chance that a "Model F-Value" this large could occur due to noise.

Values of "Prob > F" less than 0.0500 indicate model terms are significant.
In this case A, C, AC are significant model terms.
Values greater than 0.1000 indicate the model terms are not significant.
If there are many insignificant model terms (not counting those required to support hierarchy), model reduction may improve your model.

The "Lack of Fit F-value" of 4.69 implies there is a 5.76% chance that a "Lack of Fit F-value" this large could occur due to noise. Lack of fit is bad -- we want the model to fit.
This relatively low probabiity (<10%) is troubling.

Std. Dev.	1.75	R-Squared	0.9034
Mean	35.26	Adj R-Squared	0.8165
C.V. %	4.97	Pred R-Squared	0.2894
PRESS	226.36	Adeq Precision	12.674

Continued from Table A.1

"Adeq Precision" measures the signal to noise ratio. A ratio greater than 4 is desirable. Your ratio of 12.674 indicates an adequate signal. This model can be used to navigate the design space.

Factor	Coefficient Estimate	df	Standard Error	95% CI Low	95% CI High	VIF
Intercept	34.42	1	0.60	33.08	35.76	
A-Soda Conc.	-4.03	1	0.55	-5.27	-2.79	1.00
B-Temperature	0.17	1	0.55	-1.07	1.41	1.00
C-time	-2.63	1	0.55	-3.87	-1.39	1.00
AB	-0.97	1	0.62	-2.36	0.41	1.00
AC	1.85	1	0.62	0.47	3.23	1.00
BC	-0.22	1	0.62	-1.61	1.16	1.00
A^2	1.63	1	1.06	-0.73	3.98	1.82
B^2	-1.27	1	1.06	-3.63	1.08	1.82
C^2	1.33	1	1.06	-1.03	3.68	1.82

Final Equation in Terms of Coded Factors:

$$
\begin{aligned}
\text{Yield} &= \\
&+34.42 \\
&-4.03 * A \\
&+0.17 * B \\
&-2.63 * C \\
&-0.97 * A * B \\
&+1.85 * A * C \\
&-0.22 * B * C \\
&+1.63 * A^2 \\
&-1.27 * B^2 \\
&+1.33 * C^2
\end{aligned}
$$

Table A.2 ANOVA Table for Kappa Number

ANOVA for Response Surface Quadratic Model

Analysis of variance table [Partial sum of squares - Type III]

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	
Model	476.62	9	52.96	100.55	< 0.0001	significant
A-Soda Conc.	*396.90*	*1*	*396.90*	*753.55*	*< 0.0001*	
B-Temperature	*0.73*	*1*	*0.73*	*1.38*	*0.2667*	
C-time	*5.33*	*1*	*5.33*	*10.12*	*0.0098*	
AB	*0.15*	*1*	*0.15*	*0.29*	*0.6038*	
AC	*0.66*	*1*	*0.66*	*1.26*	*0.2887*	
BC	*0.061*	*1*	*0.061*	*0.12*	*0.7402*	
A^2	*33.60*	*1*	*33.60*	*63.79*	*< 0.0001*	
B^2	*1.18*	*1*	*1.18*	*2.24*	*0.1656*	
C^2	*3.01*	*1*	*3.01*	*5.71*	*0.0380*	
Residual	5.27	10	0.53			
Lack of Fit	*5.24*	*5*	*1.05*	*184.90*	*< 0.0001*	*significant*
Pure Error	*0.028*	*5*	*5.667E-003*			
Cor Total	481.89	19				

The Model F-value of 100.55 implies the model is significant. There is only a 0.01% chance that a "Model F-Value" this large could occur due to noise.

Values of "Prob > F" less than 0.0500 indicate model terms are significant.
In this case A, C, A^2, C^2 are significant model terms.
Values greater than 0.1000 indicate the model terms are not significant.
If there are many insignificant model terms (not counting those required to support hierarchy), model reduction may improve your model.

Continued from Table A.2

Std. Dev.	0.73	R-Squared	0.9891
Mean	14.55	Adj R-Squared	0.9792
C.V. %	4.99	Pred R-Squared	0.9216
PRESS	37.80	Adeq Precision	28.450

The "Pred R-Squared" of 0.9216 is in reasonable agreement with the "Adj R-Squared" of 0.9792.

"Adeq Precision" measures the signal to noise ratio. A ratio greater than 4 is desirable. Your ratio of 28.450 indicates an adequate signal. This model can be used to navigate the design space.

Factor	Coefficient Estimate	df	Standard Error	95% CI Low	95% CI High	VIF
Intercept	12.61	1	0.25	12.06	13.17	
A-Soda Conc.	-6.30	1	0.23	-6.81	-5.79	1.00
B-Temperature	-0.27	1	0.23	-0.78	0.24	1.00
C-time	-0.73	1	0.23	-1.24	-0.22	1.00
AB	0.14	1	0.26	-0.43	0.71	1.00
AC	-0.29	1	0.26	-0.86	0.28	1.00
BC	0.088	1	0.26	-0.48	0.66	1.00
A^2	3.50	1	0.44	2.52	4.47	1.82
B^2	-0.65	1	0.44	-1.63	0.32	1.82
C^2	1.05	1	0.44	0.070	2.02	1.82

A.1.2. Diagnostic Plots

Figure A-1 – Normal Plot of Residuals

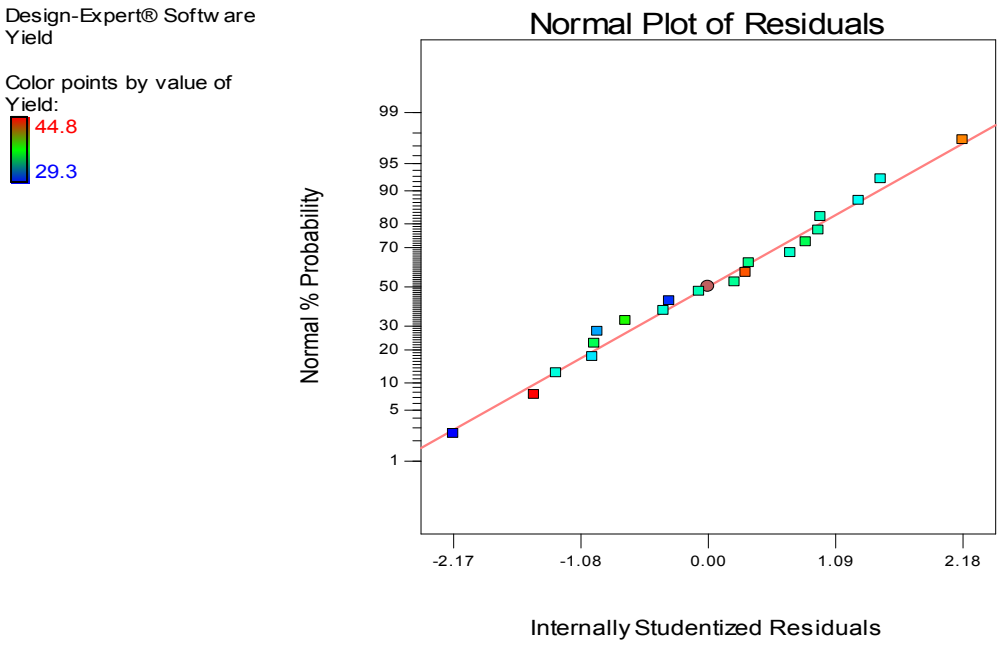


Figure A-2 – Plot of Residuals vs. Predicted Values

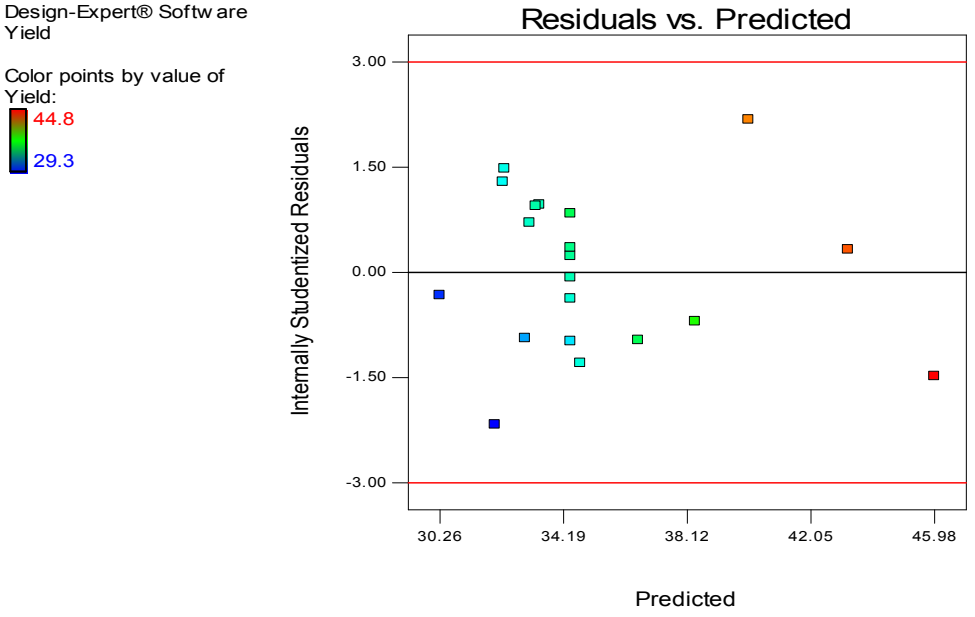


Figure A-3 – Plot of Externally Studentized Residuals

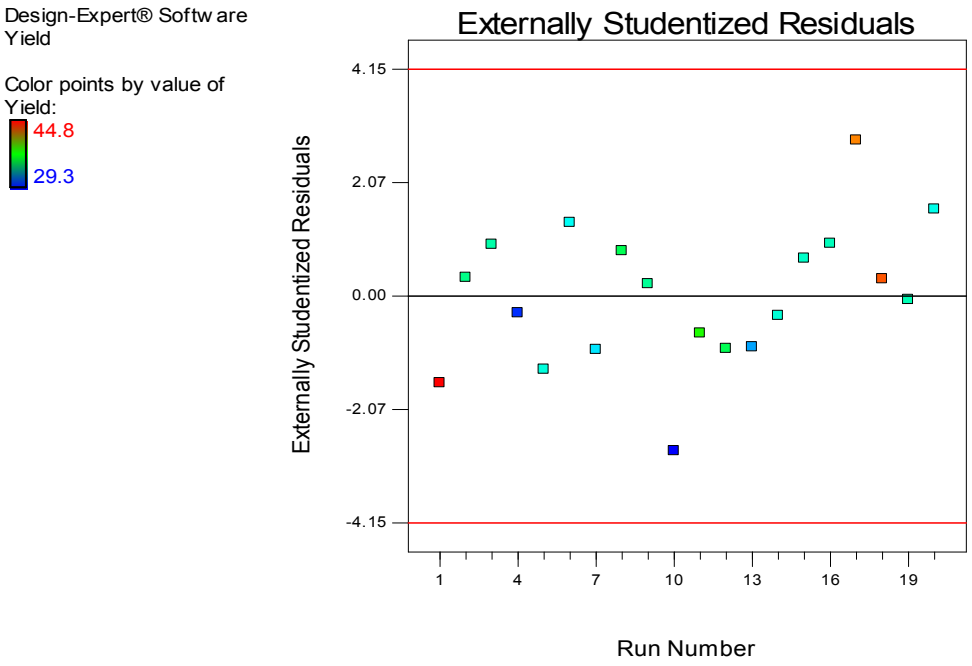


Figure A-4 – Plot of Residuals vs. Run

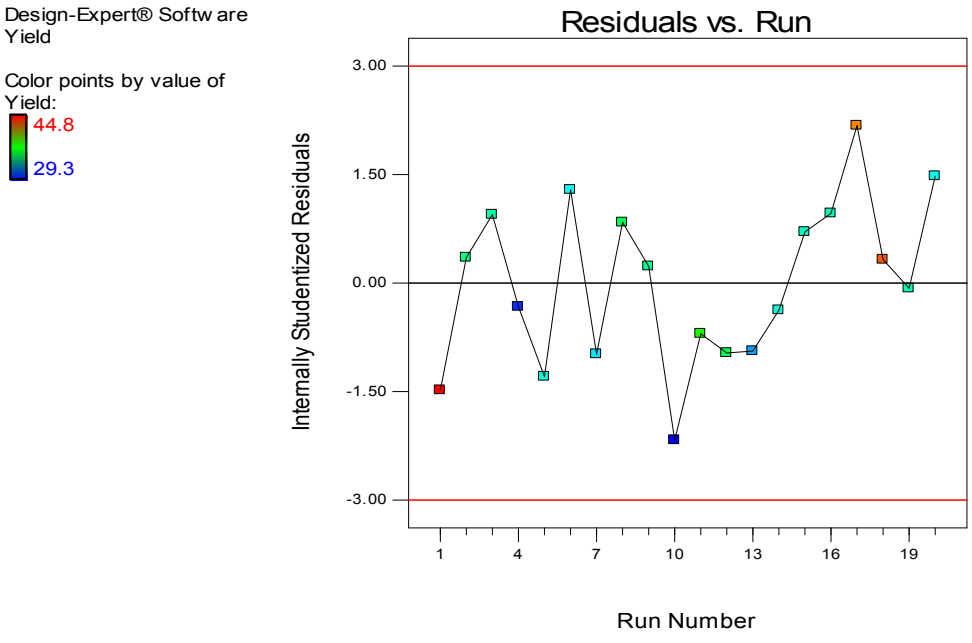


Figure A-5 – Plot of Predicted vs. Actual Percentage Yield Values

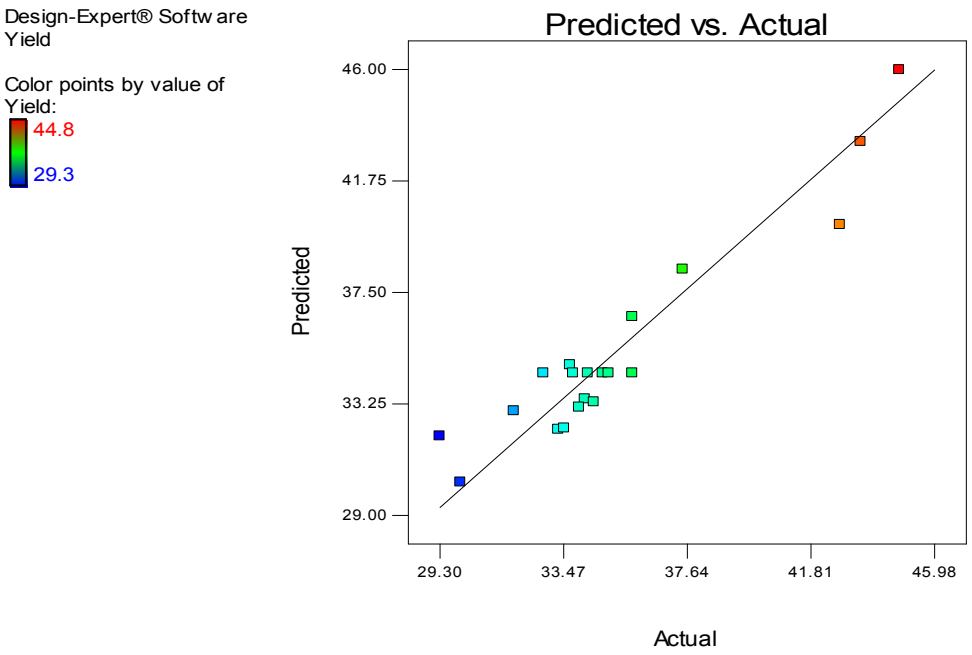


Figure A-6 – Box-Cox Plot for Power Transform

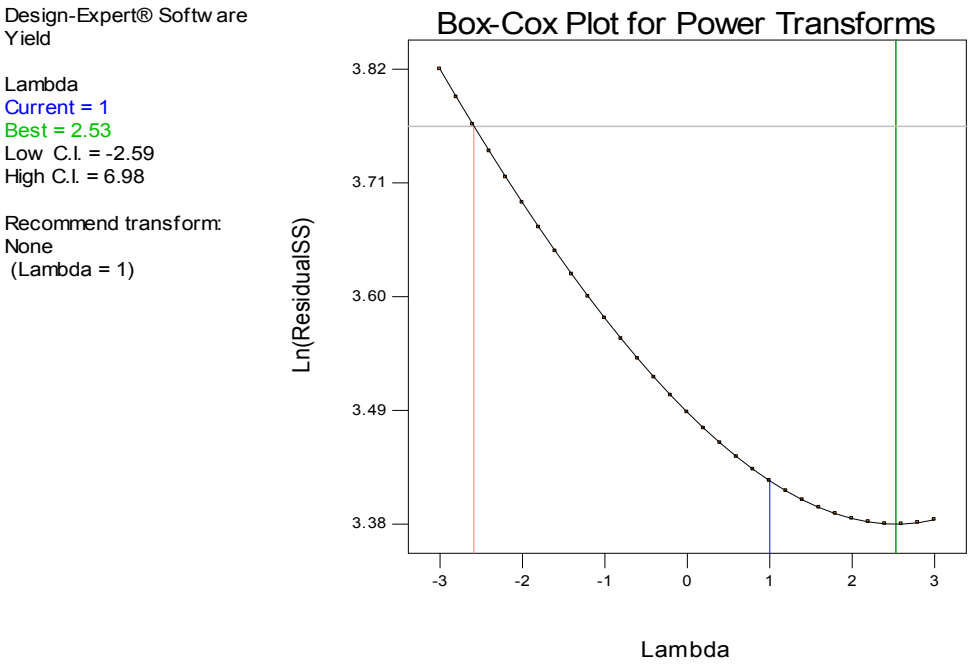


Figure A-7 – Plot of Leverage vs. Run

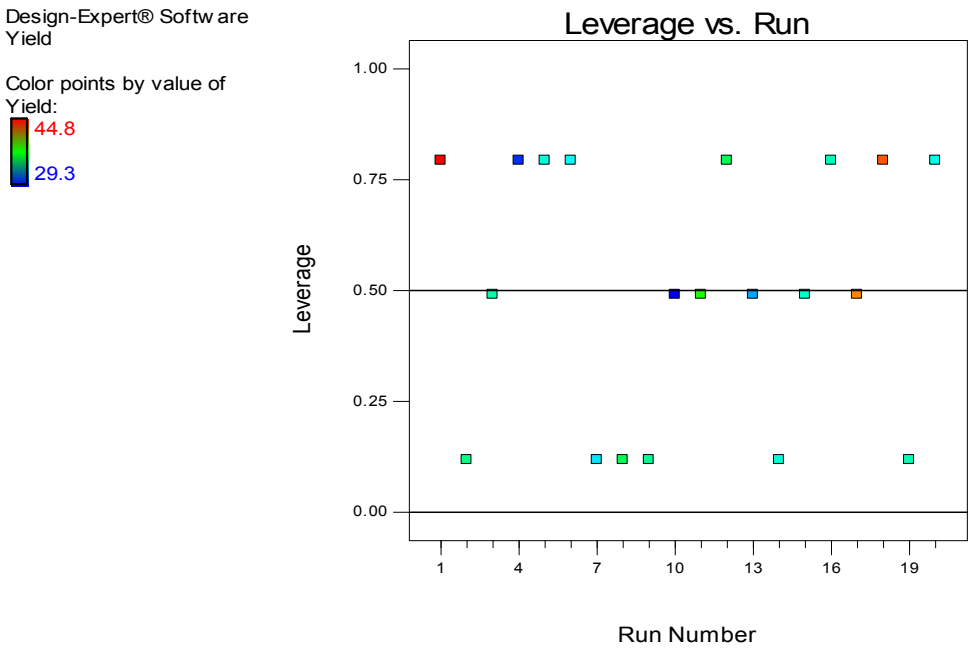
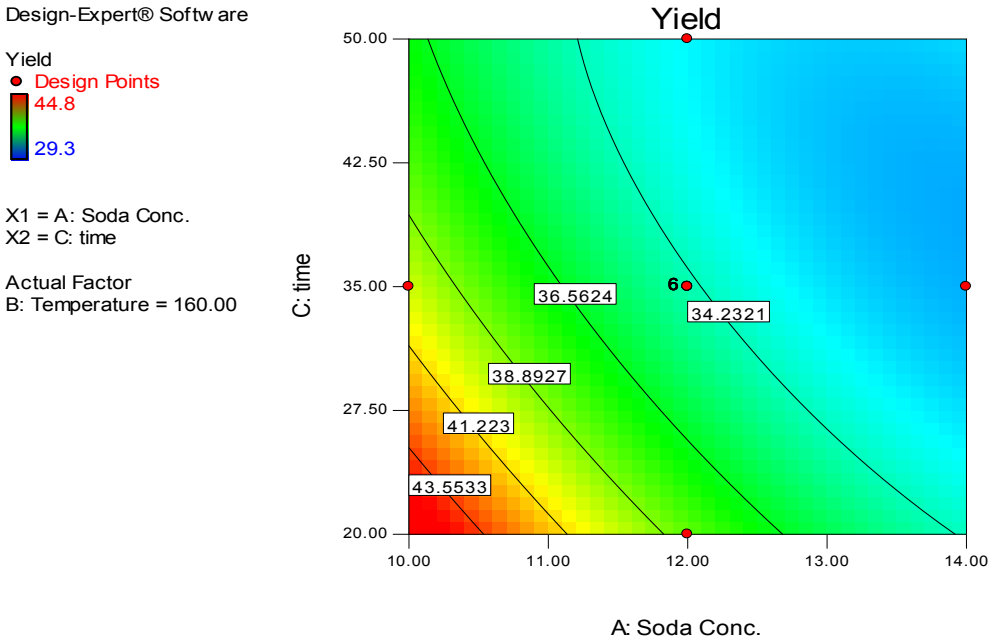


Figure A-8 - Model Graph for Percentage Yield



DECLARATION

By submitting this thesis I declare that the entirety of the work contained therein is my own, original work, that I am the sole author thereof to the extent where it is explicitly stated otherwise, that reproduction and publication thereof by any party none other than Addis Ababa University's School of Graduate Studies will not infringe any third party rights and that I have not previously submitted it entirely or in part for obtaining any qualification.

	7 July 2015
Signature (Mihretab Mezgebu)	**Date**