ADDIS ABABA UNIVERSITY

ADDIS ABABA INSTITUTE OF TECHNOLOGY

SCHOOL OF CHEMICAL AND BIO ENGINEERING

CHARACTERIZATION, UTILIZATION AND OPTIMIZATION OF ETHIOPIAN SUGARCANE BAGASSE (*SACCHARUM OFFICINARUM L.*) FOR PULP AND PAPER MAKING

MEDHANIT MAMAYE GETINET

A PhD Dissertation submitted to the School of Chemical and Bio Engineering,

Addis Ababa Institute of Technology

Presented in partial fulfillment of the requirements for the Degree of Doctor of Philosophy in Chemical Engineering (Process Engineering)

Addis Ababa University

Addis Ababa, Ethiopia

June, 2020

ADDIS ABABA UNIVERSITY

ADDIS ABABA INSTITUTE OF TECHNOLOGY

SCHOOL OF CHEMICAL AND BIO ENGINEERING

This is to certify that the PhD Dissertation prepared by Medhanit Mamaye Getinet, entitled: **"Characterization, Utilization and Optimization of Ethiopian Sugarcane Bagasse (*Saccharum officinarum L.*) for Pulp and Paper Making"** and submitted in partial fulfillment of the requirements for Degree of Doctor of Philosophy in Chemical Engineering (Process Engineering Stream) complies with the regulations of the university and meets the accepted standards with respect to originality and quality.

Signed by the Examining Committee:

Examiners

Name _____ Signature _____ Date _____

Name _____ Signature _____ Date _____

Advisors

Dr. Ing. Zebene Kiflie Signature _____ Date _____

Dr. Sisay Feleke Signature _____ Date _____

Dr. Eng. Abubeker Yimam Signature _____ Date _____

_____

School Dean/ Graduate Program Coordinator

DECLARATION

I hereby declare that the entirety of the work contained in this PhD dissertation is my own original work. To the best of my knowledge, it contains neither material previously published nor written by any other person or material which has been accepted for the award of any other academic degree in any University. Further, I have acknowledged all sources used and cited them in the reference section.

Medhanit Mamaye Getinet _____ June, 2020

Name of the PhD candidate Signature Date

ABSTRACT

Characterization, utilization, and optimization of Ethiopian sugarcane bagasse (*Saccharum officinarum L.*) for pulp and paper making

The current global awareness about the use of non-wood biomass for pulp and paper production has resulted in significant reduction of deforestation. Based on this, the dissertation investigated the suitability of Ethiopian sugarcane bagasse (ESCB) (*Saccharum officinarum L.*) for the pulp and paper production. The study is focused toward the physical fractionation pretreatment of the Ethiopian sugarcane bagasse aiming at the reduction of its lignin, extractive, silica, and ash contents to improve the pulping process. In this regard, chemical compositional analysis was carried out in order to determine the cellulose, lignin, holocellulose, ash and silica contents. Furthermore, cold, and hot water solubility, 1% NaOH solubility and the ethanol-toluene extractive contents were measured. The chemical composition analysis of Ethiopian sugarcane bagasse revealed a good level of cellulose (50%) and Klason lignin content (18%). The measurement of the bagasse fiber dimensions (fiber length of 1.86 mm, fiber diameter of 30.02 μm, cell-wall thickness of 2.53 μm) advocates its suitability for pulp and paper production. The physical fractionation pretreatment had a significant effect on reducing the lignin, ethanol-toluene extractive, ash, and silica contents in the Ethiopian sugarcane bagasse, as evidenced from the Fourier Transform Infrared Spectroscopy analysis.

Based on the above results, the physical fractionation pretreated Ethiopian sugarcane bagasse (ESCB-B) was further delignified by using soda and Kraft pulping methods followed by a single stage hydrogen peroxide bleaching. Multilevel categoric experimental design was used to assess the effects of three independent process variables (pulping temperature, chemical concentration,

and time) on the pulp yield and kappa number during the soda and Kraft pulping processes. Response surface methodology with central composite experimental design was used to assess the effect of independent bleaching variables (bleaching temperature, H_2O_2 concentration and time) on the pulp yield, brightness, and whiteness during the bleaching process. For the optimal pulping outputs, the pulp yield was 35.99% with 16.73 kappa number and 38.41% with 17.68 kappa number for soda and Kraft delignification, respectively. The bleaching response for soda pulp with kappa number of 16.73 and 8.27 were pulp yield of 88.07% and 85.17%, brightness of 62.02% and 71.86% and whiteness of 84.43% and 90.47%, respectively. The bleaching response for Kraft pulp with kappa number of 17.68 and 8.41 were pulp yield of 84.12% and 83.91%, brightness of 61.92% and 68.35% and whiteness of 85.36% and 91.43%, respectively. Paper from soda pulp with kappa number of 16.73 and Kraft pulp with kappa number of 17.68 had higher burst, tensile and tear strength than paper from soda pulp with kappa number of 8.27 and Kraft pulp with kappa number of 8.41. Results suggest that the utilization of Ethiopian sugarcane bagasse using soda and Kraft delignification at the optimum conditions of 130 ^oC cooking temperature, 10% sodium hydroxide concentration at 60 min followed by single stage hydrogen peroxide bleaching is a promising approach.

Furthermore, the black liquors generated from the untreated and physical fractionation pretreated Ethiopian sugarcane bagasse by using soda and Kraft delignification processes were characterized. The lignin, chemical oxygen demand, biochemical oxygen demand and total dissolved solid contents of pretreated sugarcane bagasse soda and Kraft black liquor were found to be (28.45 g/L, 50000 mg/mL, 328 mg/mL, 145.83 mg/L) and (23.29 g/L, 74100 mg/mL, 192 mg/mL, 157.49 g/L), respectively. On the other hand, the lignin, chemical oxygen demand, biochemical oxygen demand and total dissolved solid contents of untreated sugarcane bagasse soda and Kraft black

liquor were (40.53 g/L, 54300 mg/mL, 356 mg/mL, 157.88 g/L) and (36.51 g/mL, 77400 mg/mL, 200 mg/mL, 164.86 g/L), respectively. The untreated sugarcane bagasse soda and Kraft black liquor present higher contents of lignin, chemical oxygen demand, biochemical oxygen demand and total dissolved solid than pretreated soda and Kraft black liquor. The physical fractionation pretreatment had a significant effect on reducing the lignin, chemical oxygen demand, biochemical oxygen demand and total dissolved solid contents of the black liquor. The results clearly demonstrate the efficacy of physical fractionation pretreatment for Ethiopian sugarcane bagasse for pulp and paper production.

Keywords: Sugarcane bagasse, physical fractionation pretreatment, soda delignification, Kraft delignification, single stage hydrogen peroxide bleaching, paper mechanical properties, black liquor.

ACKNOWLEDGEMENT

This PhD dissertation is the output of the effort and support of several people to whom I am extremely grateful. First and foremost, I own it all to Almighty God and Saint Virgin Mary for giving me the opportunity, wisdom, health strength and patience throughout the entire situation and challenge that I faced for successful completion of this PhD research. Simply, thanks for being always present and doing the impossible to keep me going further.

I would like to give my profound gratitude to my major advisor, Dr. Ing. Zebene Kiflie for his advice, and support throughout my PhD study. He has been supportive since the days I began working my dissertation. I appreciate his comments, his idea for providing high quality work and insights throughout my study period.

I would like to extend my gratitude to my co-advisor, Dr. Sisay Feleke, for his continuous support, guidance, cooperation, encouragement, inspiration and facilitating laboratory space at Ethiopian Environment and Forest Institute. I appreciate his comments, motivation, and cooperation for providing high quality work and insights throughout my study period. His constant guidance and support have always kept me going ahead.

My special words of thanks should also go to my co-advisor, Dr. Eng. Abubeker Yimam who helped me truly without hesitation. He has been supported me starting from the day I started developing my PhD proposal. I appreciate his advice, motivation, and cooperation for providing high quality work, throughout my study period.

Special mention goes to Dr. Eng. Anuradha Jabasingh, for her continuous support, guidance, cooperation, encouragement, and sharing experience regarding PhD research and publication. Her

passion and essential view on research have made a deep impression on me. I am really glad to be associated with a person like Dr. Anuradha in my life.

I would also like to thank the staffs of Chemical and Bio Engineering school specially Mrs Sirgut, and Ato Hintsasilase. I would like to thank the staffs of Ethiopian Environment and forest research Institute. I would like to extend my thanks to Bahir Dar University Institution of Technology.

Special indication goes to my friends Dr. Hanna, Dr. Helen, Getnet, Elyas, Deribew, Gebeyehu, Dr. Solomon, Yisehak, Dr. Delelegne, Mebet and Mulugeta for going far beyond the call of duty. Who provided me with a friendly and inspiring environment to work and have fun. Who have been satisfied with other people achievements and who are described as kind and generous, your support were not bounded by place and time. I appreciate their motivation, cooperation, and support for providing high quality work, throughout my study period. Wish you all the best.

Finally, but by no means least, thanks go to my family who give me unbelievable support in each and every step of my life. Words cannot express how grateful I am to my Father Mamaye Getinet, and my mother Adugn Yibeltal. Special thanks to my brother Michael Mamaye, I would like to express my endless love for being a reason to started this PhD study and go forward. Special thanks to my brother Kassahun Yibeltal, my sister Hayimanot Yibeltal and my brother Yohanes Mamaye. Without their support and encouragement this would not be possible. I would like to express my endless love for being a reason to go forward. You are the most important people in my life and I dedicated this dissertation for my family.

Table of Contents

List of Figures

List of Tables

LIST OF SYMBOLS AND ABBREVIATIONS

Symbols

a*	Redness
b*	Yellowness
C-alk	Sodium hydroxide concentration
C-H_2O_2	Hydrogen peroxide concentration
L*	Lightness
R^2	Determination coefficients
R^2_{adj}	Adjusted determination coefficients
T	Temperature
t	Time
Y	Response
β_i	Linear coefficients
β_{ii}	Quadratic coefficients
β_{ij}	Interaction coefficients

Abbreviations

ANOVA	Analysis of Variance
APHA	American Public Health Association
BOD	Biochemical Oxygen Demand
CCD	Central Composite Design
Cell.	Cellulose
COD	Chemical Oxygen Demand
CWS	Cold Water Solubility

ECF	Elemental Chorine Free
ESCB	Ethiopian Sugarcane Bagasse
ESCB-A	Sample A
ESCB-B	Sample B
ESCB-C	Sample C
ESC	Ethiopian Sugar Corporation
Ext.	Extractive
FTIR	Fourier Transform Infrared Spectroscopy
GSM	Gram per Square Meter
Hol.	Holocellulose
HPB	Hydrogen Peroxide Bleaching
HWS	Hot Water Solubility
Lig.	Lignin
MCD	Multilevel Categoric Design
MOR	Ethiopian Ministry of Revenues
n.a	Not available
PFP	Physical Fractionation Pretreatment
PKBL	Pretreated Kraft Black Liquor
PSBL	Pretreated Soda Black Liquor
Pulp-SA	Soda pulp at kappa number of 16.73
Pulp-SB	Soda pulp at kappa number of 8.27
Pulp-KA	Kraft pulp at kappa number of 17.68
Pulp-KB	Kraft pulp at kappa number of 8.41

RSM	Response Surface Methodology
SCB	Sugarcane Bagasse
Sil.	Silica
SPSS	Statistical Package for Social Sciences
SS	Sum of Squares
TAPPI	Technical Association of Pulp and Paper Industry
TCF	Total Chorine Free
TDS	Total Dissolved Solid
UKBL	Untreated Kraft Black Liquor
USBL	Untreated Soda Black Liquor
Y_{BKA}	Brightness of Pulp-KA
Y_{BKB}	Brightness of Pulp-KB
Y_{BSA}	Brightness of Pulp-SA
Y_{BSB}	Brightness of Pulp-SB
Y_{KK}	Kraft kappa number
Y_{KP}	Kraft pulp yield
Y_{PKA}	Pulp yield of Pulp-KA
Y_{PKB}	Pulp yield of Pulp-KB
Y_{PSA}	Pulp yield of Pulp-SA
Y_{PSB}	Pulp yield of Pulp-SB
Y_{SK}	Soda kappa number
Y_{SP}	Soda pulp yield
Y_{WKA}	Whiteness of Pulp-KA

Y_{WKB}	Whiteness of Pulp-KB
Y_{WSA}	Whiteness of Pulp-SA
Y_{WSB}	Whiteness of Pulp-SB

CHAPTER ONE

Introduction

This chapter summarize the overall outline of the study. It clarifies about background, problem statement, research questions, objectives of the study, significance of the study, novelty of the study and structure of the dissertation.

1.1. Background

Pulp and paper industries are one of the oldest industries and helping the society in the world by manufacturing paper and paper-based products. Pulp and paper are produced almost in all countries of which USA, China, Japan, and Canada are the largest producers. They account for more than half of the world paper production (Johnston, 2012; Dillen et al., 2016). The global pulp and paper manufacturing industries have faced challenges to their products due to increased digitalization in developed countries. However, paper manufacturers are now shifting their focus towards packaging materials and sanitary products, which appear to be the two most promising segments for growth of pulp and paper demand (Dillen et al., 2016; Cortesi et al., 2018).

The demand for pulp and paper fiber resources is largely determined by the society's economic growth (Lwako et al., 2013). Despite the demands for newsprint and other printing papers are reducing due to increasing digitalization, the demand for containerboards and tissue paper will grow up. At the same time the rising awareness in renewable packaging goods around the consumer is increasing the market demand for paper-based packaging materials. As a result, the annual consumption of packaging material and tissue (hygiene products) is expected to increase

up to 2.9%. With the expansion of urbanization, increasing population and the development of industries, it is highly probable that the demand for paper and paper products will continually increase (Dillen et al., 2016; Cortesi et al., 2018).

Pulp and paper are the major products of the forestry-based industries in the world. Pulp and paper are produced from wood, recycled paper, non-wood biomass and agricultural residues (Dillen et al., 2016; Bajpai, 2017). Wood is the conventional and major raw material for the production of paper pulp and paperboard. However, the shortage of this resource due to its long growing cycle and environmental issues, the production of pulp should be supported with other non-woody biomass and recycled fibers (Caparrós et al., 2008).

The non-wood plants have short growth cycles, moderate irrigation and fertilization requirements, annual renewability, high cellulose content and low lignin content. The low lignin amount in most of these plants favors pulping process with reduced energy and chemicals consumption as compared to wood (Alila et al., 2013). Currently, non-wood raw materials are used in paper producing companies. This has happened due to the changes in the agricultural policies, shortage of wood supply and environmental concerns (Camarero et al., 2004). The most commonly used non-wood raw materials for pulp and paper making are straws, bamboo, kenaf, hemp, sisal, abaca, and cotton (Jimenez et al., 2008).

Sugarcane is one of the important non-wood plants that is largely cultivated in Ethiopia (Ayele et al., 2014). It is mainly used for production of sugar while huge amount of bagasse is produced during sugar production process as a byproduct. Currently, there are eight sugar producing industries in Ethiopia, Wonji-Shoa, Matahara, Fincha, Kessem, Arjo-Debesa, Omo-Kuraz II and III and Tendaho. In addition to these five new sugar factories are under construction (Wolkaity, Tana Bellese I and II, Omo-Kuraz I and VI) (ESC, 2019). Furthermore, it is planned to expand the

existing factories with the aim of producing 2.5 million tons of sugar and 304 million liters of ethanol. Because of this huge expansion, it is expected that large amount of sugarcane bagasse will be generated in the future. Nowadays, the sector is gaining a particular emphasis in converting this massive production of industrial residue to useful products like pulp and paper production. Sugarcane bagasse is delignified using chemical pulping methods followed by appropriate pretreatments. Pretreatment is required to decrease the pulping chemical dose and reduce pollution load of black liquor (Yirefu et al., 2013; Mekonnen et al., 2014).

In the present study, it has been attempted to investigate the suitability of Ethiopian sugarcane bagasse for pulp and paper production by conducting physical fractionation pretreatment, morphological and chemical characterizations. In addition, soda and Kraft pulping were conducted to delignify sugarcane bagasse and black liquor characterization were done.

1.2. Problem Statement

At the national level, the Ethiopian government has developed a policy that promotes agro based industrialization, known as agricultural demand led industrialization (Dube et al., 2019). Of these, pulp and paper industry are the one that required huge tones of fibrous biomass input. To satisfy the huge amount of fiber requirement, it becomes stringently necessary to look for alternative fiber sources biomass other than wood. Since wood is the main raw material used for pulp and paper production worldwide. In this regard, non-wood biomass such as agricultural residues and annual plants can be considered as an effective alternative source of cellulose fiber for producing pulp and paper with acceptable properties (Alila et al., 2013).

Non-wood biomass such as cotton stalk, Enset fiber, wheat straw and sugarcane bagasse are possible fiber sources for pulp and paper production in Ethiopia. However, there is insignificant

use of agricultural residues as industrial raw material in Ethiopian because there is lack of awareness and know-how.

Sugarcane is one of the important non-wood plants that is largely cultivated in Ethiopia for sugar production (Ayele et al., 2014). In this production process huge amount of sugarcane bagasse is produced. Ethiopian Sugar Corporation (ESC, 2019) reported that, more than 1.2 million tons of sugarcane bagasse was produced in Ethiopia annually. Form this annual production around 260 thousand surpluses are leftover and damped to environment. On the other side, pulp and paper is imported to satisfied the increasing demand of pulp and paper products in the country. Ethiopian Ministry of Revenues (2019) reported that, more than 8890 tons of pulp and 97,072 tons of paper were imported in 2018.

In this regard, the availability of these large quantities of fibrous residues (sugarcane bagasse), increasing demand for pulp and paper products in the country, and lack of information about pretreatment, pulping and bleaching parameter selection for sugarcane bagasse delignification and bleaching have activated the interest in their utilization.

From our extensive search and as of our knowledge, no work has been previously reported on the characteristics, pretreatment techniques, delignification and bleaching optimization and paper mechanical properties of Ethiopian sugarcane bagasse. Therefore, this work is the first of its kind that covers the physical fractionation pretreatment and optimization of delignification and bleaching processes. Thus, the dissertation planned to investigate the utilization of Ethiopian sugarcane bagasse as raw materials for pulp and paper manufacturing.

1.3. Objectives of the study

1.3.1. General Objective

The general objective of this research was to investigate the suitability of Ethiopian sugarcane bagasse (*Saccharum officinarum L.*) as alternative raw material for pulp and paper production.

1.3.2. Specific objectives

The specific objectives were

- To characterize the chemical composition of untreated and pretreated sugarcane bagasse (*Saccharum officinarum L.*) and morphological properties.
- To study soda delignification and single stage hydrogen peroxide bleaching of SCB and optimize the respective processing conditions.
- To study Kraft delignification and single stage hydrogen peroxide bleaching of SCB and optimize the respective processing conditions.
- To characterize the black liquor resulting from soda and Kraft pulping of untreated and pretreated SCB.

1.4. Significance of the study

This study attempts to tap the potential of the abundantly available non-wood biomass, sugarcane bagasse, as a source of raw material for the production of pulp and paper. This is achieved by investigating the suitable pretreatment, pulping, and bleaching conditions for maximum utilization of sugarcane bagasse for the pulp and paper manufacturing. In addition, this research is believed to contribute towards mitigating the environmental problems resulting from the use of large amount of chemicals during pulping and bleaching, reducing the accumulation of dumped sugarcane bagasse through conversion and deforestation due to paper pulp production. The outputs

can be used by the pulp and paper industries, Ethiopian sugar factories, Universities, and researchers by providing valuable data regarding the morphological properties, chemical composition, pretreatment, pulping and bleaching methods and parameters for Ethiopian sugarcane bagasse.

1.5. Novelty of the research

The novelty of this research is the thorough characterization both for untreated and physical fractionation pretreatment sugarcane bagasse to assessed its suitability for pulp and paper production. Evaluation and optimization of sugarcane bagasse soda and Kraft pulping at mild cooking condition and single stage hydrogen peroxide bleaching, which to the best of our knowledge has never being published. Also, the demonstration of physical fractionation pretreatment using 1 mm size sieve prior to pulping and bleaching. The physical fractionation pretreatment is economically and prevent fiber damage by pretreatment compared with other pretreatment methods used for sugarcane bagasse.

1.6. Structure of the dissertation

The dissertation is organized into seven main chapters.

In chapter one, short introduction, the objectives, problem statement, and significance of the study are presented. The overview of the chapters depending on the specific objectives are specified.

In chapter two, presents the introduction about the main concepts and the gaps in the literature within the scope of the dissertation.

In chapter three, characterization of Ethiopian sugarcane bagasse to assess its suitability for pulp and paper production are discussed. In this chapter, the morphological properties and chemical composition of physical fractionation pretreated and untreated sugarcane bagasse (*Saccharum*

officinarum L.) is reported. Moreover, comparison with wood and other non-wood raw materials used for pulp and paper production is presented and discussed.

In chapter four, the optimization of the soda delignification and single stage hydrogen peroxide bleaching are presented and discussed. In this chapter, optimum of soda delignification conditions using multilevel categoric experimental design is presented. Moreover, optimum of single stage hydrogen peroxide bleaching conditions using response surface methodology, central composite experimental design is presented and discussed. The mechanical properties of the hand sheet paper made based on the optimized condition were also discussed.

In chapter five, the optimization of the Kraft delignification and single stage hydrogen peroxide bleaching are presented and discussed. In this chapter, the optimum Kraft delignification conditions using multilevel categoric experimental design is presented. Moreover, the optimum single stage hydrogen peroxide bleaching using response surface methodology, central composite experimental design is presented. The mechanical properties of the hand sheet paper made based on the optimized condition were also discussed.

In chapter six, characterization of black liquor prepared from pretreated and untreated sugarcane bagasse are presented and discussed. The effects of pretreatment and pulping methods on the physical and chemical properties of the black liquor are also reported.

Chapter seven provides the conclusions drawn from the work performed within the study. Furthermore, this chapter points out to some remarkable areas where future work based on the overall finding of this study can be carried out. Figure 1.1 show the overall structure of the dissertation.

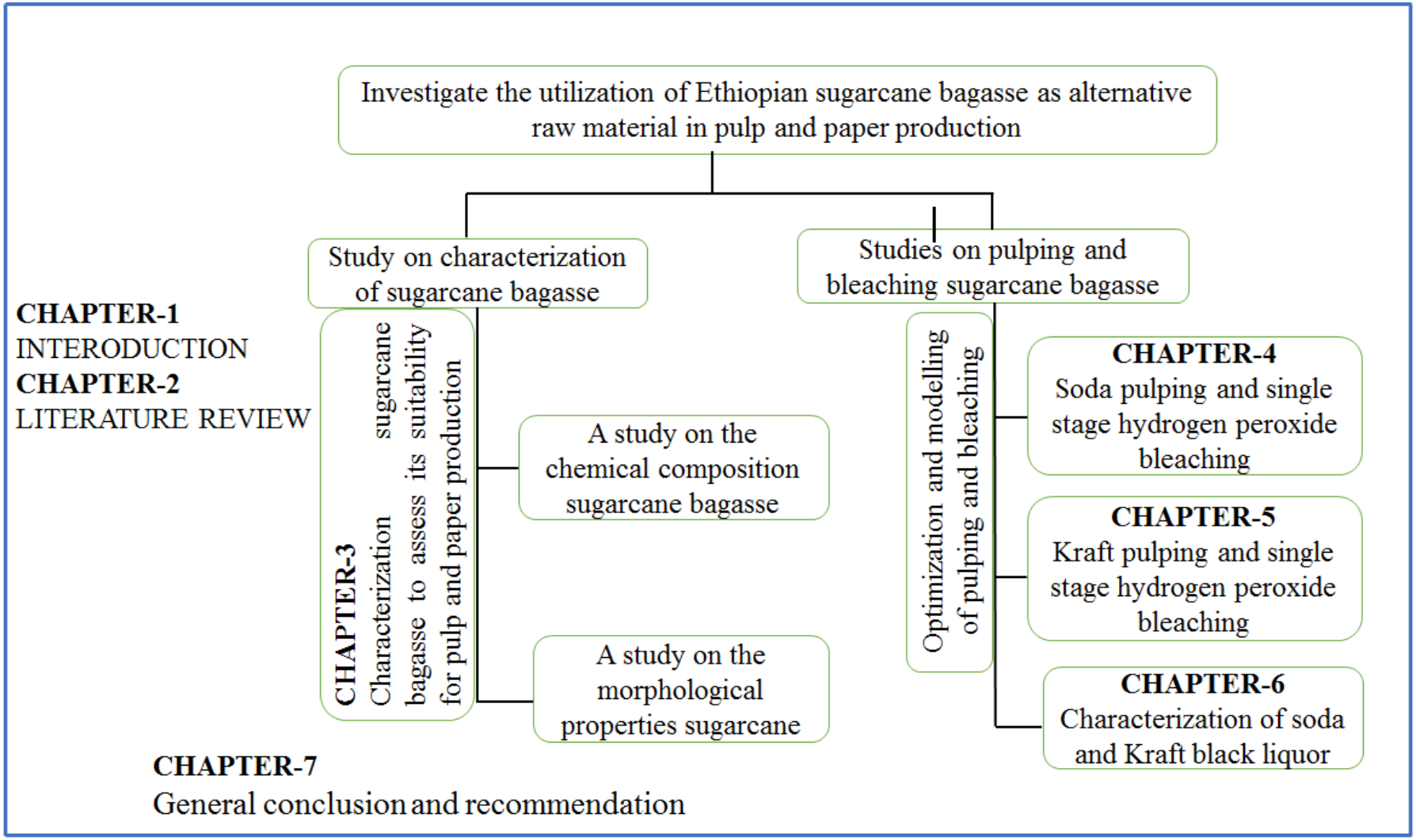


Figure 1.1 Structure of the dissertation

CHAPTER TWO

Literature review

2.1. Introduction

The word paper is derived from the papyrus plant. Papyrus plants were used for writing words by pressing and drying it. The earliest papermaking process was chemical free method. Its description was done by Cai Lun in 105 AD (Johnston, 2012; Lwako et al., 2013). The paper making process spread from the Middle East to Egypt (around 900 AD) and to Morocco. Then it was spread toward North and East Europe: France (1157), Italy (1276), Germany (1390), Poland (1491), Great Britain (1495), Spain in 1500 and Russia (1576) (Johnston, 2012).

Fiber products as a consumer goods have proved critical in driving most sensitive needs of mankind, notably in areas of education, sanitation, and communication. Its production and consumption have steadily increased. This is due to global socio-economic realities (such as burgeoning world population, advancement in technology and global economic prosperity) and its physiochemical properties (such as durability and flexibility) (Jimenez et al., 2008; Feria et al., 2012; Johnston, 2012; Cortesi et al., 2018; Ezeudu et al., 2019). Global pulp and paper production by region are shown in Figure 2.1 (Cortesi et al., 2018; Ezeudu et al., 2019).

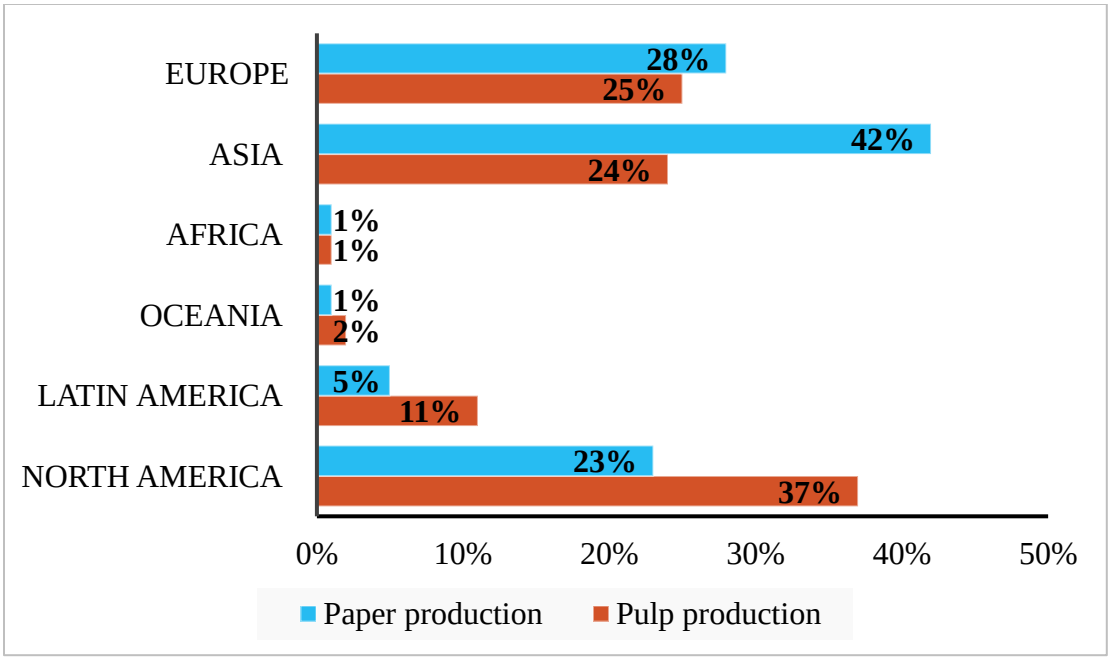


Figure 2.1 Pulp and paper production in the world (Cortesi et al., 2018).

The paper and paperboard consumption in 1963 was 165 million tons per year, in 1993 it was approximately 253 million tons per year, in 1997 it was 300 million tons per year and in 2010 it was 400 million tons per year (Ashori, 2006; Ververis et al. 2007). World paper consumption latterly exceeded 490 million tons per year. More than half of the consumption occurred in America and Asia with further quarter in Europe, while the entire continent of Africa accounts for 2% of global paper consumption Figure 2.2 (Cortesi et al., 2018; Ezeudu et al., 2019). This large consumption of paper required large tons of paper production from wood biomass. Nowadays over 6×10^8 m^3 of wood is used for pulp and paper production worldwide annually. This causes serious global issue, because wood is also a raw material for many other industries (fuel, tools, weapons, structures, and for furniture) and a balancing factory for climate (Johnston, 2012; Dillen et al., 2016).

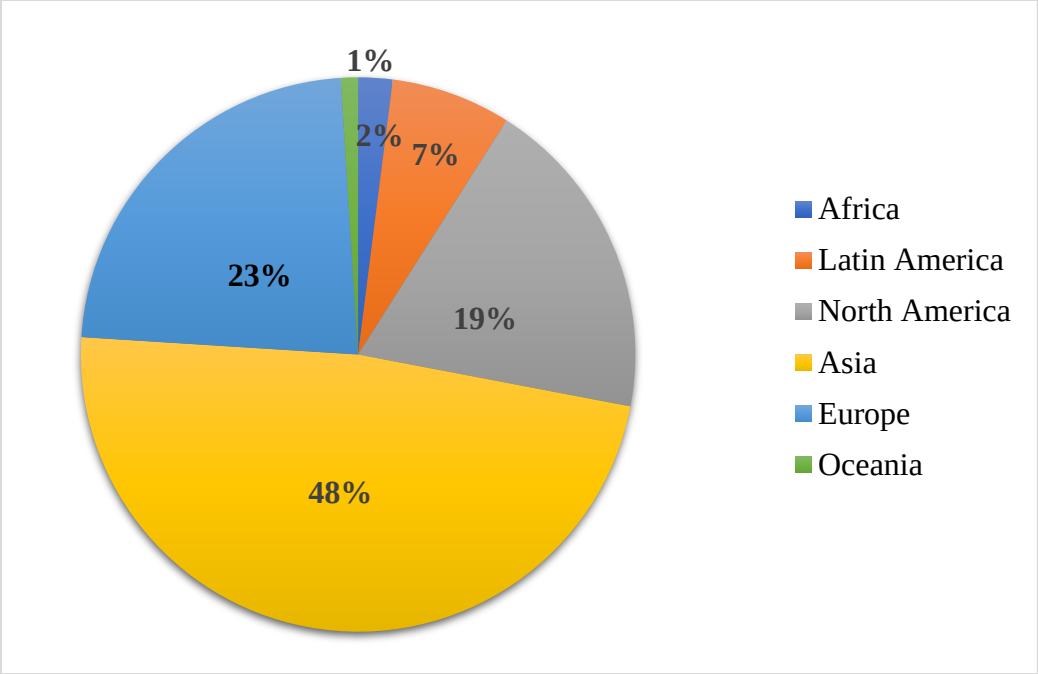


Figure 2.2 Global paper consumption (Cortesi et al., 2018).

The pulp and paper industries are aware with the hot issues of sustainability, renewable materials, green chemistry, recycling materials and environmental issues (Johnston, 2012). Due to this the pulp and paper industries are searching new source of cellulosic fibers other than wood fiber sources. Currently, more than half of paper is produced from virgin pulp (55%) and the rest is produced from recycled wood-based paper (38%) and non-wood biomass (7%), (Feria et al., 2012; Dillen et al., 2016).

2.2. Pulp and paper demand in Ethiopia

The demand for pulp and paper products in Ethiopia is increasing due to the population growth, improved economy, expansion of educational institutions and increasing of the manufacturing sector that use paper and/or paper products (Fenta, 2010). According to the Ethiopian Ministry of Revenues (MOR, 2019) report, the demand for paper is increasing by 17% per annum in

2017/2018. Table 2.4 shows the pulp and paper imported data in the period of 2014 to 2018 (MOR, 2019).

Table 2.1 Pulp and paper imported data from 2014-2018.

Year	Pulp imported Gross wt. (tons)	Paper imported Gross wt. (tons)
2014	8,528.16	54,755.31
2015	8,329.94	65,018.27
2016	8,556.29	77,214.32
2017	8,786.79	89,410.38
2018	8,993.37	104,735.32

Presently, there are around 25 companies involved in papermaking and packaging in Ethiopia. Ethiopian pulp and paper Share Company and Barguba private limited company are the only paper products manufacturing companies that use imported pulp and waste paper as input raw materials. The rest companies are imported paper and convert the paper in the form of customer need like printing and packaging (ECCIDI, 2016).

In order to narrow the gap between the demand and supply of pulp and paper products beside the expansion of the production capacity, the sector should look for sustainable, cheap, environmental, and economically sound raw material. The traditional source of raw material for pulp production which is the forest with the current situation of the country may not be viable. Therefore, we have to look for some other raw materials like sugarcane bagasse, bamboo and enset residues (Fenta, 2010; Berhanu, et al., 2018).

2.3. Raw materials used for pulp and paper production

2.3.1. Wood

Wood is the principal raw material for pulp and paper production worldwide. Wood pulp is used for printing and writing paper, cardboard and fiberboard, as well as rayon (artificial silk), cellophane manufacturing and other cellulose derivative products (Brostow et al., 2010; Sugesty et al., 2015; Dillen et al., 2016; Bajpai, 2017). Wood pulps are basically grouped into three different categories: softwood, hardwood and residues from mechanical wood processing (sawmill chips and sawdust) (Dillen et al., 2016).

Softwood: These are commonly known as conifer species, with more tracheid cells having long fiber length. Some of the softwoods used for pulp and paper production are spruces, firs, scots pine and lodgepole pine (Sable et al., 2012; Dillen et al., 2016). Softwoods are the preferred raw material for strong papers production, due to their long fiber length and slenderness of the fibers. The fibers of softwood are long and thin-walled, which are predominantly preferred for papers with high demands of bonding related strength characteristics, such as tensile, burst and surface strength (Dillen et al., 2016).

Hardwood: Tree species belonging to this class are known as broadleaved or deciduous plants and have more cell types than the softwood. Some of the hardwoods used in pulp and paper production are birch, eucalyptus (*E. globulus, E. camaldulensis, E. microtheca and E. tereticornis*), acacia and aspen (Miranda et al., 2012; Dillen et al., 2016). Hardwoods are the preferred raw material for printing papers. Hardwood fibers are characterized with short fiber length, which implies a high number of fibers per unit mass of pulp. This is important for the formation characteristics like uniformity, opacity and surface smoothness, all of which are vital for printing

paper (Dillen et al., 2016). On the other hand, the short fibers of hardwood are chosen for making soft tissue, because they improve the tactile softness of the product (Dillen et al., 2016).

Due to the increasing demand of fiber products worldwide, approximately 50% of the harvested wood is used for pulp and paper manufacturing in industrialized nations. A clear feeling of forest resource for pulp production contributing to the global warming and deforestation which alerted for the search of an alternative biomass substituents with fast growing, short cycle, economical and environmentally sound. So it is found to be very important to substitute wood pulp with another alternative raw materials such as non-wood resources from agricultural residues (wheat straw, rice straw), fast growing species like bamboo and industry byproducts like sugarcane bagasse (Brostow et al., 2010; Sugesty et al., 2015).

2.3.2. Non-wood

Non-wood fiber sources are non-woody cellulosic plant materials of annual plants, agricultural and agroindustry residues (Ashori, 2006; Requejo et al., 2012). Some of the non-woody plant species have short and fast growing cycles at moderate irrigation requirement, renewability and high cellulose yield (Alila et al., 2013). Some of the non-wood plants used for pulp and paper making are bamboo, enset fiber, abaca, sisal, kenaf, jute and hemp (Ai and Tschirner, 2010; Alila et al., 2013; Yuan et al., 2016).

Agricultural and agro-processing residues: are abundant and easily available non-wood biomass, which are considered as residues after the valorization of the important parts. Some of the agricultural residues used as an alternative raw material for pulp and paper making are sugarcane bagasse and rice straw (Johar et al., 2012; Mansouri et al., 2012; Kaur et al., 2017; Berhanu et al., 2018).

In addition, the non-wood raw materials are categorized into two based on the fiber length: shorter fiber and longer fiber categories. The shorter fiber sources category, which substitutes the hardwood pulp contains sources like sugarcane bagasse, bamboo, corn stalks, sorghum stalk, wheat straw and rice straw. The longer fiber sources category, which may be used as substitute to softwood pulp, contains cotton and linters, flax, hemp, sisal, and abaca (Lwako et al., 2013).

Non-wood fiber sources are low in lignin content but have comparable chemical composition and dimensional properties with wood fiber sources. The advantages of using non-wood fiber sources are many. They contribute in the reduction of deforestation and the need for replanting. Non-wood sources are characterized by fast growth, high annual yields per hectare, little refining requirement. They are cheaper than wood and can be sourced from byproducts (agricultural residues and industrial byproducts) (Ashori, 2006; Rodrıguez et al., 2008; Mohieldin, 2014; Yuan et al., 2016). In large and mechanized farming system agricultural residues are burned in the field, which can cause environmental problems such as fog, particulate matter, plagues and CO_2 emissions to the atmosphere (Requejo et al., 2012). These problems can be reduced by utilizing the biomass effectively by determining the chemical composition and fiber dimension (Watkins et al., 2014).

2.4. Chemical composition

The chief constituents of lignocellulosic biomass are cellulose, hemicellulose and lignin (Watkins et al., 2014). The cellulose is known as the framework forming the microfibrillar structures, hemicellulose as matrix and lignin is known as encrusting substance of the cell wall. The percentage composition of these structural components differs from species to species, plant part, growing condition and geographical location (Galbe and Zacchi, 2012; Kumar and Kumari, 2014). The amount of cellulose in a given plant is an indicator for the feasibility of the plant material for pulp and paper making. For example, plant materials with cellulose content of 34% and above are

regarded as potential source for pulp and paper manufacturing (Udohitinah and Oluwadare, 2011; Watkins et al., 2014). As result characterization of lignocellulosic materials based on their chemical composition like cellulose, lignin and hemicellulose contents are vital. Those characteristics are used as an indication for the suitability of the lignocellulosic material for pulp production. In addition, the chemical composition also shows the chemical consumption during pulping and bleaching and selection of pulping and bleaching parameters.

2.4.1. Cellulose

Cellulose is one of the most abundantly available natural polymer in lignocellulosic biomass and the demand for it is progressively rising as a result of its environment-friendly and bio-compatible nature (Watkins et al., 2014). Cellulose is a linear and parallel oriented homopolymer macromolecules made of β-D-glucopyranosyl units with (1-4)-β-D-glycosidic linkage (Johnston, 2012; Kumar and Kumari, 2014). It is an organic compound composed of carbon, hydrogen and oxygen causing a universal formula of $(C_6H_{10}O_5)_n$, a polysaccharide consisting of a linear chain of several hundreds to over ten thousand linked β-D-glucose units. The linearity structure of cellulose is maintained due to the 180^o rotation of the glucose units to each other in the formation of 1-4-β-D-glyosidic linkage (Figure 2.3). Cellulose has two regions of very tightly packed (crystallite) owing to inter and intramolecular hydrogen bonds reaching 60-95% depending on the source of cellulose fiber and an irregular amorphous (Galbe and Zacchi, 2012; Johnston, 2012; Lwako et al., 2013; Kumar and Kumari, 2014; Chen et al., 2015).

The variance in degree of polymerization depends upon the source of cellulose (Kumar and Kumari, 2014). The cellulose microfibers have an ordered polymer chains that contain tightly packed crystalline and amorphous regions, which are embedded with hemicellulose and lignin (William et al., 2011). Cellulose is insoluble in most common solvents including water and also

resistant to enzymatic hydrolysis, due to the high intra and inter molecular hydrogen bonding which reduces water access to its functional groups (Johnston, 2012; Galbe and Zacchi, 2012; Wong et al., 2013).

Cellulosic fibers are normally negatively charged when suspended in water due to the presence of acidic ionization. The population of ionized groups is highly dependent on the origin of fiber cell wall constituents and on the chemical treatments during pulping and bleaching of fibers (Lin et al., 2014). The hydrophilic natures of the cellulose within paper structure are very important for good fiber-fiber bonding (Sahin and Arslan, 2008). Nowadays, cellulose is used for many products such as pulp and paper production, composites, building materials, textiles, chemical derivatives and fabric fibers (Pereira et al., 2011). The percentage composition of cellulose in lignocellulosic biomass is important to identify its suitability for pulp and paper production.

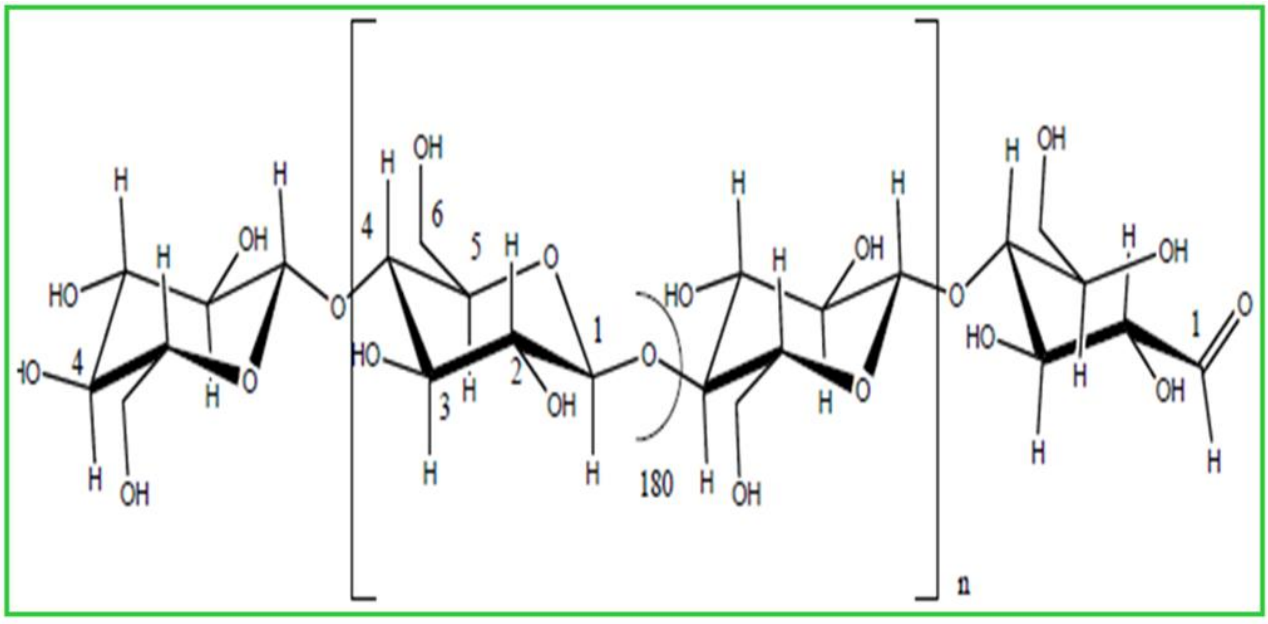


Figure 2.3 Structure of cellulose (Watkins et al., 2014)

2.4.2. Lignin

Lignin is composed of mainly three types of monomers highly cross-linked macromolecule, which include coniferyl, sinapyl and p-coumaryl alcohols (Figure 2.4). The polymerization of the monomers yields structure of lignin (Figure 2.5) (William et al., 2011; Li et al., 2012; Watkins et al., 2014). Lignin is a heterogeneous biopolymer in lignocellulose biomass. It is formed by radical mediated oxidative coupling of phenyl-propane units linked together through various types of ether and carbon-carbon bonds (William et al., 2011; Li et al., 2012; Gellerstedt, 2015).

Lignin occupies the spaces in cell-wall between cellulose, hemicellulose and pectin components and acts as the "glue" that connects cellulose and hemicellulose. Thus, it gives strength to the cell-wall of the plant as a whole. Furthermore, lignin has been setup to act as a major role in protecting the cellulose/hemicelluloses from harsh environmental conditions, provide mechanical strength for the plant, and prevent the absorption of water through the cell-wall due to insolubility in water (hydrophobic nature) (Lwako et al., 2013; Wong et al., 2013; Watkins et al., 2014; Kumar and Kumari, 2014). Lignin has high resistance to thermal degradation compared with cellulose and hemicellulose, due to its high level of aromaticity, size and structural arrangement (Pereira et al., 2013).

Lignin is used for numerous applications due to its polyphenolic structure, such as activated carbons, flocculants, surfactants, production of charcoal, emulsifiers, dyes, synthetic floorings, sequestering, binding, thermosets, dispersal agents, paints, and fuels to treatments for roadways and for bioplastic manufacturing. In the pulp and paper production process the lignin dissolved in the spent liquors is burned to generate energy (Li et al., 2012; Pereira et al., 2013; Watkins et al., 2014).

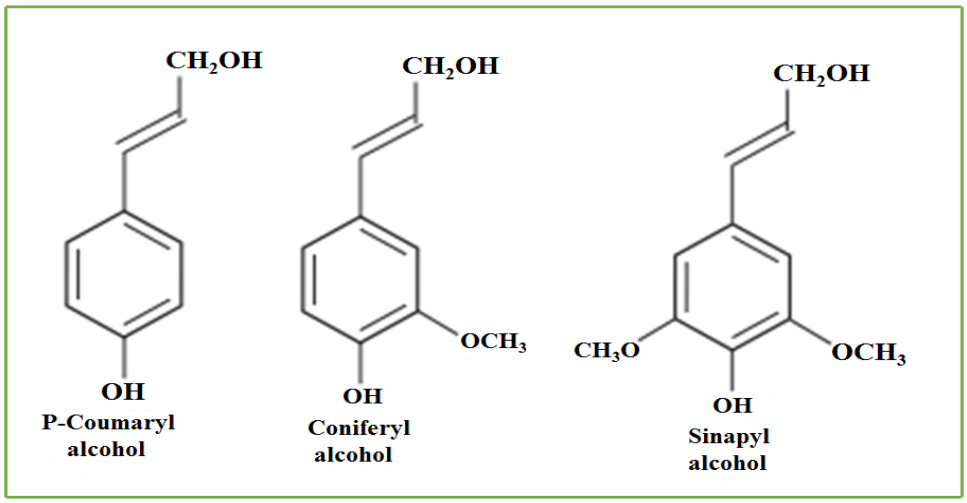


Figure 2.4 Lignin building blocks (Watkins et al., 2014)

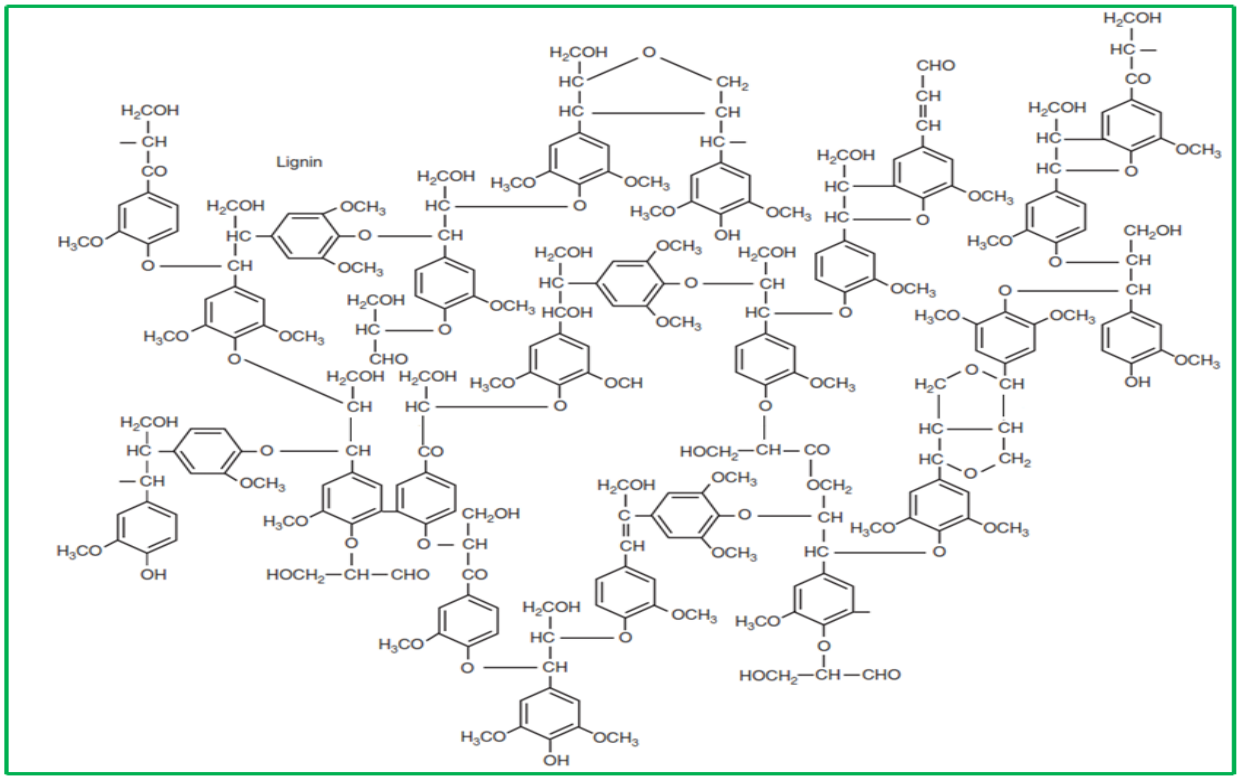


Figure 2.5 Lignin structure (Watkins et al., 2014)

2.4.3. Hemicelluloses

Hemicelluloses are most abundant branched and low-molecular weight polymers in the cell-wall of lignocellulosic biomass (Liu et al., 2011; Peng et al., 2012; Kumar and Kumari, 2014; Bajpai,

2017). It is mainly composed of pentose sugar (xylose and arabinose) and the hexoses (glucose, mannose, galactose). On the side chain of the hemicellulose, uronic acids of glucose and galactose are found. The degree of polymerization of hemicellulose is much lower than cellulose. It is bonded to other cell-wall components such as cellulose by hydrogen bonds, and lignin by covalent bonds. These linkages could be either of ester or ether type of glycosidic bonds (Mousavioun and Doherty, 2010; Peng et al., 2012).

Large variations in hemicellulose content and chemical structure can occur between different lignocellulosic biomass (Figure 2.6) (Peng et al., 2012). Softwood biomass contains both hexose and pentose while hardwood contains more pentose monomer units (Mousavioun and Doherty, 2010). Hemicellulose from hardwood also highly acetylated compared to its softwood analogue. Hemicellulose can be used as viscosity modifiers in food packaging film, as wet strength additive in paper making, a gelling agent and as tablet binder (Peng et al., 2012; Kumar and Kumari, 2014).

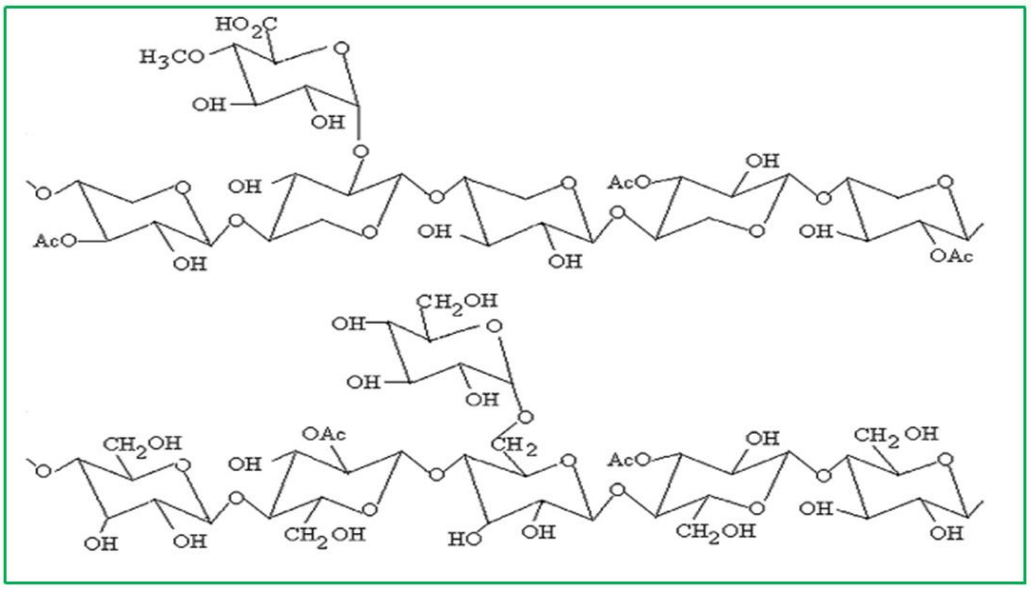


Figure 2.6 Structure of hemicelluloses (Watkins et al., 2014)

The chemical composition of wood/non-wood biomass varies, depending on the type of species, climate condition, soil property, and cultivation mechanism (Kumar and Kumari, 2014). Table 2.1 shows the chemical composition of wood and non-wood fiber source biomass.

Table 2.2 Chemical composition of some typical lignocellulosic biomass.

Source		Percentage chemical composition			
		Cellulose	Hemicelluloses	Lignin	Extractive substances
Wood	Hardwood	43-47	25-35	16-24	2-8
	Softwood	40-44	25-29	25-31	1-5
Non-wood	Bagasse	40	30	20	10
	Corn stalks	35	25	35	5
	Hemp	70	22	6	2
	Wheat straw	30	50	15	5
	Flax	71	21	2	6

2.5. Morphological properties

Fiber morphological properties of lignocellulosic biomass are expressed by fiber length, fiber width, cell-wall thickness, and lumen diameter. Fiber dimensions are the most significant parameters for selecting a lignocellulosic fiber for pulp and paper making (Udohitinah and Oluwadare, 2011) and also to estimate the qualities of pulp and paper (Lin et al., 2014; Mercy et al., 2017).

Fiber length: It is an essential characteristic that determines the quality of lignocellulosic biomass for paper production. Fiber length is one of the morphological properties that affects tensile

strength and breaking strength of paper (Kiaei et al., 2014). According to Khakifirooz et al. (2013), fibers with fiber length less than 0.9 mm are classified as short fibers, those having length between 0.9 mm and 1.9 mm as average length fibers and fibers having length greater than 1.9 mm a long fiber. The fiber strength depends on the number of bonding sites that are available on an individual fiber to form an interwoven network of fibers (Kiaei et al., 2014). Fiber strength is an important factor in determining sheet formation and structure, tear strength, breaking strength and drainage properties in paper manufacturing process (Ai and Tschirner, 2010; Kiaei et al., 2014; Mercy et al., 2017). For instance long fibers result in better pulp performance creating strong bond formation between the fibers while short fibers result in more uniform and denser sheet formation properties, which slows drainage on the paper machine and increases moisture content after the press section going into the dryer section (Ai and Tschirner, 2010).

Fiber Lumen diameter: It is the internal hollow diameter of the fiber. It has an effect during the pulping process and pulp beating. Larger lumen diameter fibers result in better diffusion of cooking chemicals and pulp beating. This happened due to the penetration of liquid into empty spaces of the fibers (Kiaei et al., 2014; Mercy et al., 2017).

Fiber cell-wall thickness: is the thickness of the cell-wall of the fibers. It has an effect on the burst strength, tensile strength, and folding endurance of paper sheet. Thick cell-wall fibers results in paper with coarse surface. They give higher pulp yield, high tear strength and also low burst and tensile strength and folding endurance of paper (Kiaei et al., 2014; Mercy et al., 2017).

Generally, morphological properties of fibers are important to determine the strength properties of paper. Cell-wall thickness and fiber length have greatest influence on strength properties of paper (Fiserova et al., 2011). For example, paper properties like density, mechanical strength, optical and surface properties are affected by the initial pulping raw material, pulping method and

bleaching condition used (Anjos et al., 2015). Factors affecting the overall quality of natural fibers such as chemical composition and morphological properties are summarized in Table 2.2 (Kumar and Kumari, 2014; Dillen et al., 2016).

Table 3.2 Factors affecting fiber quality of natural fiber production.

Conditions	Factors affecting fiber quality
Plant growth	Species of plant
	Crop management
	Cell-wall thickness
	Fiber orientation in the plant and local climate
	Plant maturity
Harvesting	Fiber ripeness, which affects:
	Coarseness of fibers and adherence between fibers
Fiber extraction	Decortications process and type of retting method
Supply	Transportation and Storage conditions

2.6. Sugarcane bagasse in Ethiopia

Sugarcane is a potential source with large amount of natural fibers worldwide which has not yet been adequately exploited (Wong et al., 2013). It is an herbaceous perennial crop plant that belongs to the grass family, Poaceae. There are six types of known sugarcane species which are *Saccharum officinarum L.*, *Saccharum barberi*, *Saccharum endul*, *Saccharum spontaneum*, *Saccharum revannae*, and *Saccharum sinense* (Mekonnen et al., 2014; Tolera et al., 2014). Form these species *Saccharum officinarum L*. is extensively cultivated in Ethiopia for sugar production. In Ethiopia,

the commercial cultivation of sugarcane for sugar production started in 1954 at Wonji and in 1962 at Shoa (together named as Wonji-Shoa), in 1969 at Metahara and in 1998 at Finchaa (Tadesse et al., 2014). Currently, in Ethiopia about 145,030 ha of land is cultivated for sugarcane. It is planned to increase sugarcane plantation to 200,000 ha of land (Yirefu et al., 2013; Mekonnen et al., 2014). During sugar production, bagasse and molasses are obtained as byproducts. Currently, only a portion of the sugarcane bagasse is burned for generation of steam and electricity for the sugar mills while almost all of the remaining bagasse is dumped in the environment without being used (Alena and Sahu, 2013; Mekonnen et al., 2014; Evangelina et al., 2015).

On average, a mass 270 kg of bagasse with 50% moisture content per metric ton of sugarcane is generated. As has been already mentioned, it is readily available source of renewable lignocellulosic biomass around the sugar mills (Samariha and Khakifirooz, 2011; Khakifirooz et al., 2013; Wong et al., 2013). The sugarcane bagasse chemical composition depends on the sugarcane variety, the climatic condition, geographical location, the type of soil and the stage of maturity of sugarcane (Wong et al., 2013). Sugarcane bagasse can be considered either as a waste, affecting the environment if not utilized, or as a resource when appropriate utilization technologies are implemented (Pereira et al., 2011).

Currently, large amount of surplus sugarcane bagasse is available for other applications, such as production of pulp and paper, cellulosic ethanol, etc. (Mousavioun and Doherty, 2010). According to Ethiopian Sugar Corporation report (ESC, 2019), around 22% surplus sugarcane bagasse is available annually. Table 2.5 summarizes the amount of sugarcane bagasse generated at the Ethiopian sugar factories (ESC, 2019).

Table 2.4 The annual sugarcane bagasse production in Ethiopian sugar factories from 2014-2018.

Year	Produced sugarcane Bagasse (ton)							
	Wonj-shoa	Metehara	Fencha	Tendaho	Kessem	Arjo-Dedesa	Omo-kuraz II	Omo-kuraz III
2014	269,492	235,035	332,696					
2015	278,560	375,834	382,582		118,011	12,914		
2016	275,373	213,467	316,774	22,131	173,827	39,140		
2017	327,127	318,599	406,830	63,677	124,240	20,405	43,376	
2018	278,286	271,031	346,089	40,586	91,256	23,305	39,117	78,008

The interesting feature of sugarcane bagasse for pulp and paper production can be attributed to its ease of delignification, requiring milder and shorter cooking conditions than wood biomass (Vena et al., 2013). Sugarcane bagasse has two portions: the pith which is a non-fibrous tissue and the fiber part. The pith is not suitable for pulp and papermaking as it consumes large amount of chemicals in pulping process. Its content reaches 30-35% of sugarcane bagasse. Pith has high content of extractive substance, lignin, ash, and silica. It can cause drainage problem in pulp and paper production process and also in chemical recovery. So, to overcome these problems pretreatment of the raw material aimed at lowering of the pith content is important (Vena et al., 2013).

2.7. Pretreatment of lignocellulosic biomass

Lignocellulosic biomasses have complex chemical composition and structure. This complexity has hindered the delignification process. Pretreatment of lignocellulosic material improves the chemical and enzymatic delignification process (Abril et al., 2012; Galbe and Zacchi, 2012).

Pretreatment is a very important step in converting lignocellulosic biomass to pulp. The degree of polymerization, moisture content, available surface area, wax, pectin, hemicellulose and lignin content are some of the factors that affect the pulping process, yield and qualities of pulp and paper by consuming large amount of chemicals and damage the fibers (Karp et al., 2013; Pereira et al., 2011). Good pretreatment should be less destructive and generating low waste, avoid fiber breakage, preserve the pentose (hemicellulose) fractions, low formation of degradation products, minimum energy demands, and the pretreatment agent should have low cost and be capable of recycling inexpensively. Some of the pretreatment methods used in non-wood biomass are pre-hydrolysis, dilute acid pre-hydrolysis, hot water extraction and dry and wet depithing (Karp et al., 2013; Mohieldin, 2014).

Pre-hydrolysis pretreatment is one of the widely employed pretreatment method for the pretreatment of non-wood lignocellulosic biomass (Karp et al., 2013). It uses steam at high temperature and pressure. Quick decomposition is carried out, which results in the explosion of the cellular tissue and the separation of its components (Abril et al., 2012). The advantage of pre-hydrolysis pretreatment is because it is chemical free and have low environmental impact since it use water (Vila et al., 2011). The drawback of pre-hydrolysis is the degradation of hemicellulose and lignin transformation due to the high temperature (Karp et al., 2013).

Dilute acid pre-hydrolysis pretreatment is another pretreatment method for non-wood lignocellulosic biomass. Sulfuric acid is the most commonly used acid in the pretreatment but other reagents such as hydrochloric, nitric and phosphoric acids can also be used (Karp et al., 2013). Dilute acid pretreatment is performed by soaking the lignocellulosic material in appropriate acid in a controlled moderate temperature for effective penetration and treatment of the biomass for subsequent delignification process (karp et al., 2013; Galbe and Zacchi, 2012).

Hot water extraction is a hydrothermal pretreatment method, where pressure is applied to maintain the water in the liquid state at elevated temperature of 170-230 °C and pressure higher than 5 MPa. In this pretreatment method over 50% of the biomass could be solubilized; all of the hemicellulose together with more than 60% of the acid-insoluble lignin and less than 10% of the cellulose could be solubilized in the liquid phase (Karp et al., 2013).

Depithing pretreatment operations are used for the removal of pith fraction from the fiber in the case of sugarcane bagasse. This treatment decreases pith content almost by 20% in paper production (Hemmasi et al., 2011).

Generally, different pretreatment methods are employed in modification of the lignocellulosic material for specific products separating and breaking down lignin-carbohydrate complex structure (Wei et al., 2018). Pretreatment of lignocellulosic material increases the suitability for pulp production enabling mild pulping conditions (save chemical and energy), lowering the lignin content, minimizing the load of bleaching chemicals and to minimizing associated problems caused by pith and sticky materials (Vila et al., 2011; Mohieldin, 2014).

The pretreatment methods that are used for non-wood biomass pretreatment employ chemicals (like NaOH and H_2SO_4), water and steam which may damage the fibers and reduce the pulp yield and mechanical properties (tensile, buster and tear strength) of paper. To overcome this problem physical fractionation pretreatment is used, which separates the unwanted components of lignocellulosic material for pulp production by size difference using appropriate sieves.

2.8. Pulping methods

Pulping is the process of reducing the non-fibrous mass from wood and non-wood biomass by breaking the bonds within the structure of the call-wall, to release and soften the cellulose fibers.

Pulping process can be classified as mechanical, chemical and semi-chemical pulping (Sridach, 2010a; Bajpai, 2017). Chemical pulping is one of the major pulping methods which uses chemicals in the presence of heat and pressure. In chemical pulping, cooking the raw material with appropriate chemical in an aqueous solution at elevated temperature of 150 -175 ^{o}C and pressure between 7-11 atm., which degrades and dissolves away the lignin and leaves most of the cellulose and some hemicellulose in an intact form of the fibers (Figure 2.7) (Ibarra et al., 2006; Bassiouni and Ghazy, 2016; Bajpai, 2017). In chemical pulping the main factors that affect pulp and paper properties are chemical concentration (white liquor), pulping temperature, pressure, chips size, pulping time and liquor to material ratio (Wutisatwongkul et al., 2016).

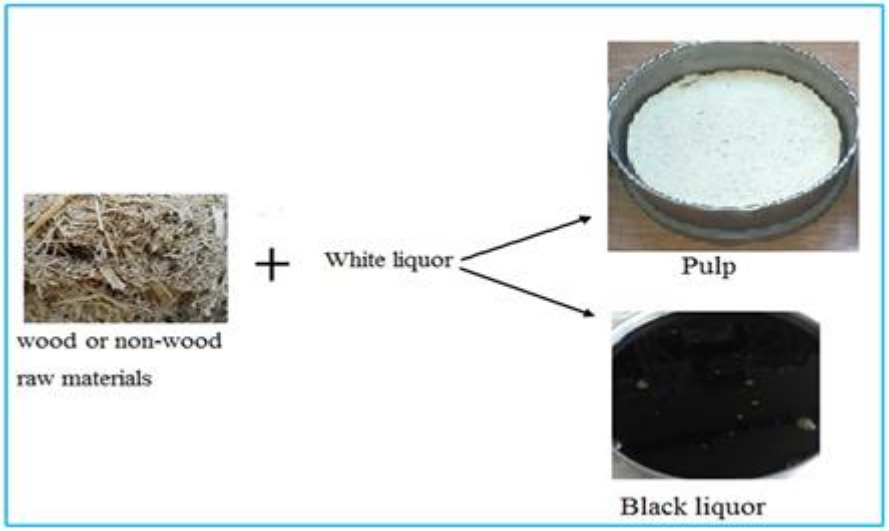


Figure 2.7 Chemical pulping process flow diagram

2.8.1. Kraft pulping

Kraft (sulfate) pulping was invented by Carl F. Dahl in 1889 and one of the predominant chemical pulping technologies worldwide (Johnston, 2012). It uses a solution of sodium hydroxide and sodium sulfide to convert wood or non-wood biomass to a pulp. In this process, lignocellulosic materials are cooked in a digester to degrade lignin and hemicellulose into fragments and dissolved

in the strong basic liquor. Then the fibers are separated and cleaned from the black liquor by series of washing (Santos et al., 2011; Moshkelani et al., 2013; Bassiouni and Ghazy, 2016; Bajpai, 2017). The removal of lignin is affected by the cooking temperature, alkali charge and cooking time (Bassiouni and Ghazy, 2016).

The advantage of Kraft pulping process lies in its capacity to give good fiber strength compared to the sulfite process. The disadvantage in this process is its low pulp yield because of carbohydrate instability and degradation during the reaction (Santos et al., 2011). To overcame this limitation, it is important to know the raw material properties and optimize the process conditions (interaction between process parameters) (Santos et al., 2011).

2.8.2. Soda pulping

Soda pulping was invented by Watt and Burgess in 1853. It uses sodium hydroxide as a cooking chemical. It is the first and the most traditional chemical pulping method suitable for various non-wood fiber source raw materials (Doherty and Rainey, 2006; Johnston, 2012; Andrade and Colodette, 2014). Nowadays, it is the predominant chemical pulping method for non-wood lignocellulosic materials like sugarcane bagasse, straw and reeds other than wood lignocellulosic materials (Akgül and Tozluo, 2010).

The advantages of soda pulping are significantly lower the ash content in the pulp which is the major problem in the case of non-wood raw materials, the sulfur-free medium of cooking process, its lower cooking time and temperature and suitable for delignification of non-wood biomass (Khakifirooz et al., 2013; Mohammad et al., 2013; Kaur et al., 2017). The limitation of soda pulping is the high chemical charge which is a problem for the pulp mills and environment, the difficulty in chemical recovery, and low pulp yield (Vishtal and Kraslawski, 2011; Khakifirooz et al., 2013; Mohammad et al., 2013; Kaur et al., 2017).

2.8.3. Organosolv pulping

Organosolv is one of the chemical pulping processes which uses organic solvents to solubilize the lignin in the biomass. The organosolv pulping method is mostly an experimental and to some extent a pilot-scale production system. The process is carried out by using either the low boiling solvents like ethanol, methanol and acetone or the high boiling solvents like ethyleneglycol and ethanolamine. Addition of sodium hydroxide or acidification ratio and concentration in organosolv pulping process is common for delignification of lignocellulosic biomass. It is used for all type of lignocellulosic materials like wood, non-wood and agricultural residues (Kaur et al., 2017; Berhanu et al., 2018).

The advantages of organosolv pulping are the ease of recovery of solvents using distillation, the less pollution load compared with Kraft pulping, prevention of polysaccharide degradation, its high pulp yield, low residual lignin content, high brightness and good paper strength (Sridach, 2010a; Kaur et al., 2017; Berhanu et al., 2018).

All pulping methods used different cooking chemicals and processing conditions. As result of pulping methods and processing parameters the pulp yield, pulp quality and paper mechanical properties are varied. Therefore, the selection of appropriate delignification parameters is vital, especially for non-wood biomass like sugarcane bagasse in order to increase the pulp yield and paper mechanical properties.

2.9. Pulp bleaching

Bleaching is a process which is employed to improve the brightness of the pulp by removing the residual lignin (Ibarra et al., 2006; Bajpai, 2010). Bleaching process increases pulp brightness. Brightness is widely used as an indication of its whiteness and provides a convenient way of

evaluating the degree of bleaching. Pulp brightness levels ranged from about 15% for unbleached alkaline pulp to about 93% for fully bleached alkaline pulps (Bajpai, 2010; Bajpai, 2017).

The purposes of bleaching are to increase the pulp brightness, to disintegrate the fiber bundles and shaves as well as the removal of dark fragments for chemical pulps and to remove the residual lignin in unbleached pulp as it eliminates the problem of yellowing of paper. During bleaching resin and other extractives are also removed, which stained in unbleached chemical pulps, and this improve the absorbency, brightness, whiteness and softness of pulp (Bajpai, 2010; Bajpai, 2017).

Pulp bleaching is carried out in a multistage process (alternative delignification and extracting the dissolved materials). Chemical pulp bleaching has been classified into a stepwise progression of chemical reaction, following from single stage hypochlorite bleaching to multi-stage bleaching process, involving chlorine (Cl_2), chlorine dioxide (ClO_2), hydrogen peroxide (H_2O_2) and ozone (O_3). The conventional bleaching sequence is CEHDED (Chlorine, Extraction with sodium hydroxide, Hypochlorite, Chlorine dioxide, Extraction with sodium hydroxide and Chlorine dioxide) (Bajpai, 2010). In Pulp and paper production, the pulp bleaching stage is the most polluting, due to the use of chlorine and chlorine based compounds such as Cl_2, ClO_2 and NaOCl (Moldes et al., 2010; Kiaei et al., 2014). Chlorine bleaching method has a negative environmental effect due to the release of chlorinated compounds; and also the degradation ability of the carbohydrate components (Ibarra et al., 2006). Therefore, the substitution of chlorine in bleaching sequences is a great concern for the pulp and paper industry from environmental point of view (Mussatto et al., 2008). Under stringent regulation and market demands for chlorine free bleached products, the pulp and paper industries are in fast-track for the implementation of elemental chlorine free (ECF) and total chlorine free (TCF) bleaching processes (Bajpai, 2010).

Nowadays, peroxide, oxygen, ozone and lignolytic enzymes are some of the methods used as chlorine free pulp bleaching method. They are the best potential alternative chlorine free bleaching technologies both from environment and economy point of view. Among these chlorine free chemicals, hydrogen peroxide is recognized as an important bleaching chemical, and environmentally friendly (Ibarra et al., 2006; Loureiro et al., 2011). It is an oxidant compound widely used for bleaching sequences in chemical pulp bleaching (Requejo et al., 2012). It is applied in combination with alkali to decrease kappa number and to increase brightness (Shatalov and Pereira, 2005). In this bleaching process, the permanent removal of most of the chromophoric groups present in the lignin molecule occurred, due to the reaction of lignin with peroxide (Mussatto et al., 2008). Alkaline hydrogen peroxide are enough to bleach non-wood chemical pulps to high brightness by keeping high yield and strength properties (Shatalov and Pereira, 2005). The advantage and disadvantage of some pulp bleaching chemicals are summarized in Table 2.3.

The bleaching methods listed are effective to bleach non-wood biomass pulps. However, they use different chemicals in multi-stage processes. This can damage the fibers and reduce yield and mechanical properties of paper. The reduction of number of bleaching stages and selection of appropriate bleaching parameters (like temperature, bleaching chemical concentration and time) for single stage hydrogen peroxide bleaching is important.

Table 2.5 Bleaching chemicals: advantages and disadvantages

Chemicals	Designation	Advantage	Disadvantage
Chlorine	C	Effective, economical delignification	Can cause loss of pulp strength if used improperly, environmental hazard
Hypochlorite	H	Easy to make and use	Can cause loss of pulp strength if used improperly, environmental hazard
Chlorine dioxide	D	Achieve high brightness without pulp degradation	Must be made at mill site
Oxygen	O	Low chemical cost	Used in large amounts, requires expensive equipment, can cause loss of pulp strength
Hydrogen peroxide	P	Easy to use and high pulp yield	Relatively expansive
Reductant hydrosulfite		Easy to use, low capital	Decomposes readily, limited brightness gain
Alkali sodium hydroxide	E	Effective & economical	Darkens pulp

2.10. Process condition optimization

Experimental design is a plan for collecting and analyzing data or is a planned approach for determining cause and effect relationships in the process. Response surface methodology (RSM) is a collection of statistical and mathematical techniques for designing experiments, building models, evaluating the effects of several factors and their interactions, searching optimal conditions for desirable responses and reducing the number of experiments (Myers et al., 2009; Wang et al., 2011; Subramonian et al., 2015; Birjandi and Younesi, 2016). Response surface methodology has been proposed to determine the influence of individual and their interactive input variables on the response variables. The input variables are subjected to the control of an experiment and called independent variables. The independent variables affect the quality characteristics of the product or process output called response (Myers et al., 2009; Wang et al., 2011; Birjandi and Younesi, 2016)

The experimental design such as the central composite design (CCD) and Multilevel categoric design are widely used in experiments involving several factors in order to fit a model by the least squares technique, where the adequacy of the proposed model is then revealed using the diagnostic examination tests (Birjandi and Younesi, 2016). This method has been widely used for the optimization of various processes in food chemistry, material science, chemical engineering and biotechnology (Myers et al., 2009; Wang et al., 2011; Subramonian et al., 2015; Birjandi and Younesi, 2016). Furthermore, it has important applications in the design, development and formulation of new products as well as in the improvement of existing product designs (Myers et al., 2009).

2.11. Paper sheet formation

Paper is a sheet constituted of pulp fibers bonded together with hydrogen bond, which are normally produced by separating wood fiber cells using mechanical or chemical processes. The isolated fibers are subsequently rearranged and randomly distributed into a sheet structure (Figure 2.8) (Sridach, 2010b; Johnston, 2012).

In paper making process, the pulp slurry is pumped to the fourdrinier machine. The fourdrinier machine forms web of fibers and removes large amount of water. Moreover, additional dewatering occurs in pressing and drying section. As the paper enters the press section, it undergoes compression between two rotating rolls to squeeze out more water. These cases continue into a second drying operation before entering the calendaring stacks that are part of the finishing operation. At the end of the paper machine, paper continues onto a reel for winding to the desired roll diameter (Bajpai, 2010; Bajpai, 2012).

The extent and intensity of paper properties are dependent on the biological species and pulp fiber processing which have an interlinked effect on the paper quality (Anjos et al., 2015). Paper mechanical properties are dependent on the fiber morphology such as fiber length, fiber width and cell-wall thickness. The mechanical properties of paper which include tensile strength, tear strength and burst strength are affected by the morphological properties and chemical composition of the raw material and also by the pulping method and associated parameters (Fiserova et al., 2011).

The burst and tensile strength of paper sheet are affected by fine particles of lignocellulosic materials in addition to morphological properties. Fiber flexibility is another property of paper which affects tensile and burst strength and printing ability of paper. Tensile strength is affected

by mechanical and chemical treatments of lignocellulosic materials and inter-fiber bonding abilities (Fiserova et al., 2011).

Figure 2.8 Electronic microscopy observation of paper structure (magnification ×35 and ×80 in red frame) (Johnston, 2012).

2.12. Pulp and paper wastes

Pulp and paper industries consume large volume of fresh water and release large amount of wastewater. In pulp and paper mills huge quantity of sludge and significant amount of wastewater are generated at different stages of paper making processes of sorting, pulping, screening, cleaning, bleaching and fiber recycling processes. This wastewater contains variety of organic and inorganic matters mostly originating from the raw material cooking chemicals, bleaching chemicals, and dyeing both in the liquid and solid form (Abdullah et al., 2015; Ashra et al., 2015).

Pulp and paper industries generate a liquid waste called black liquor. Black liquor is composed of organic compounds of the raw material, the hemicellulose and lignin, dissolved in the cooking chemicals and inorganic chemicals. The chemical and physical properties of black liquor depend on the nature of raw material, dose of cooking chemicals, pulping methods, and the black liquor dry solids contents. The liquid waste normally burnt to produce electricity and steam in pulp and paper mill, while caustics are recovered (Lei et al., 2010; Bajpai, 2017).

Solid wastes are rejected, fine fibers, significant amounts of ash and trace quantities of heavy metals, chlorinated organic compounds, and pathogens. The amount and the composition of the solid waste depend on the type of raw materials used (wood or non-wood), the pulping method, process technology applied and the amount of water used in particular process (Pokhrel and Viraraghavan, 2004; Monte et al., 2009).

Some solid wastes are non-hazardous, which require particular management as a waste material or as a byproduct. Most solid wastes are removed after primary mechanical treatment, resulting in the sludge that contains large quantities of fibers and paper making fillers. Most of the sludge are used as landfill, reused in other pulp and paper mills, it could be recycled into production on-site, or used in other products (Alda, 2008).

The most widely researched non-conventional management alternative has been the reuse of primary sludge as feedstock in the manufacture of hardboard, fiber-board, building materials such as composites of cement, bricks, ceramics, concrete and landfill cover material. These management alternatives upgrade the use of high fiber content of some primary sludge in fiberboard, the high filler content of others (in building materials) or in landfill cover materials (Alda, 2008; Andrés et al., 2015).

The waste generated from pulp and paper manufacturing cause environmental pollution. To overcome those problems, use of chemical free raw material pretreatment method like physical fractionation pretreatment, selection of delignification and bleaching method, reduction of chemical dose in pulping and bleaching is important. The pulp and paper production flow diagram show in Figure 2.9.

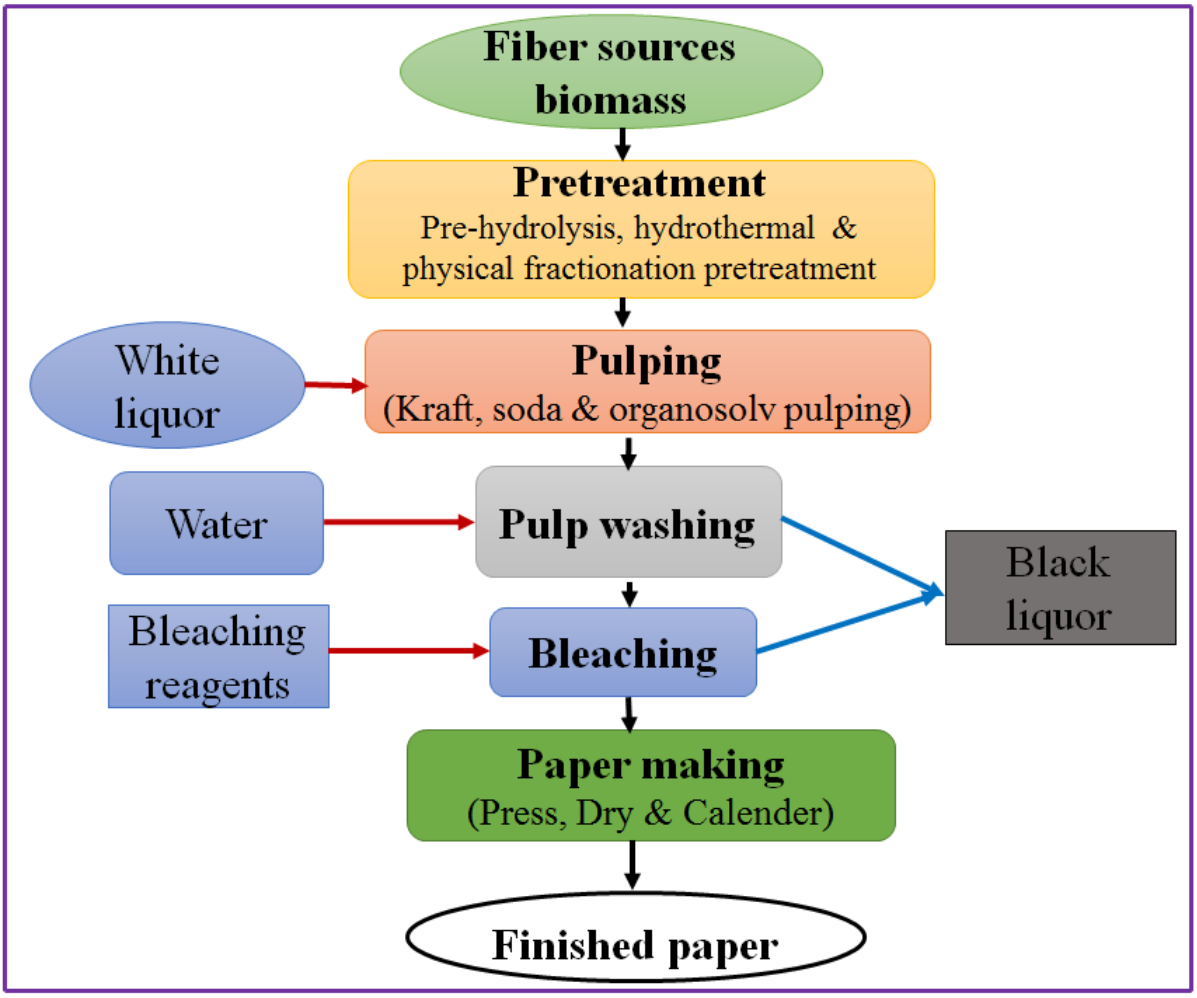


Figure 2.9 Process flow diagram showing pulp and paper manufacturing from non-wood biomass.

2.13. Concluding Remarks

The production of paper and paper related material increased with annual growth rate of 2.8% worldwide. Remarkable variation has been observed in annual production of pulp and paper products among regions of the world. Form global annual production of paper, Ethiopia covers less than 0.01%. This is because pulp and paper production required vast capital investment and enormous tons of fibrous raw materials. To satisfied the pulp and paper demand, enormous amount of foreign currency has been used to the import of pulp and paper products to the country.

Agricultural residues are one of suitable and sustainable raw material for pulp and paper production. The chemical and morphological characteristics of biomass are different based on species, location, and plant maturity. So far, pulp and paper production potential of numerous non-wood plants and agricultural residues have been investigated (Tripathi et al., 2016; Shao et al., 2017; Berhanu et al., 2018).

Sugarcane is largely cultivated in Ethiopia for sugar production, and large amount of bagasse are surplus without significant commercial value. Around 260 thousand tons of bagasse are discarded annually from 1.2 million tons of bagasse annually produced in the sugar factories. However, Ethiopian sugarcane bagasse characterization and utilization for paper production has not been previously studied. Moreover, any pulping method for Ethiopian sugarcane bagasse delignification and bleaching have not been tried before.

CHAPTER THREE

Characterization of Ethiopian sugarcane bagasse

3.1. Introduction

Sugarcane bagasse (SCB) is an abundant agro-industrial byproduct, inexpensive and a readily available source of renewable lignocellulosic biomass (Jabasingh and Nachiyar, 2011, 2012). Sugarcane bagasse as lignocellulosic materials contain cellulose, lignin, hemicellulose, ash, silica and ethanol-toluene extractive substances (Samariha and Khakifirooz, 2011; Andrade and Colodette, 2014). Suitability of the lignocellulosic material for the paper pulp production depends on its chemical composition and pretreatment method. Pretreatment of any lignocellulosic material is crucial to remove any unwanted components. The selection of an appropriate pretreatment method depends on maintaining of cellulose structure, operational cost, simplicity of the system and chemical consumption (Zhao and Liu, 2012; Biswas and Ahring, 2016).

Some of the pretreatment methods applied for various lignocellulosic materials specifically for sugarcane bagasse are the pre-hydrolysis treatment (Andrade and Colodette, 2014), combination of dry depithing and wet depithing (Agnihotri et al., 2010), and hot water extraction (Lei et al., 2010). In this study, we used a cost-effective, physical fractionation pretreatment (PFP) to process the ESCB. The method reduces the chemical used during pulping and bleaching, prevents fiber damage, and enhances pulp quality. Also, the residue after the PFP can be used for the co-energy generation (Vila et al., 2011). There is hardly any damage to the fibers, and the pulp and paper quality is enhanced (Mohieldin, 2014). The fiber morphology of lignocellulosic materials is an

important parameter for estimating the quality of pulp and paper. Fibers are conventionally classified as short, average and long based on their fiber length (Khakifirooz et al., 2013). Fibers with Runkel ratio less than 1 are suitable for paper making. At this Runkel ratio, fibers are more flexible, collapse easily and form paper with large bonded area (Mercy et al., 2017). The degree of this fiber bonding depend on the individual fiber flexibility, characterized by the flexibility coefficient (Hemmasi et al., 2011; Kiaei et al., 2014).

Henceforth, in this chapter, the suitability and effectiveness of the PFP on the ESCB were scrutinized, in order to shore up its application for pulp and paper production. Furthermore, ESCB were compared to the woods, which are traditionally used in paper production.

3.2. Materials and Methods

3.2.1. Materials

ESCB samples were collected from Wonji-Shoa sugar factory, Ethiopia. The samples were air dried and categorized accordingly. Untreated (sample A) and pretreated (sample B and sample C) were referred to as ESCB-A, ESCB-B and ESCB-C, respectively, based on their sizes. The samples were ground-using hammer mill, and the fraction that passed through a 40 mesh screen and retained in the 60 mesh screen was collected and stored in airtight bags for further chemical characterization and analysis (Andrade and Colodette, 2014). The sample preparation was carried out using standard methods of the Technical Association of Pulp and Paper Industry (TAPPI). For the morphological characterization (fiber length, fiber diameter, cell-wall thickness, and lumen diameter), samples were taken from top, middle, and bottom parts of the sugarcane.

3.2.2. Methods

3.2.2.1. Fiber dimension and derived values

Fiber length was determined by macerating small slivers of ESCB in 10 mL of 67% HNO_3. This is followed by boiling for 10 min, to separate the fiber bundles. The slivers were washed with distilled water, and the fiber bundles were separated into individual fibers and placed on a slide (standard, 7.5 cm×2.5 cm) using a dropper. Fiber samples were viewed under the calibrated microscope (Motic microscope, model BA210) with magnification of 40X. A total of 120 randomly chosen fibers were measured using Motic images plus 2.0 software. Sugarcane cross section at the base, middle and top of the stem were taken for determination of the fiber diameter, lumen diameter and cell-wall thickness. The samples were then sliced using a surgical blade and the slices with clear visibility were employed for the cell structure dimension analysis. The slices were stained using the aniline sulphate-glycerin mixture for 5 min. They were then washed with different concentration of ethanol (30%, 60%, 90%) for drying. The slices were then placed on a slide (standard, 7.5 cm×2.5 cm) and then covered with a cover clip after dropping hematoxylin as a binder. The cell visualization was carried out with a magnification of 100X. The Motic microscope observation of ESCB, showing the lumen diameter, indicated by 1, and cell-wall thickness indicated by 2, and the fiber length is shown in Figure 3.1. Three derived values were calculated using the fiber dimensions: slenderness ratio (fiber length/diameter), flexibility coefficient (fiber lumen diameter/fiber diameter×100) and Runkel ratio (2 × fiber cell-wall thickness/lumen diameter) (Agnihotri et al., 2010; Cao et al., 2014). These values were then compared to those of softwood, hardwoods, and non-wood lignocellulosic biomass, which are used as reference, in order to assess the suitability of ESCB for pulp and paper production.

3.2.2.2. Physical fractionation pretreatment

The physical fractionation pretreatment (PFP) of ESCB was carried out using two different sieve sizes to separate the rest of the bagasse. Sample ESCB-B was fractionated by using 1mm and sample ESCB-C by 1.5 mm sieve size. The air-dried ESCB sample was fractionated to remove the unwanted components like pith and dust. The fractionated sample that was retained by the 1 mm and 1.5 mm sieve was collected and used for the chemical compositional and FTIR analysis.

3.2.2.3. Chemical characterization

ESCB was subjected to chemical composition characterization using the following standard procedures: cellulose content was measured using nitric acid method and holocellulose content by chlorite method (Hamzeh et al., 2013). TAPPI standards were used in the measurement of lignin (TAPPI T222 om-02), ash (TAPPI T211 om-02), silica (TAPPI T245 cm-07), cold and hot water solubility (TAPPI T207 cm-99), 1% NaOH solubility (TAPPI T212 om-02) and ethanol-toluene extractive (TAPPI T204 cm-97). All the tests were run in triplicate, and the average values were recorded.

3.2.2.4. Statistical analysis

The data collected was subjected to statistical analysis using (Statistical Package for Social Sciences) SPSS software, to determine the significant differences in the chemical composition of the untreated and pretreated ESCB. This approach provides a more accurate picture of standard error and allows a direct visual comparison of the means, for accuracy in analysis within each sample.

3.2.2.5. FTIR analysis

FTIR spectra of ESCB was measured by the direct transmittance using the KBr pellet technique (Chen et al., 2010; Poletto et al., 2012). The pretreatment was carried out by tableting the mixture of each sample and KBr (where KBr has a proportion of 0.5 wt%.) into a film. Spectra were recorded from 4000 to 400 cm^{-1} at a resolution of 4 cm^{-1} using Perkin-100 FTIR spectrometer (PerkinElmer Inc., USA).

3.3. Results and Discussion

3.3.1. Fiber dimensions and derived values

The fiber dimensions and their derived values for ESCB, reference non-wood and wood fiber source are presented in Table 3.1. The ESCB had a very good fiber dimension and derived values compared to those of the softwood, hardwood, bamboo, *Sacchuarum officinerum*-Co 89003 bagasse and Iranian sugarcane bagasse. According to the classification made by Khakifirooz et al. (2013), the fiber length of the ESCB lies in the average fiber length category. The longer fibers produce good surface contact and fiber-to-fiber bonding (Kiaei et al., 2014), resulting in a good pulp beating with satisfactory paper tear indices and bursting strength, a stringent requirement for the printing and writing purposes papers (Ververis et al., 2004). The ESCB had a very good (>60) slenderness ratio, basically due to its longer fibers, leading to an enhanced tearing resistance. ESCB had an excellent fiber diameter and cell-wall thickness and was shown to possess a good Runkel ratio (<1) (Table 3.1) (Kiaei et al., 2014; Mercy et al., 2017).

Table 3.1 Fiber dimension and derived value of ESCB compared with wood and non-wood fiber sources

Materials	Ethiopian sugarcane bagasse[a]	*Eucalyptus globulus* labill[b]	Scots pine[c]	Bamboos (A*pus*)[d]	*Saccharum officinerum* -Co 89003 bagasse[e]	Iranian sugarcane bagasse[f]
L(mm)	1.86±0.49	0.98	2.15	2.34	1.51±0.08	1.59
D (µm)	30.02±5.09	18.8	33.1	14.54	21.4±1.6	20.96
W (µm)	27.26±4.91	n.a	15.5	6.12	6.23±0.4	9.72
t (µm)	2.53±0.76	4.9	2.2	4.21	7.74±0.2	5.64
Rr (2W/L)	0.18	n.a	0.28	1.18	2.46	1.16
Sr (L/D)	61.96	n.a	64.95	160.94	70.56	75.86
Fc(L/D)*100	90.82	n.a	46.82	42	29.29	46.37
Rc (W/D)	0.08	n.a	0.06	0.29	0.72	0.73

L: Fiber length; D: Fiber diameter; W: Lumen diameter; t: Cell-wall thickness; Rr: Runkel ratio; Sr: Slenderness ratio; Fc: Flexibility coefficient; Rc: Rigidity coefficient; n.a: not available; '±' refers to standard deviation.

Source: [a]Current study, [b](Miranda et al., 2012), [c](Sable et al., 2012), [d](Sugesty et al., 2015), [e](Agnihotri et al., 2010), [f](Hemmasi et al., 2011).

The lumen diameter of ESCB was greater than that of some of the woods species, basically resulting in high flexibility coefficient. Fibers with high flexibility coefficient can in turn complement a higher mechanical strength (tensile, burst and folding endurance) (Ververis et al., 2004; Hemmasi et al., 2011; Kiaei et al., 2014). Therefore, papers made from ESCB fibers are expected to be appropriate even for wrapping and packaging needs.

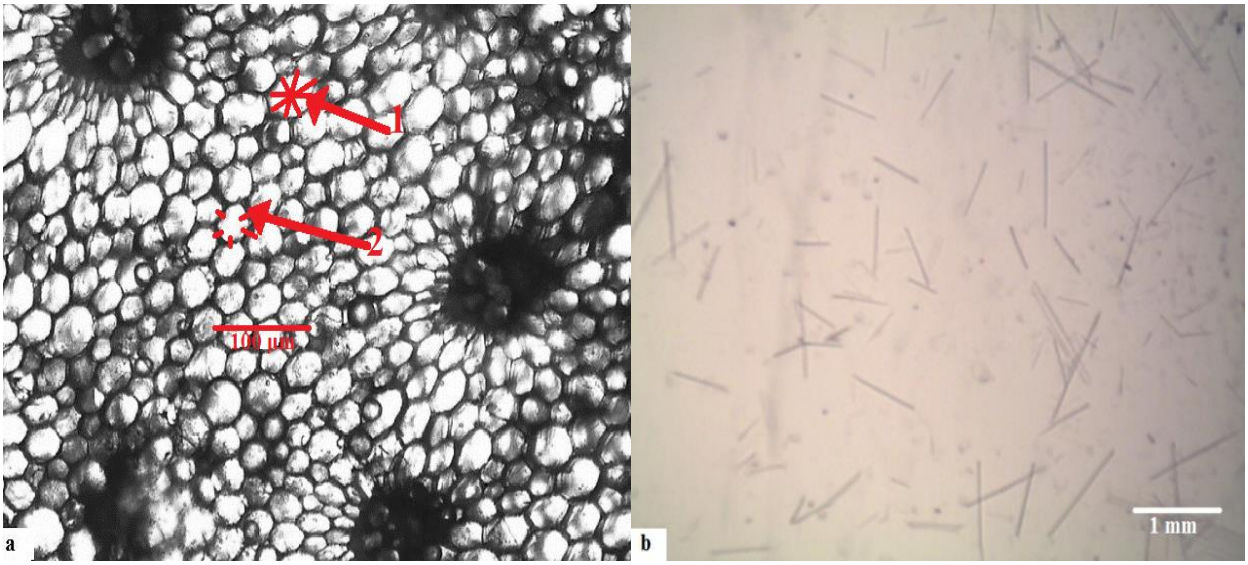


Figure 3.1 Motic microscopic observation of ESCB fiber dimensions: a) Cross sectional view, lumen diameter (1) and cell-wall thickness (2) of the fibers, b) fiber length

3.3.2. Chemical characterization

The chemical compositions of the samples (ESCB-A, ESCB-B, ESCB-C), reference woods (hardwood and softwood) and non-woods (bamboo, Iranian sugarcane bagasse and *Saccharum officinerum*-Co 89003 bagasse) is presented in Table 3.2. The cellulose content of all samples ESCB-A, ESCB-B and ESCB-C was satisfactory (closer to 50%). Plant materials with cellulose content > 34% were considered as suitable for pulp and paper production (Hemmasi et al., 2011). The Klason lignin contents were also satisfactory (<30%) for all the samples. The ESCB-B and ESCB-C showed the lowest lignin content, eventually due to the physical fractionation pretreatment (PFP) comprehending the fact that ESCB-B and ESCB-C will require milder pulping and bleaching conditions (lower temperatures and chemicals) to arrive at a satisfactory kappa number, at the same time less energy and chemical consumption, when compared with ESCB-A, and other conventional woods (Agnihotri et al., 2010; Hemmasi et al., 2011).

Table 3.2 Chemical composition of ESCB compared with wood and non-wood biomass (% dry weight).

Chemical composition	Cell	Lig	Hol	Ext	1% NaOH	HWS	CWS	Ash	Sil
ESCB-A*	48±0.40	27.6±1.47	67.87±0.81	3.90±1.08	37.7±1.08	8.5±0.70	5±1.08	13.65±1.47	2.65±0.40
ESCB-B*	50±0.81	18±0.70	80±0.70	1.95±0.81	27.2±0.40	4±0.40	4±0.70	4.8±0.40	1.30±0.40
ESCB-C*	53±0.70	18±0.40	80±0.40	1.90±1.08	26.7±0.40	4±0.70	4±0.81	4.65±0.40	1.15±0.40
Eucalyptus globulus[a]	56.9	17.8	n.a	1.4	12.2	n.a	n.a	1.0	n.a
Scots pine[b]	49.0	27.1	n.a	2.9	n.a	n.a	n.a	0.3	n.a
Bamboos (*apus*)[c]	47.56	22.41	63.23	4.89	29.89	12.67	10.89	6.09	n.a
Saccharum officinerum-Co 89003 bagasse[d]	42.34±0.36	21.7±0.35	71.03±0.5	1.85±0.01	32.29±0.1	7.42±0.05	3.02±0.02	2.10±0.05	0.98±0.007
Iranian sugarcane bagasse[e]	55.75±0.4	20.5±1.7	n.a	3.25±4.3	n.a	n.a	n.a	1.85±3.7	n.a

Cell: Cellulose; Lig: Lignin; Hol: Holocellulose; Ext: Extractive; 1% NaOH: 1% NaOH solubility; HWS: Hot Water Solubility; CWS: Cold Water Solubility; Sil: Silica content; n.a: not available; '±' refers to standard deviation.

Source:*current study, [a](Miranda et al., 2012), [b](Sable et al., 2012), [c](Sugesty et al., 2015), [d](Agnihotri et al., 2010), [e](Hemmasi et al., 2011).

Holocellulose content was lower for ESCB-A, compared to ESCB-B and ESCB-C. This indicates the efficiency of pretreatment of the ESCB, with high holocellulose content to produce pulp with higher yield (Sugesty et al., 2015). The alcohol-toluene solubility of the ESCB decreased in the order of ESCB-A, ESCB-B and ESCB-C, after the PFP. The alcohol-toluene solubility of ESCB-B and ESCB-C was actually less than the bamboo (*Apus*) and Iranian sugarcane bagasse, but was higher than Eucalyptus *globulus* labill, and similar to Saccharum *officinerum*-Co 89003 bagasse. Such solubility values shows the presence of huge amounts of substances, resembling wax, fats, resins, phytosterols, non-volatile hydrocarbons, low molecular weight carbohydrates, salts and other water-solubile substances in ESCB-A, which could be challenging for the production of good-quailty pulp, since these extractives make stain upon pulping, enhancing the tendency to leave stains on the resulting paper sheets (Rodrıguez et al., 2008; Cao et al., 2014).

The ash and silica content of the ESCB decreased in the order of ESCB-A, ESCB-B and ESCB-C, after the PFP (Figure 3.2). ESCB had a high amount of minerals, especially silica, then the conventional sample used in this study. Higher silica content can cause problems during refining and recovery of the cooking liquor, used in the first stage of the pulping process. Since PFP on the ESCB significantly reduces the silica content, the problems during the cooking liquor recovery would be eliminated (Rodrıguez et al., 2008). The 1% NaOH, hot and cold water-soluble components in ESCB decreased in the order of ESCB-A, ESCB-B and ESCB-C. The 1 % NaOH solubility in all the samples were higher than *Eucalyptus globulus* labill. Nevertheless, solubility in 1 % NaOH was lower for ESCB-B and ESCB-C, when compared with bamboo (*Apus*) and *Saccharum officinerum*-Co 89003 bagasse (Table 3.2). The measure of 1% NaOH solubility indicates the presence of high amount of sugar components which increase the susceptibility of ESCB-A to degradation, by either microorganisms, heat, light or oxidation (Agnihotri et al., 2010).

Hence, adequate precaution should be taken during the storage of the ESCB. The higher content of hot water-soluble components including starch, sugar and proteins indicates the incomplete extraction of the sugarcane, which can in turn increase the consumption of pulping chemicals (Rodrıguez et al., 2008). The pretreatment of bagasse brought a significant decrease in lignin, extractives, 1% NaOH and hot water solubility, ash, and silica contents. The high content of unwanted materials can affect the quality and yields of pulp, increase the chemical consumption and cause problem during the production process (Vila et al., 2011). Thus, the treatment is more attractive, since it bears considerable practical and economic advantage (Przybysz et al., 2018).

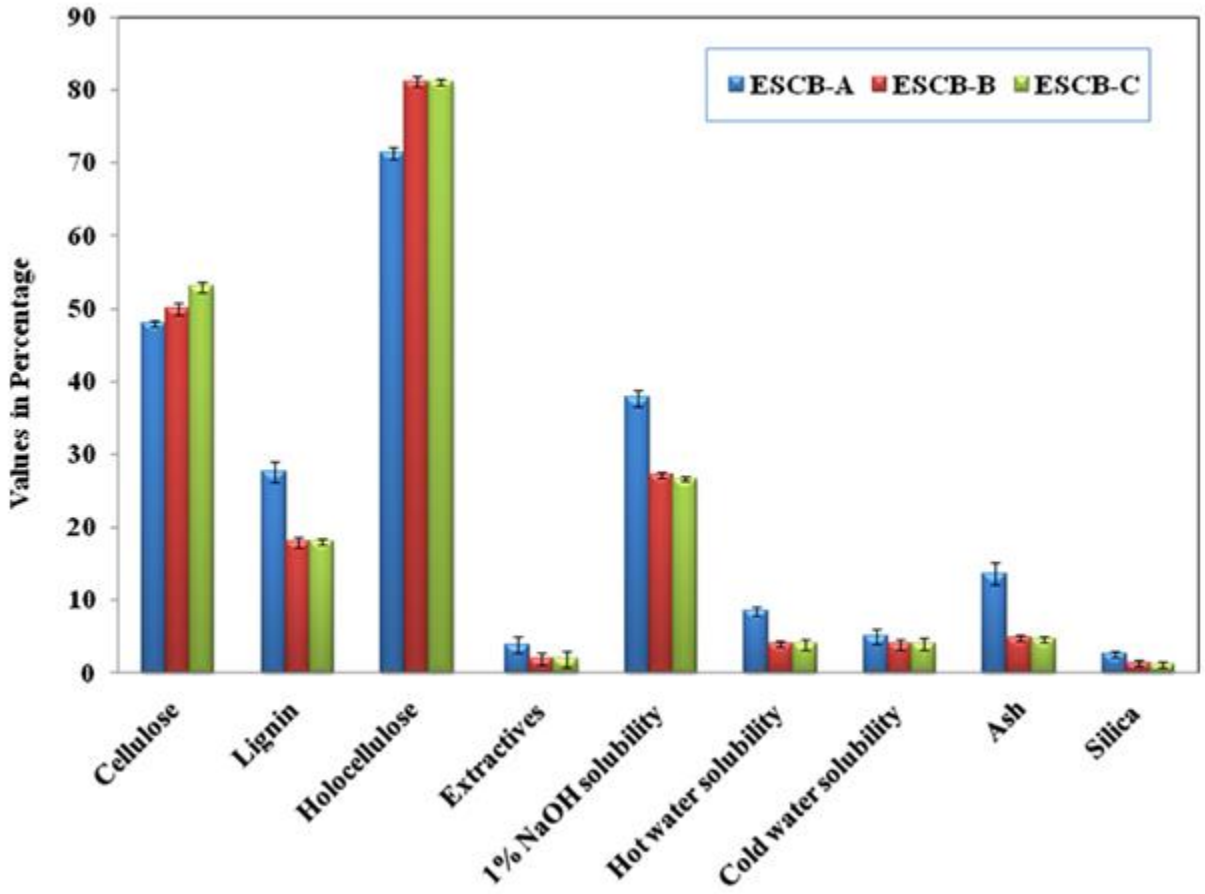


Figure 3.2 Comparative compositional analysis of ESCB-A, ESCB-B and ESCB-C

3.3.3. Fourier Transform Infrared Spectroscopy (FTIR) Analysis

The FTIR spectrum is presented in Figure 3.3, and the band observed and the corresponding functional groups are summarized in Table 3.3 (Adel et al., 2010; Poletto et al., 2012).

Table 3.3 FTIR assignment band of ESCB samples

Band wavenumber (cm^{-1})	Functional group	Polymer
668	Aromatic ring	Lignin
840, 834	Glycosidic linkage	Cellulose, Hemicellulose
899	C-H deformation	Cellulose
1036, 1034	C-H, C-O-C stretching	Cellulose, hemicellulose, lignin
1245, 1242	C-O stretching	Lignin
1327	C-H vibration, O-H in plane bending	Cellulose, hemicellulose, lignin
1384	C-H stretching	Cellulose, hemicellulose, lignin
1420-1430	C-H in plane deformation	Cellulose
1515, 1517	C=C stretching of aromatic ring	Lignin
1604, 1606	Aromatic ring stretching	Lignin
1735	Carbonyl stretching	Lignin
2854, 2919	C-H stretching	Lignin
3422, 3429	O-H stretching	Lignin

Sources: (Chen et al., 2010; Iskalieva et al., 2012; Li et al., 2012; Poletto et al., 2012; Wong et al., 2013; Xu et al., 2013; Borges et al., 2016)

There is a strong band at around 3422 cm^{-1}, which is assigned to different O-H stretching bands of lignin (Xu et al., 2013). The two bands around at 2919 cm^{-1} and 2854 cm^{-1}, mainly due to the higher content of lignin and extractives and more prominent in the ESCB-A, are related to the

asymmetric and symmetric methyl and methylene stretching groups present in the spectra of all the ESCB components (Chen et al., 2010; Poletto et al., 2012).

The bands at 1604, 1515 and 1245 cm^{-1} are assigned to C=C, C-O stretching or bending vibrations of the different groups present in lignin. The bands at 1425, 1327, 1220 and 1110 cm^{-1} are characteristic of C-H, C-O deformation, bending or stretching vibrations of the groups in lignin and carbohydrates. The bands at 1735, 1384, 1242 and 1034 cm^{-1} are assigned to C=O, C-H, C-O-C, C-O deformation or stretching vibrations of different groups in carbohydrates. The absorption peak at 1515 and 668 cm^{-1}, most prominent in the ESCB-A is the characteristics of the aromatic skeletal vibration C=C of the benzene ring is the lignin (Wong et al., 2013; Borges et al., 2016).

The bands at 1735 cm^{-1} are assigned to the C=O stretching vibrations of the carboxyl and acetyl groups in hemicellulose (Poletto et al., 2012). The strong and broad band at 1735 cm^{-1} shown by ESCB-B and ESCB-C due to the higher holocellulose content (Chen et al., 2010; Poletto et al., 2012; Wong et al., 2013). The bands at 1420-1430 cm^{-1} and 899 cm^{-1} are assigned to the aromatic skeletal vibrations associated with C-H in plane deformation and C-H deformation of cellulose, respectively. They are associated with the amount of crystalline structure of cellulose, while the bands at 899 cm^{-1} are related to the amorphous region in cellulose (Borges et al., 2016). The absence of the band at 2348 cm^{-1} from ESCB-B and ESCB-C are due the reduction of lignin and extractives. The FTIR results were found to be in agreement with the chemical compositional analysis results (Table 3.3). This indicates the effectiveness of PFP for the reduction of unwanted components to facilitate application in the pulp and paper production.

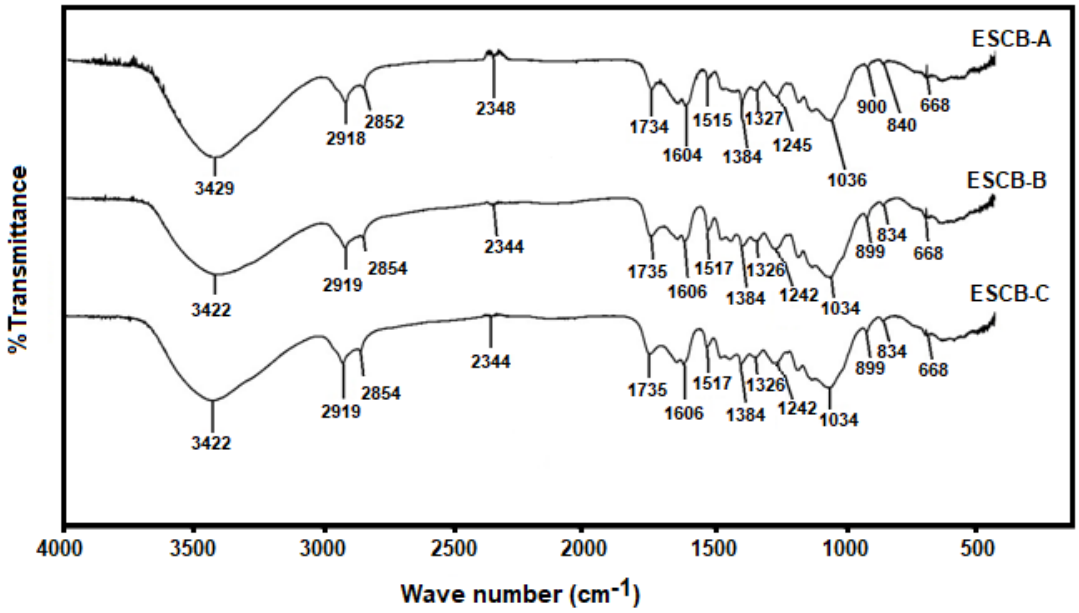


Figure 3.3 FTIR spectra of ESCB samples

3.4. Conclusion

The Ethiopian sugarcane bagasse (ESCB) had a very good fiber length (1.86 mm), cell-wall thickness (2.53 µm), flexibility coefficient (90), Runkel ratio (<1), cellulose content (50%) and Klason lignin content (18%), making its suitable for pulp and paper production. Nevertheless, many unwanted components, including the lignin, extractive, ash, and silica, increase the lignocellulosic recalcitrance of ESCB toward pulping. The physical fractionation pretreatment (PFP) adopted for the (ESCB) in this study is an effective pretreatment method to remove these unwanted components, prior to its application for pulp and paper production, as could be evident from the FTIR spectrum. The research could thus be a boon, in terms of two facets: to manufacture good quality paper and to provide an eco-friendly substitution for the woody forest resources.

CHAPTER FOUR

Optimization of soda delignification and single stage hydrogen peroxide bleaching

4.1. Introduction

Sugarcane bagasse has suitable chemical composition, morphological properties, and high carbohydrate content (51-78%), which makes it a very promising raw material for the pulp and paper production (Jabasingh and Nachiyar, 2012; Jabasingh et al., 2016; Carvalho et al., 2014). Most of the bleachable grade pulps were produced by the Kraft, soda and organosolv delignification methods (Wutisatwongkul et al., 2016).

Soda pulping is a sulfur-free medium of cooking process, which requires lesser cooking time and lower temperature (Enberg et al., 2013; Kaur et al., 2017). One approach to upgrade the utilization of soda delignification technology is to select the apt process parameters, which includes the pulping temperature, sodium hydroxide (NaOH) concentration, time, liquid to solid ratio, and the raw material purity. From these parameters pulping temperature, sodium hydroxide (NaOH) concentration, and time are the primary factors which significantly affect the pulp yield and kappa number (Wutisatwongkul et al., 2016; Anupam et al., 2018). The optimization of these pulping parameters become necessary because of the influence of these parameters on the quality of pulp and paper (Anupam et al., 2018). Moreover, prior to this optimization study, the raw material purity of the Ethiopian sugarcane bagasse was performed using the physical fractionation pretreatment (PFP) (Mamaye et al., 2019). Response surface methodology and multilevel categoric

design are the optimization methods commonly applied in the chemical and biochemical processes, including for the delignification and bleaching studies. This method allows the analysis of the simultaneous effects of the multiple independent process variables. In addition, response surface methodology requires a small number of experiments (Myers et al., 2009; Anupam et al., 2018; Berhanu et al., 2018). So far, the soda delignification conditions reported are the temperatures between 160 to 180 °C, NaOH concentration of 12.5% to 15%, time above 60 min and the liquid to biomass ratio of 8:1 and 4:1 L/kg (Agnihotri et al., 2010; Andrade and Colodette, 2014). A combination of dry-wet depithing and pre-hydrolysis pretreatments were adopted prior to the delignification (Andrade and Colodette, 2014). The introduction of physical fractionation pretreatment (PFP) prior to soda delignification helps to produce pulp with a satisfactory quality (Mamaye et al., 2019). The soda pulp is dark, and in order to facilitate the decrease in this darkness, the pulp should be bleached using total chlorine free (TCF) bleaching method (Hu et al., 2017).

Hydrogen peroxide bleaching (HPB) is one of the total chlorine free (TCF) bleaching methods applicable for the chemical pulping of non-wood biomass (Maryana et al., 2017). Brightness and whiteness are the most important characteristics measured during the pulp bleaching. The characteristics are affected by raw material, pulping method, bleaching chemical type, bleaching conditions (temperature, chemical concentration, and time) and sequence (stages) of bleaching (Hu et al., 2017; Li et al., 2011). Hydrogen peroxide bleaching has more than three stages and uses hydrogen peroxide (H_2O_2) and sodium hydroxide (NaOH) as a major bleaching chemical in all the stages (Maryana et al., 2017; Pereira et al., 2011). The common HPB stages used are OQP. O-stage refers to the oxygen delignification, where the chemicals used are H_2O_2, oxygen, peroxymonosulfuric acid (H_2SO_5) and NaOH. Q-stage refers to the chelating treatment stage, where Diethylenetriamine pentaacetic acid (DTPA), sodium silicate (Na_2SiO_3), hydrogen peroxide

(H_2O_2), NaOH and sulfuric acid (H_2SO_4) are employed. And the last P-stage refers to the hydrogen peroxide stage. In this stage, H_2O_2, $MgSO_4$, NaOH and Na_2SiO_3 are used. The single stage HPB suggested in this study, would be a significant step in meeting the required pulp brightness, whiteness, and paper mechanical properties.

The mechanical properties of paper have a significant role in the selection of paper for various applications (printing, writing, and packaging) (Hu et al., 2017). These properties (tensile, burst and tear strength) determine the resistance of the paper to stress, which are important for its performance in printing. For example, in printing paper, tensile strength can be used as a potential indicator of the resistance to web breaks during converting (Anjos et al., 2015). The mechanical properties chiefly depend upon the preparation method, fiber length, fiber strength, bond strength and bonded area, which in turn depend on the characteristics of the raw material, pulping method and process parameters adopted. The application of sulfur-free soda delignification in combination with single stage HPB would be a significant step in meeting environmental and economic concerns related to conventional methods followed in the paper and pulp industries (Shendye et al., 2016).

However, SCB depithing, pre-hydrolysis, and pulping parameters require additional investments. Appropriate selection of soda delignification process conditions, after the adoption of an integrated physical fractionation pretreatment (Mamaye et al., 2019) will ensure the possibility of pulp production using the single stage HPB of ESCB and hence the determination of the mechanical properties. The process modeling and optimization were carried out using the multilevel categories experimental design for the soda delignification process and by using the response surface methodology (RSM) for the bleaching step. The results are then presented and discussed elaborately in this chapter.

4.2. Materials and Methods

4.2.1. Materials

The SCB was air dried and subjected to physical fractionation pretreatment using 1 mm size sieve to separate the rest of the bagasse and to remove the unwanted components (pith and dust) (Mamaye et al., 2019). The fraction retained on the 1 mm size sieve was oven dried (50 ^{o}C) for 12 h and then subjected to the soda delignification process.

4.2.2. Methods

4.2.2.1. Soda pulping

Soda delignification of the fractionated SCB was carried out in an autoclave, equipped with digital timer and temperature controller. The soda delignification process was performed under different experimental conditions at reaction temperatures of (130, 140 and 150 ^{o}C), NaOH concentration of (10, 15 and 20%) and reaction time of (60, 90 and 120 min), in order to optimize the pulp yield and kappa number. However, the solid to liquid ratio was kept constant at 1:10 (amount of SCB (kg): volume of liquor (L)). After cooking, the contents were transferred to a stainless-steel sieve of 150 mesh and washed thoroughly with tap water until neutral pH. This was followed by oven drying at 50 ^{o}C. The dried product was then analyzed for total pulp yield (gravimetrically) and kappa number (TAPPI T236 om-06). The pulps that showed the maximum and minimum pulp yield were chosen for the further studies (bleaching and paper mechanical property tests). These soda pulps with the maximum and the minimum pulp yield corresponded to the kappa number of 16.73 and 8.27, and hence were named as pulp-SA and pulp-SB, respectively.

4.2.2.2. Hydrogen peroxide bleaching

Soda pulps of pulp-SA and pulp-SB were bleached by single stage HPB method using H_2O_2 and NaOH. The process was performed under different experimental conditions: reaction temperatures of (80-90 ^oC), H_2O_2 concentration of (2-3%) and reaction time of (60-120 min). The experiments were designed using Design Expert ® version 10 software, in order to optimize the pulp yield, brightness and whiteness. The NaOH concentration (1.5%), H_2O_2: NaOH ratio (3:1) and pulp to liquid ratio (1:4) kg/L were kept constant in this study. The analysis of the bleached pulp was carried out using the following standard procedures: the pulp yield (gravimetrically), diffuse brightness of pulp (TAPPI T525 om-06) and whiteness (TAPPI T1216 sp-98).

4.2.2.3. Experimental design

A systematic experimental method for the statistical modeling and optimization of soda delignification conditions was premeditated using the multilevel categoric experimental design. The main and interaction effects of the independent process variables including the reaction temperature, NaOH concentration and reaction time were determined. A total of 27 experiments with replicate were performed to formulate the model equations and to study the linear, and interaction effects of each independent process variable on each response. An optimum set of delignification conditions, giving maximum forecast pulping output (pulp yield and kappa number) was recognized after fitting the linear polynomial model equation (Eq. (4.1)) into the experimental data.

A statistical modeling and optimization of single stage HPB were carried out using the response surface methodology (central composite design). The main and interaction effects of the independent process variables, including the reaction temperature, H_2O_2 concentration and reaction time were determined. A total of 15 experiments were performed to formulate the model

equations and to see linear, quadratic and interaction effects of each independent process variable on each response. An optimum set of bleaching conditions, giving maximum forecast of pulp yield, brightness, and whiteness were recognized after fitting the second order polynomial model equation (Eq. (4.2)) to the experimental data. The regression coefficients and estimated effect and the model for experimental results, statistical significance was confirmed by using analysis of variance (ANOVA). Design Expert ® version 10 software was used for regression analysis and ANOVA.

$$Y = \beta_o + \sum_{i=1}^{3} \beta_i X_i + \sum_{i=1}^{3} \beta_{ij} X_i X_j \quad (4.1)$$

$$Y = \beta_o + \sum_{i=1}^{3} \beta_i X_i + \sum_{i=1}^{3} \beta_{ii} X_i^2 + \sum_{i<j=2}^{3} \beta_{ij} X_i X_j \quad (4.2)$$

Where Y is the response, β_o, β_i, β_{ii} and β_{ij} are an intercept, linear, quadratic and interaction coefficients, respectively and X_i and X_j are the independent variables.

4.2.2.4. Measurements of mechanical properties of paper

The hand sheets paper with a diameter of 15 cm and 60 g/m^2 were prepared as per TAPPI T205-02 standard method from pulp-SA and pulp-SB. These sheets were subjected to the following tests for the determination of their mechanical properties. Bursting strength was measured according to TAPPI T403 om-97 (PN-BSM 6000 burst tester), tearing strength was measured according to TAPPI T414 om-98 (L&W AB tearing tester) and tensile strength was measured according to TAPPI T404 cm-92 (L&W AB tensile strength tester).

4.3. Results and Discussion

4.3.1. Soda pulping: optimization and modeling

Multilevel categoric design (MCD) was used for the optimization of the soda pulping process. The soda delignification statistical model was developed based on the three factors with three-levels MCD. It had three independent process variables (reaction temperature, NaOH concentration and reaction time, referred to as X_T, $X_{C\text{-}alk}$ and X_t, respectively) and two pulping outputs (pulp yield and kappa number, referred to as Y_{SP} and Y_{SK}, respectively). The MCD modeling was assigned based on data corresponding to the experimental point matrix of the independent process variables in 27 combinations with replicate (Table 4.1).

Table 4.1 Multilevel categoric experimental design matrix and soda pulping responses used for optimization and modeling.

Run	Temperature X_T (^oC)	NaOH concentration $X_{C\text{-}alk}$ (%)	Time X_t (min)	Pulp yield Y_{SP} (%)	Kappa number Y_{SK}
1	150	20	120	26.87	8.27
2	140	20	60	30.42	13.55
3	140	20	90	30.66	12.83
4	130	10	90	33.92	14.29
5	150	10	120	27.75	8.76
6	150	20	60	28.45	9.57
7	130	10	120	33.73	13.96
8	140	15	90	31.25	12.95
9	130	20	90	31.93	12.96
10	140	20	120	30.07	11.74
11	150	20	90	27.94	8.96
12	150	15	90	29.24	9.16
13	130	15	60	35.09	15.37
14	130	15	90	32.59	13.55
15	130	20	60	33.84	14.28
16	130	10	60	35.99	16.73
17	140	10	120	31.94	12.87
18	150	15	60	29.96	10.21
19	140	10	90	32.41	13.36
20	130	20	120	31.98	12.41
21	150	10	90	29.29	9.93
22	130	15	120	32.97	13.37
23	140	10	60	32.54	14.75
24	140	15	120	30.81	12.37
25	140	15	60	31.52	13.75
26	150	10	60	30.42	10.94
27	150	15	120	27.80	8.79

The statistical significance of the model, individual terms, and their interactions on the responses (pulp yield and kappa number) were investigated through ANOVA. Table 4.2 summarizes the statistical significance of each variable, sum of squares, P-value, F-value, and lack of fitness. It was found that the models are significant with p-value less than 0.05. The linear equations representing the model in terms of coded factors are presented as Eq. (4.3) and Eq. (4.4). For process modeling, only statistically significant regression coefficients were used.

$$Y_{SP} = 31.17 + 2.4X_{T1} + 0.13X_{T2} + 0.84X_{C-alk1} + 0.08X_{C-alk2} + 0.86X_{t1} - 0.14X_{t2} + 0.15X_{T1}X_{C-alk1} + 0.17X_{T2}X_{C-alk1} - 0.09X_{T1}X_{C-alk2} - 0.18X_{T2}X_{C-alk2} + 0.55X_{T1}X_{t1} - 0.66X_{T2}X_{t1} - 0.61X_{T1}X_{t2} + 0.29X_{T2}X_{t2} + 0.12X_{C-alk1}X_{t1} + 0.08X_{C-alk2}X_{t1} + 0.01X_{C-alk1}X_{t2} - 0.08X_{C-alk2}X_{t2} \quad (4.3)$$

$$Y_{SK} = 12.12 + 1.89X_{T1} + 0.92X_{T2} + 0.63X_{C-alk1} - 0.04X_{C-alk2} + 1.03X_{t1} - 0.21X_{t2} + 0.26X_{T1}X_{C-alk1} - 0.1X_{T2}X_{C-alk1} + 0.03X_{T1}X_{C-alk2} - 0.06X_{T2}X_{C-alk2} + 0.33X_{T1}X_{t1} - 0.14X_{T2}X_{t1} - 0.29X_{T1}X_{t2} + 0.13X_{T2}X_{t2} + 0.27X_{C-alk1}X_{t1} - 0.08X_{C-alk2}X_{t1} - 0.1X_{C-alk1}X_{t2} - 0.07X_{C-alk2}X_{t2} \quad (4.4)$$

The equations obtained after the analysis of ANOVA indicate the determination and adjusted determination coefficients were found to be R^2=0.99 (R^2_{Adj}=0.99) and R^2=0.99 (R^2_{Adj}=0.98) for pulp yield and kappa number, respectively, show high statistical significance of the models. In addition, the higher adjusted determination coefficient values indicate the used independent process variables are significant which affect the responses (pulp yield and kappa number) (Anupam et al., 2018). Besides the linear effects of reaction temperature, NaOH concentration and reaction time show confidence interval of 95% (p=0.05).

Table 4.2 ANOVA table obtained for linear and interaction effects of pulping factors on pulp yield (Y_{SP}) and kappa number (Y_{SK}) of soda pulping.

	Pulp yield (Y_{SP})			Kappa number (Y_{SK})			
Factors	SS	F-value	P-value	SS	F-value	P-value	
Model	282.16	15.68	0.0001	272.00	264.32	0.0001	Significant
X_T	218.70	2638.05	0.0001	222.11	1942.58	0.0001	
$X_{C\text{-}alk}$	28.04	338.18	0.0001	13.57	118.65	0.0001	
X_t	23.26	280.54	0.0001	31.86	278.63	0.0001	
$X_T X_{C\text{-}alk}$	1.66	10.01	0.0001	1.43	6.24	0.0007	
$X_T X_t$	9.87	59.52	0.0001	1.78	7.77	0.0001	
$X_{C\text{-}alk} X_t$	0.64	3.88	0.0104	1.26	5.51	0.0015	
Lack of fit	0.41	1.34	0.2669	0.53	1.23	0.3217	Not significant

SS: Sum of squares

The multilevel categoric plots for the pulp yield and kappa number as a function of the three variables are illustrated in Figures 4.1 and 4.2. As can be seen from MCD graphs and F-values in Table 4.2, the effect of reaction temperature is a primary, which is decisive for the degree of pulp delignification and kappa number during the soda pulping. This is followed by the effect of NaOH concentration and process time. The pulp yield and kappa number obtained in the experiment are found to be in the range of 26.87-35.99% and 8.27-16.73, respectively (Table 4.1). Similar optimum pulp yield was reported for the pre-hydrolysis soda pulping of SCB, providing the dissolved pulp yield of 35.1% at kappa number of 16.9 (Andrade and Colodette, 2014).

With respect to the regression coefficient shown by the response models (Table 4.2), pulp yield and kappa number are significantly influenced by the reaction temperature, NaOH concentration,

reaction time and their linear interaction. In addition, the interaction between reaction temperature and NaOH concentration, the interaction between the reaction temperature and time and the interaction between the reaction time and NaOH concentration are observed to have considerable influence on the pulp yield and kappa number, as shown in Figure 4.1a, b, c, and Figure 4.2a, b, c. In these plots, it can be observed that pulp yield and kappa number decreased with the increase in reaction temperature, NaOH concentration, and time. The changes in the temperature and sodium hydroxide concentration were observed to have a greater effect on the pulp yield and the kappa number than the time. The linear polynomial functions with respect to each independent process variable gave a set of optimum reaction conditions at the extreme points of the 3D plots. The optimum conditions established to obtain a maximum expected pulp yield during the pulping were a temperature of 130 °C, 10% NaOH concentration and a time of 60 min.

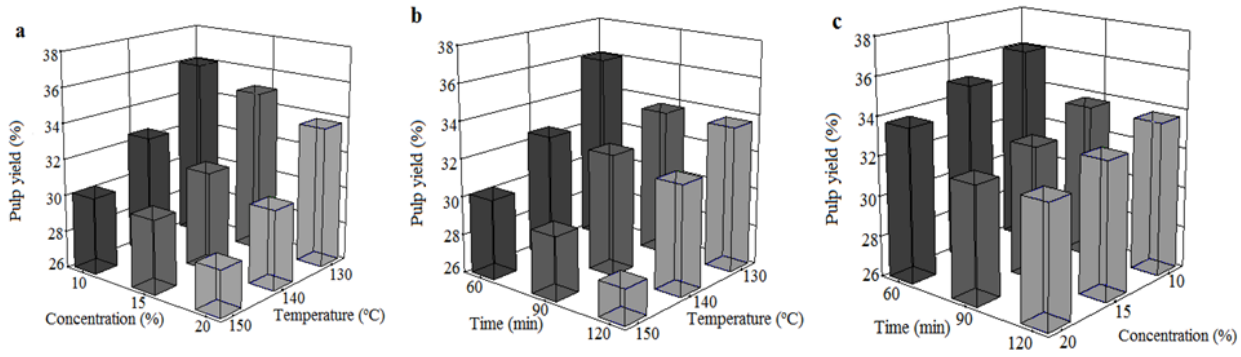


Figure 4.1 Multilevel categoric design plots of pulp yield under variable condition of soda pulping a) at 60 min time b) at 10% NaOH concentration c) at 130 ^{o}C temperature.

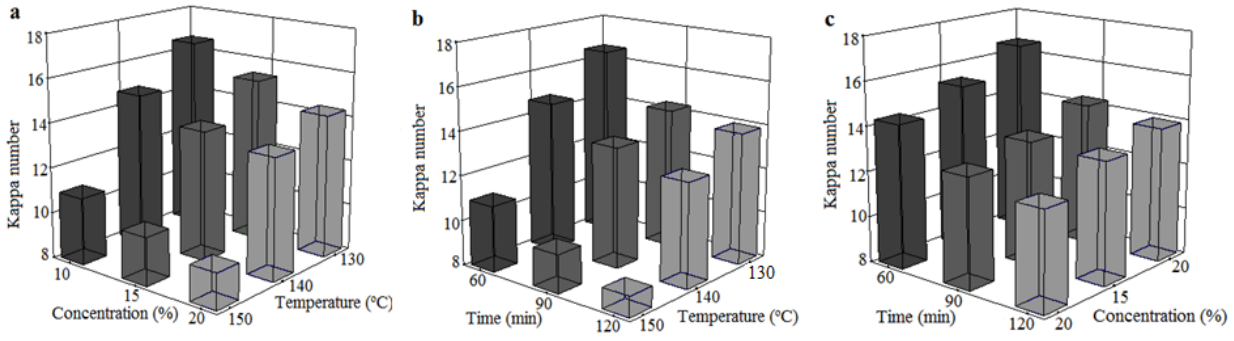


Figure 4.2 Multilevel categoric plots of kappa number under variable condition of soda pulping a) at 60 min time b) at 10% NaOH concentration c) at 130 ^{o}C temperature.

4.3.2. Hydrogen peroxide bleaching: modeling and optimization

A response surface methodology (central composite design) was used for the optimization of single stage HPB (Myers et al., 2009). The single stage HPB statistical model was established with three independent process variables (process temperature, H_2O_2 concentration and process time, referred to as X_T, $X_{C\text{-}H_2O_2}$ and X_t, respectively). It has three responses each for pulp-SA and pulp-SB (bleached pulp yield, brightness, and whiteness, nominated as Y_{PSA} and Y_{PSB}, Y_{BSA} and $Y_{BSB,}$ and Y_{WSA} and Y_{WSB}, respectively). The independent process variables for the RSM modeling were based on the experimental data from the bleaching tests. As shown in Table 4.3, the experimental CCD matrix having total of 15 runs was built to identify the statistical significance of bleaching factors.

Table 4.3 Central composite design (CCD) experimental design matrix and single stage hydrogen peroxide bleaching responses used for optimization and modeling.

Run	Coded variables			Decoded variables			Pulp-SA			Pulp-SB		
	A	B	C	X_T	$X_{C\text{-}H2O2}$	X_t	Y_{PSA}	Y_{BSA}	Y_{WSA}	Y_{PSB}	Y_{BSB}	Y_{WSB}
1	-1	0	0	80	2.5	90	87.57	61.56	84.21	83.11	71.18	88.35
2	0	0	-1	85	2.5	60	88.55	61.38	84.28	84.83	71.13	90.66
3	-1	-1	-1	80	2	60	88.14	61.15	84.27	83.65	71.62	89.3
4	-1	1	1	80	3	120	88.54	62.02	82.23	83.73	72.57	87.94
5	0	0	1	85	2.5	120	88.01	61.51	83.51	82.57	71.65	89.22
6	1	-1	1	90	2	120	87.47	61.78	84.19	82.08	72.05	86.94
7	1	0	0	90	2.5	90	87.78	61.21	83.81	82.51	71.43	89.4
8	0	1	0	85	3	90	87.44	61.66	82.67	82.65	71.42	88.73
9	0	-1	0	85	2	90	87.58	59.83	83.65	82.36	71.33	88.73
10	1	1	-1	90	3	60	87.31	59.67	84.43	82.1	70.42	89.08
11C	0	0	0	85	2.5	90	87.76	61.37	83.51	82.98	71.37	88.52
12C	0	0	0	85	2.5	90	87.75	61.36	83.54	82.96	71.36	88.48
13C	0	0	0	85	2.5	90	87.72	61.32	83.59	82.93	71.35	88.57
14C	0	0	0	85	2.5	90	87.68	61.39	83.53	82.96	71.36	88.48
15C	0	0	0	85	2.5	90	87.68	61.35	83.55	82.94	71.35	88.58

A (X_T): Temperature (^oC), B ($X_{C\text{-}H2O2}$): H_2O_2 concentration (%), C (X_t): Time (min), Y_{PSA}: pulp yield of pulp-SA, Y_{PSB}: pulp yield of pulp-SB, Y_{BSA}: Brightness of pulp-SA, Y_{BSB}: Brightness of pulp-SB, Y_{WSA}: Whiteness of pulp-SA, Y_{WSB}: Whiteness of pulp-SB

Analysis of variance was used for checking the statistical significance of the parameters involved in bleaching. In addition, the quadratic effects of H_2O_2 concentration, process temperature and time

showed a confidence interval of 95% (P=0.05), which indicate its high statistical significance. The interaction effects between temperature and H_2O_2 concentration, temperature, and time, and H_2O_2 concentration and time were studied to determine their effect on the pulp yield, brightness, and whiteness.

Higher temperatures above the value mentioned was found to decrease the bleached pulp yield and hence the paper quality, whereas an increase in the treatment time beyond 75 min resulted in an overcooked pulp; furthermore, it lead to the formation of grey spots, mainly due to the condensation of the residues of lignin monomers. For simulation of single stage HPB, the second-order polynomial function Eq. (4.2) was fitted to experimental data. This gives six model equations describing pulp yield, brightness and whiteness developed after the single stage HPB of pulp-SA Eqs. ((4.5), (4.6), (4.7)) and pulp-SB Eqs. ((4.8), (4.9) and (4.10)), respectively. For the process modeling, only statistically significant regression coefficients were used. The quadratic equations representing the model in terms of the coded factors were used to make forecast regarding the response for the given levels of each factors.

$$Y_{PSA} = 87.72 + 0.074X_T - 0.049X_{C-H_2O_2} - 0.19X_t - 0.33X_TX_{C-H_2O_2} - 0.11X_TX_t + 0.55X_{C-H_2O_2}X_t - 0.024X_T^2 - 0.11X_{C-H_2O_2}^2 - 0.28X_t^2 \quad (4.5)$$

$$Y_{BSA} = 61.35 - 0.12X_T + 0.65X_{C-H_2O_2} + 0.046X_t - 0.7X_TX_{C-H_2O_2} + 0.96X_TX_t + 0.31X_{C-H_2O_2}X_t + 0.026X_T^2 - 0.29X_{C-H_2O_2}^2 + 0.056X_t^2 \quad (4.6)$$

$$Y_{WSA} = 83.54 - 0.14X_T - 0.35X_{C-H_2O_2} - 0.27X_t + 0.3X_TX_{C-H_2O_2} + 0.1X_TX_t - 0.67X_{C-H_2O_2}X_t + 0.24X_T^2 - 0.19X_{C-H_2O_2}^2 + 0.18X_t^2 \quad (4.7)$$

$$Y_{PSB} = 82.93 - 0.074X_T - 0.2X_{C-H_2O_2} - 0.61X_t - 0.73X_TX_{C-H_2O_2} - 0.12X_TX_t + 0.62X_{C-H_2O_2}X_t - 0.22X_T^2 - 0.27X_{C-H_2O_2}^2 + 0.53X_t^2 \quad (4.8)$$

$$Y_{BSB} = 71.37 - 0.11X_T + 0.22X_{C-H_2O_2} + 0.018X_t - 0.47X_TX_{C-H_2O_2} + 0.24X_TX_t + 0.47X_{C-H_2O_2}X_t + 0.061X_T^2 + 0.18X_{C-H_2O_2}^2 - 0.11X_t^2 \quad (4.9)$$

$$Y_{WSB} = 88.53 - 0.17X_T - 0.63X_{C-H_2O_2} - 0.82X_t - 0.56X_TX_{C-H_2O_2} - 0.21X_TX_t - 0.48X_{C-H_2O_2}X_t + 0.23X_T^2 - 0.34X_{C-H_2O_2}^2 + 0.49X_t^2 \quad (4.10)$$

The determination and the adjusted determination coefficients were found to be R^2=0.99 (R^2_{Adj}= 0.99) for the pulp yield, brightness, and whiteness, pointing to high statistical significance. The simulated bleaching effects described by Eqs. ((4.5), (4.6), (4.7)) and Eqs. ((4.8), (4.9), (4.10)) are demonstrated by the response surface plots in the Figure 4.3 and Figure 4.4, respectively. These plots allow us to describe the maximum predictable levels of single-stage HPB outputs, at the necessary regions of the respective process variables.

Table 4.4 ANOVA table obtained for quadratic and interaction effects of bleaching factors on pulp yield, brightness, and whiteness of pulp bleaching.

Source	Y_{PSA}		Y_{BSA}		Y_{WSA}		Y_{PSB}		Y_{BSB}		Y_{WSB}		
	F	P	F	P	F	P	F	P	F	P	F	P	
Model	157.4	0.0001	547.65	0.0001	689.7	0.0001	338.1	0.0001	2587.06	0.0001	554.55	0.0001	Significant
A	16.57	0.0096	52.05	0.0008	97.96	0.0002	9.71	0.0264	401.86	0.0001	66.46	0.0005	
B	7.36	0.0421	1423.05	0.0001	588.00	0.0001	71.56	0.0004	1557.6	0.0001	886.93	0.0001	
C	109.5	0.0001	7.18	0.0438	363.00	0.0001	651.63	0.0001	9.81	0.0259	1477.08	0.0001	
AB	164.5	0.0001	830.57	0.0001	217.13	0.0001	470.3	0.0001	3501.97	0.0001	343.16	0.0001	
AC	18.02	0.0081	1556.69	0.0001	26.24	0.0037	12.48	0.0167	887.23	0.0001	50.17	0.0009	
BC	453.3	0.0001	159.42	0.0001	1104.02	0.0001	336.77	0.0001	3495.16	0.0001	258.56	0.0001	
A^2	3.06	0.1408	4.28	0.0933	535.31	0.0001	164.48	0.0001	227.49	0.0001	224.47	0.0001	
B^2	64.48	0.0005	568.39	0.0001	330.12	0.0001	247.74	0.0001	2045.38	0.0001	495.86	0.0001	
C^2	452.9	0.0001	20.23	0.0064	307.94	0.0001	963.63	0.0001	682.94	0.0001	1043.32	0.0001	
Lack of fit	0.082	0.7888	4.78	0.0941	0.64	0.4685	5.87	0.0725	0.25	0.6453	1.57	0.2778	Not significant

F: F-value, P: P-value, A: Temperature (°C), B: H_2O_2 concentration (%), C: time (min), Y_{PSA}: pulp yield of pulp-SA, Y_{PSB}: pulp yield of pulp-SB, Y_{BSA}: Brightness of pulp-SA, Y_{BSB}: Brightness of pulp-SB, Y_{WSA}: Whiteness of pulp-SA, Y_{WSB}: Whiteness of pulp-SB

Pulp yield

The bleached pulp yield obtained in the experiment is found to be in the range of 87.31-88.55% and 82.08-84.83% for pulp-SA and pulp-SB, respectively (Table 4.3) with regard to the regression coefficients shown by the response models (Table 4.4). Pulp yield is significantly affected by the H_2O_2 concentration, temperature, and time besides to the quadratic and an interaction effect, as shown in Figure 4.3a, b, c and Figure 4.4a, b, c.

Brightness

As can be seen from Table 4.4, H_2O_2 concentration is a primary factor in defining the pulp brightness during single stage HPB, followed by the effect of temperature and time. Bleaching temperature negatively affects the highly correlated response, the pulp brightness Eqs. (4.6), (4.9). The interaction of H_2O_2 concentration with temperature and time have a significant effect on the brightness (Table 4.4). In these equations, the interaction between temperature and time, and H_2O_2 concentration and time showed a positive effect, while H_2O_2 concentration and temperature displayed a negative effect on brightness. In addition, the H_2O_2 concentration and time had a significant quadratic effect on the pulp brightness (Figure 4.3d, e, f, and Figure 4.4d, e, f). As it could be anticipated, the lignin-derived chromophores have a leading role on the brightness of the chemical pulp (Shatalov and Pereira, 2014).

Whiteness

As shown in Figure 4.3 g, h, i and Figure 4.4 g, h, i, H_2O_2 concentration, temperature and time had significant effect on the pulp whiteness. Moreover, the quadratic variables (H_2O_2 concentration, temperature, and time) and their interaction had a significant influenced on the pulp whiteness (Table 4.4).

The above indicated values closely agree with those required to achieve the maximum pulp brightness and whiteness. The fitted polynomial functions with respect to each independent variable provided the optimum bleaching conditions at maximum points on the surface plots. Hence, the following optimum conditions were established for pulp-SA and pulp-SB, respectively, 80 and 90 ^{o}C temperature, 2.3 and 2% H_2O_2 concentration and 60 min. To validate these data, the replicated single-stage HPB experiments were performed under optimized conditions for the Pulp-SA and pulp-SB. The bleached pulp having pulp yield of 88.27 and 85.79%, brightness of 61.96 and 71.16% and whiteness of 84.14 and 90.17% for pulp-SA and pulp-SB, respectively were produced. The results proved to have a very good correlation of the experimental data and data predicted by the model.

The single stage HPB was chosen among a group of potential stages of HPB. It has verified to be very effective for the removal of the residual lignin and for polysaccharide preservation of pulps. It increased the initial brightness of pulp-SA and pulp-SB from 36.33% and 40.49% to 62.02% and 71.86%, respectively. When compared with O-D-EP-P steps (O: oxygen delignification stage, D: chlorine dioxide delignification stage, EP: alkaline extraction with hydrogen peroxide stage and P: hydrogen peroxide bleaching stage), ECF bleaching, used H_2O_2, NaOH, chlorine dioxide and oxygen delignification at different stages (Andrade and Colodette, 2014). Nevertheless, single stage HPB, adopted in this study, uses only H_2O_2 and NaOH, incurs a low bleaching cost, causes less environmental pollution, decreases fiber damage by chemicals and minimizes the bleaching time (Kumar et al., 2013; Shatalov and Pereira, 2014). Compared with the number of treatment stages, the simplicity of the bleaching process employed, and the usage of chlorine free bleaching chemicals, the brightness and whiteness obtained by this treatment are remarkable and admirable.

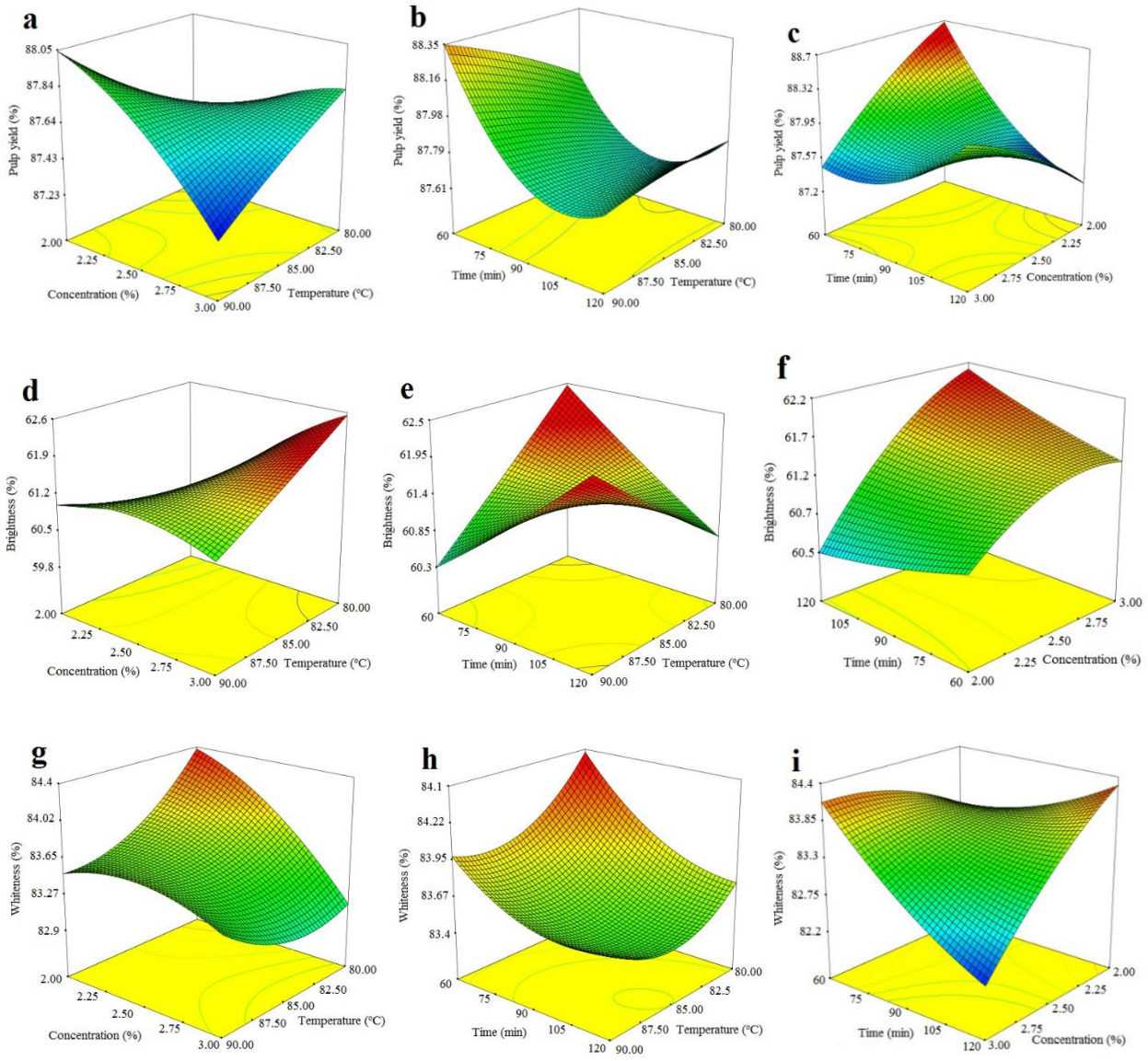


Figure 4.3 Response surface plot of pulp yield, brightness, and whiteness under variables conditions of single stage hydrogen peroxide bleaching of pulp-SA.

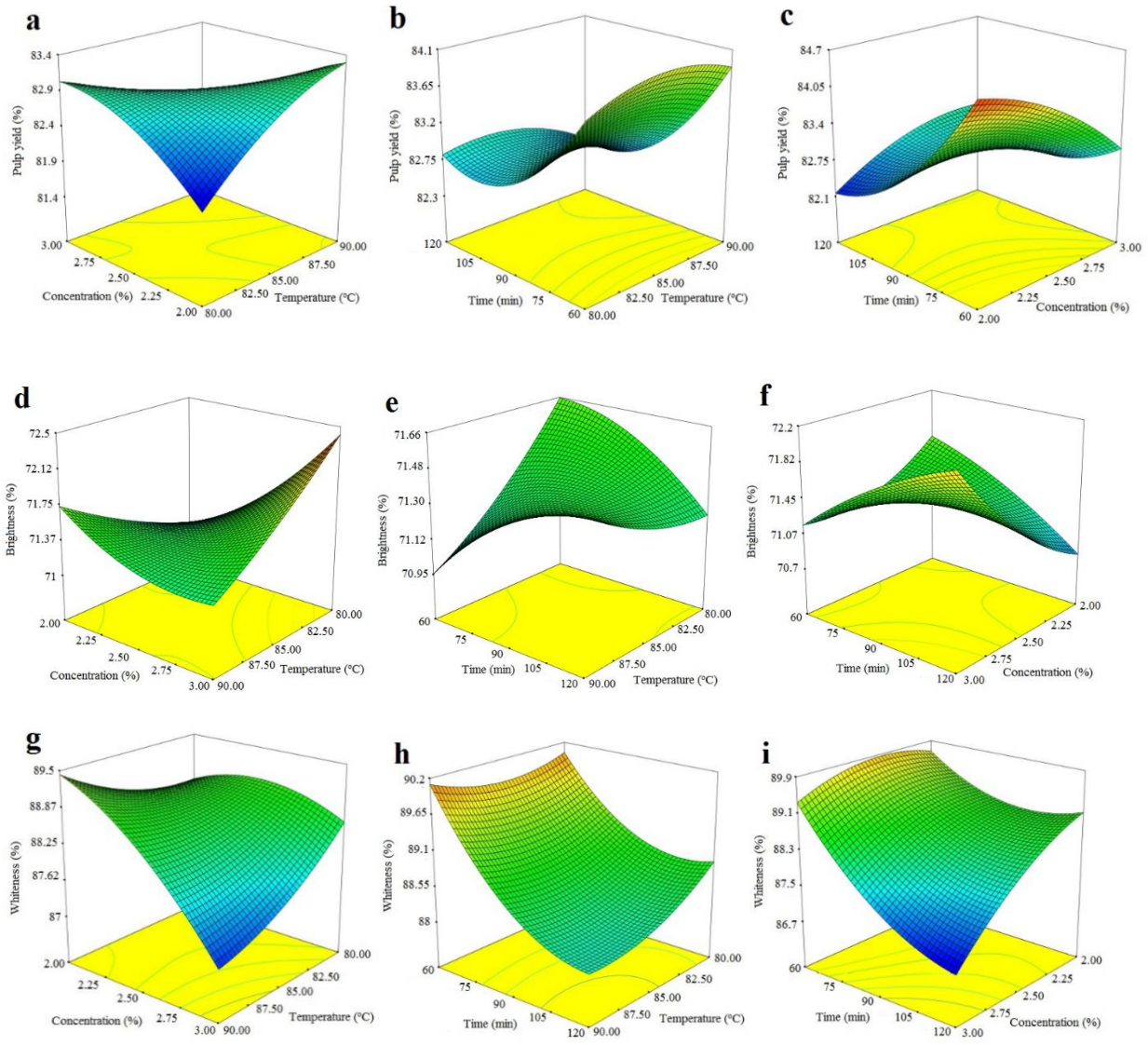


Figure 4.4 Response surface plot of pulp yield, brightness, and whiteness under variables conditions of single stage hydrogen peroxide bleaching of pulp-SB.

4.3.3. Mechanical properties of paper from pulp-SA and pulp-SB

The paper prepared from the pulp-SA and pulp-SB are presented in Figure 4.5. The comparative study was done at 130 ^{o}C, 10% NaOH concentration, and 60 min for the paper from pulp-SA and at 150 ^{o}C, 20% NaOH concentration at 120 min for the paper from the pulp-SB. The research findings revealed the significant differences in mechanical properties of 60 gm/m^2 paper made from pulp-SA and pulp-SB. Paper obtained from pulp-SA and pulp-SB had a burst index of 6.53 and 3.13 kPam^2/g, tensile index of 14.7 and 5.98 Nm/g, and tear index of 5.22 and 3.92 mNm^2/g, respectively. The paper made from pulp-SA is found to be of higher quality for the production of paper-based products, when compared with the pulp-SB, in terms of its mechanical properties. Generally, the mechanical properties of paper made from SCB soda pulp are significantly affected by the pulping conditions in addition to the physical properties of raw materials (Sharma et al., 2018). Hence, in addition to the raw material properties, the selection of pulping variables, studied in this research, is highly significant, in view of the effect it had on the mechanical properties of the paper produced (Anupam et al., 2016; Kamoga et al., 2016).

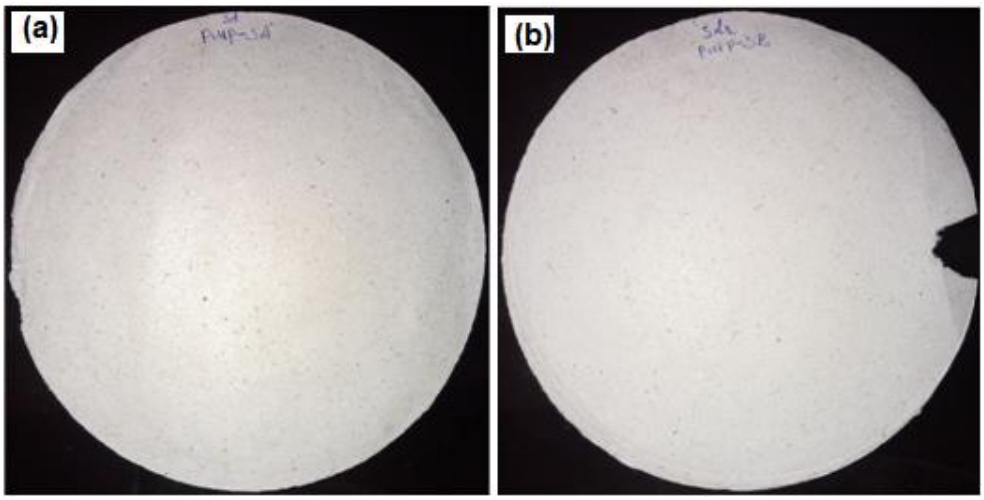


Figure 4.5 Paper from the (a) Pulp-SA and the (b) Pulp-SB.

4.4. Conclusion

The study emphasizes the delignification of ESCB using a sulfur free soda pulping process and the bleaching of the resulting pulp using the single-stage HPB. The pulping parameters investigated in this study were vital in that they strongly affected the mechanical properties of paper as well as their brightness and whiteness. A maximum pulp yield of 35.99 % with 16.73 kappa number was obtained at the optimum soda delignification conditions: 130 °C, 10% NaOH concentration at 60 min. The results have shown that the brightness and whiteness of pulp-SB were higher than those of pulp-SA. Studies carried out on the mechanical properties of the papers, clearly indicated the dominance of the pulp-SA, in terms of the tensile index (14.7 Nm/g), tear index (5.22 mNm^2/g) and burst index (6.53 $kPam^2/g$). Based on the results, it can be concluded that the utilization of Ethiopian sugarcane bagasse using soda delignification and single stage hydrogen peroxide bleaching are a promising approach to manufacture good quality pulp and paper from this non-woody biomass, sugarcane bagasse.

CHAPTER FIVE

Optimization of Kraft delignification and single stage hydrogen peroxide bleaching

5.1. Introduction

Kraft pulping is the predominant alkaline process which uses a mixture of sodium hydroxide (NaOH) and sodium sulfide (Na_2S) to liberate the fiber and degrade the lignin from wood and non-wood fibrous materials (Moshkelani et al., 2013). The introduction of physical fractionation pretreatment (PFP) prior to the Kraft pulping process helps increase the purity of SCB to produce pulp with a satisfactory quality (Mamaye et al., 2019). The Kraft delignification process produces pulp with high strength, but with darker in color. The murky color of the pulp is adjusted by using bleaching technology by lowering the remaining lignin (Loureiro et al., 2011; Ibarra et al., 2006). Pulp bleaching is the most chemical consuming and poisoning step in pulp and paper production. The chemicals often used are compounds based on chlorine such as Cl_2, ClO_2 and NaOCl (Moldes et al., 2010; Kamoga et al., 2016). To overcome the environmental pollution released from pulp bleaching chemicals, environmentally friendly bleaching chemicals are needed. Hydrogen peroxide bleaching (HPB) is one of the total chlorine free (TCF) pulp bleaching methods it has many stages and uses different bleaching chemicals in each sequence of bleaching (Maryana et al., 2017; Hosseinpour et al., 2015). Selection of bleaching chemicals, reduction of bleaching stages

and optimization of bleaching and pulping parameters are important to upgrade utilization of SCB (Hu et al., 2017; Fischer et al., 2017).

This chapter focused on the possibility of pulp production using Kraft delignification condition and single stage hydrogen peroxide bleaching of physical fractionated Ethiopian sugarcane bagasse (ESCB). Process optimization and modeling were carried out using multilevel categoric experimental design for Kraft delignification and response surface methodology for bleaching. Meanwhile, the mechanical properties of hand sheets paper were investigated.

5.2. Materials and Methods

5.2.1. Materials

As detailed in section 4.2.1 the physical fractionation SCB was subjected to Kraft delignification process.

5.2.2. Methods

5.2.2.1. Kraft pulping

Kraft delignification was carried out using the same process variables and responses as detailed in section 4.2.2.1 and Table 5.1. Though, NaOH to sulfide ratio of 3:1 L/L (Udohitinah and Oluwadare, 2011), and sulfidty of 20% (w/v) were kept constant in this study. The pulps that showed the maximum and minimum pulp yield were chosen for further studies (bleaching and paper mechanical property tests). Hence, the pulp with maximum pulp yield having a kappa number of 17.68 was named as pulp-KA and the one with minimum pulp yield having a kappa number of 8.41 was named as pulp-KB.

5.2.2.2. Hydrogen peroxide bleaching

The selected Kraft pulps, i.e. pulp-KA and pulp-KB were then bleached by the single stage HPB. The bleaching experiments were carried out at the same process conditions and responses as detailed in section 4.2.2.2 and Table 5.3.

5.2.2.3. Experimental design

A systematic experimental method for statistical modeling and optimization of the Kraft pulping process was planned using the multilevel categoric design (MCD) (Myers et al., 2009). Table 5.1 represents the experimental combination of independent process variables and the equivalent response values of the Kraft pulping. An optimum set of delignification conditions, giving maximum estimated pulping output (pulp yield and kappa number) was recognized after fitting the linear polynomial model equation (Eq. (4.1)) into the experimental data. Single stage hydrogen peroxide bleaching of Kraft pulp experimental point matrix and the equivalent response values are presented in Table 5.3. An optimum set of bleaching conditions, giving maximum estimated pulp yield, brightness and whiteness were obtained after fitting the second order polynomial model equation (Eq. (4.2)) to the experimental data.

5.2.2.4. Measurements of paper mechanical properties

Hand sheets paper with a diameter of 15 cm and 60 g/m^2 were prepared from pulp-KA and pulp-KB as per TAPPI T205-02 standard method. These sheets were subjected to the burst strength, tear strength and tensile strength using the standard methods listed in section 4.2.2.4.

5.3. Results and Discussion

5.3.1. Kraft pulping: optimization and modeling

The Kraft delignification statistical model was established based on the three independent process variables (pulping temperature, NaOH concentration and pulping time, nominated as X_T, $X_{C\text{-}alk}$ and X_t, respectively) and two output responses (pulp yield and kappa number, designated as Y_{KP} and Y_{KK}, respectively). The MCD modeling was assigned based on the data corresponding to the experimental point matrix of the independent process variables in 27 combinations with replicate (Table 5.1).

The statistical significance of the model, individual terms, and their interactions on the responses (pulp yield and kappa number) were investigated by ANOVA. The statistical significance of each variable, sum of squares, p-value, F-value, and lack of fitness were summarized in Table 5.2. It was found that the models are significant with p-value (<0.05).

Table 5.1 Multilevel categoric experimental design matrix and Kraft pulping responses used for optimization and modeling.

Run	Temperature X_T (^oC)	NaOH concentration $X_{C\text{-}alk}$ (%)	Time X_t (min)	Pulp yield Y_{KP} (%)	Kappa number Y_{KK}
1	130	20	90	34.41	14.50
2	150	15	120	27.91	8.54
3	130	10	120	35.54	15.45
4	150	10	60	29.65	10.17
5	140	10	120	32.43	11.87
6	130	10	60	38.41	17.68
7	140	15	120	31.48	11.34
8	140	10	60	34.15	15.23
9	150	10	90	29.33	9.54
10	150	15	90	29.37	9.05
11	130	20	60	35.73	15.96
12	130	20	120	33.17	13.14
13	130	15	120	34.26	15.16
14	140	15	60	33.73	14.92
15	150	20	90	27.97	8.94
16	140	15	90	32.04	11.95
17	150	15	60	29.92	10.25
18	140	20	120	30.52	10.54
19	130	10	90	35.91	16.24
20	150	20	60	28.35	9.24
21	130	15	60	36.78	16.73
22	130	15	90	36.64	15.18
23	140	10	90	33.32	12.95
24	150	20	120	27.81	8.41
25	140	20	90	31.45	11.06
26	140	20	60	32.70	13.40
27	150	10	120	27.67	8.87

The linear equations representing the model in terms of coded factors can be used to make evaluation regarding the responses for the given levels of each factors as presented in Eq. (5.1) and Eq. (5.2). For the process modeling, only statistically significant regression coefficients were used.

$$Y_{KP} = 32.21 + 3.33X_{T1} + 0.22X_{T2} + 0.78X_{C-alk1} + 0.08X_{C-alk2} + 1.12X_{t1} - 0.1X_{t2} + 0.47X_{T1}X_{C-alk1} + 0.09X_{T2}X_{C-alk1} - 0.23X_{T1}X_{C-alk2} - 0.08X_{T2}X_{C-alk2} + 0.49X_{T1}X_{t1} - 0.02X_{T2}X_{t1} - 0.29X_{T1}X_{t2} - 0.04X_{T2}X_{t2} \quad (5.1)$$

$$Y_{KK} = 12.49 + 3.13X_{T1} + 0.10X_{T2} + 0.63X_{C-alk1} + 0.13X_{C-alk2} + 1.26X_{t1} - 0.28X_{t2} + 0.23X_{T1}X_{C-alk1} + 0.13X_{T2}X_{C-alk1} + 0.08X_{T1}X_{C-alk2} + 0.02X_{T2}X_{C-alk2} - 0.05X_{T1}X_{t1} + 0.68X_{T2}X_{t1} + 0.11X_{T1}X_{t2} - 0.32X_{T2}X_{t2} \quad (5.2)$$

The regression equation obtained after the analysis of ANOVA indicates the determination coefficient (R^2=0.98 and 0.98) and adjusted determination coefficients (R^2_{adj}=0.97 and 0.98) for pulp yield and kappa number, respectively, show high statistical significance of the model. The model has high R^2, significant p-value and insignificant lack-of-fit indicating its excellency in anticipating the solution to our problem. Moreover, the higher adjusted determination coefficient values indicate the selected independent process variables are significant which affect the pulp yield and kappa number (Anupam et al., 2018).

Table 5.2 ANOVA table obtained for linear and interaction effects of pulping factors on pulp yield and kappa number of Kraft pulping.

	Y_{KP}			Y_{KK}			
Factors	SS	F-value	P-value	SS	F-value	p-value	
Model	502.32	155.11	0.0001	440.67	204.11	0.0001	Significant
X_T	427.05	923.08	0.0001	364.45	1181.65	0.0001	
$X_{C\text{-}alk}$	24.70	53.38	0.0001	18.10	58.69	0.0001	
X_t	41.25	89.17	0.0001	46.85	151.91	0.0001	
$X_T X_{C\text{-}alk}$	4.95	5.35	0.0016	3.38	5.48	0.0013	
$X_T X_t$	4.38	4.73	0.0033	7.89	12.79	0.0001	
Lack of fit	3.96	1.76	0.1083	2.18	1.28	0.2879	Not significant

With respect to the F-values Table 5.2 and the MCD graphs (Figure 5.1 and Figure 5.2), the effect of temperature is seen as a major factor, crucial for the degree of pulp delignification and kappa number, during the Kraft delignification. This is followed by the effect of the NaOH concentration and time. In addition, the pulp yield and kappa number were significantly affected by the concurrent effect of temperature and NaOH concentration, and temperature and time. In addition, the interaction of time and NaOH concentration has insignificant effect for both pulp yield and kappa number. As follows from Figure 5.1 and Figure 5.2, when temperature, NaOH concentration and time increased, both pulp yield and kappa number decreased. Mansouri et al. (2012) have also reported similar finding. The decrease in pulp yield with increasing temperature and NaOH concentration is because of the unsteady nature of carbohydrate (cellulose and hemicellulose) in alkaline solution, which promote a split in carbohydrate and form more soluble compounds

(Khakifirooz et al., 2013; Sharma et al., 2018). In this regard, the prolonged pulping at high temperature, NaOH concentration and time can cause further cellulose degradation leading to a significant drop in pulp yield. The linear polynomial function with respect to each independent process variable gave a set of maximum degree of delignification at the extreme points of the 3D plots. The optimal pulp yield was 38.41% with kappa number of 17.68 at the delignification condition of 130 ^{o}C temperature, 10% NaOH concentration and pulping time of 60 min. Similar optimal condition was obtained in soda delignification of ESCB, where the pulp yield was 35.99% with kappa number of 16.73 (Mamaye et al., 2020).

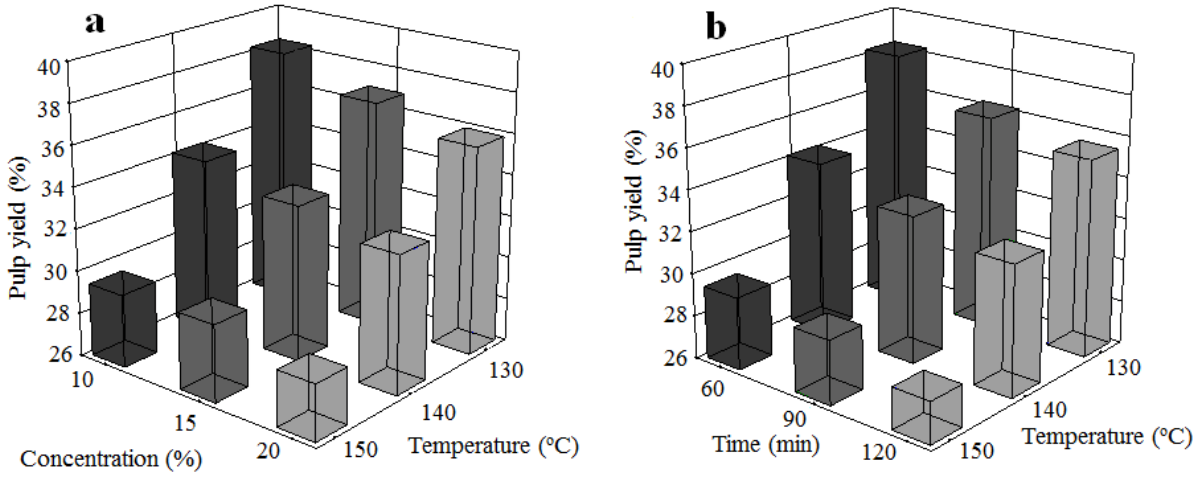


Figure 5.1 Multilevel categoric design plots for pulp yield under variable condition of Kraft pulping a) at 60 min time b) at10% NaOH concentration.

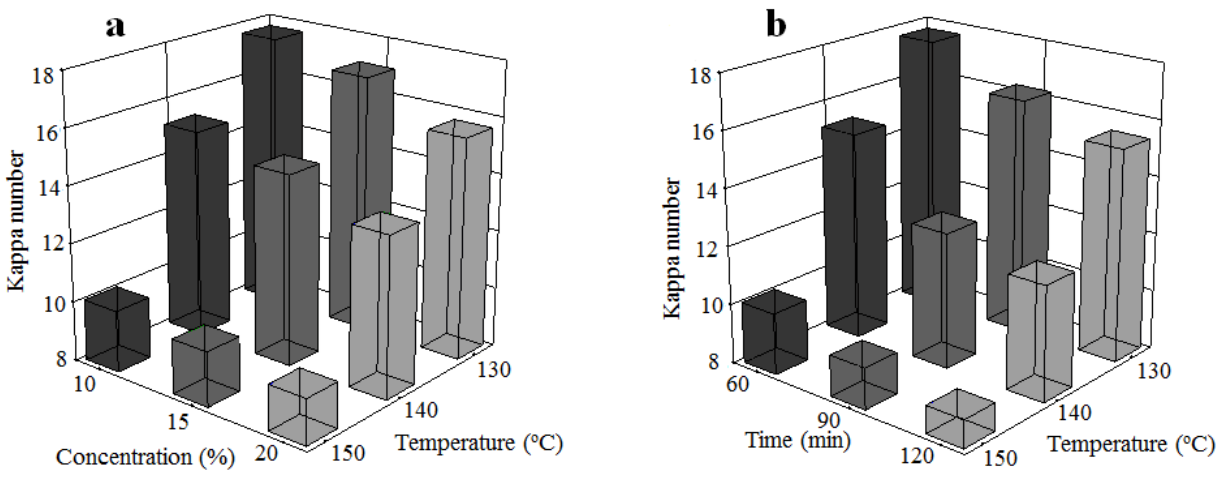


Figure 5.2 Multilevel categoric design plots for kappa number under variable condition of Kraft pulping a) at 60 min time b) at 10% NaOH concentration.

5.3.2. Hydrogen peroxide bleaching: optimization and modeling

The single stage HPB statistical model was established with independent process variables (reaction temperature, H_2O_2 concentration and time, nominated as X_T, $X_{C\text{-}H_2O_2}$ and X_t, respectively). Pulp-KA and pulp-KB have three outputs each (bleached pulp yield, brightness, and whiteness, nominated as Y_{PKA} and Y_{PKB}, Y_{BKA} and Y_{BKB}, and Y_{WKA} and Y_{WKB}, respectively). The CCD modeling was assigned based on the data corresponding to the experimental point matrix of the three independent process variables in 15 combinations (Table 5.3).

Table 5.3 Experimental central composite design (CCD) matrix and single stage hydrogen peroxide bleaching responses used for optimization and modeling.

Run	Coded variables			Decoded variables			Pulp-KA			Pulp-KB		
	A	B	C	X_T	$X_{C\text{-}H_2O_2}$	X_t	Y_{PKA}	Y_{BKA}	Y_{WKA}	Y_{PKB}	Y_{BKB}	Y_{WKB}
1	-1	-1	-1	80	2	60	84.79	61.51	85.18	83.92	64.28	91.76
2	0	-1	0	85	2	90	83.9	61.25	85.11	83.31	68.35	90.55
3	-1	1	1	80	3	120	82.63	63.81	85.55	81.14	65.75	91.48
4	0	0	1	85	2.5	120	82.15	62.79	85.91	80.98	66.88	90.17
5	0	1	0	85	3	90	82.27	62.68	86.91	81.06	64.38	91.66
6	0	0	-1	85	2.5	60	83.08	60.71	83.61	82.77	64.82	88.93
7	1	1	-1	90	3	60	82.33	61.19	85.16	82.09	67.68	89.49
8	1	0	0	90	2.5	90	82.09	63.75	86.99	82.18	68.19	91.25
9	1	-1	1	90	2	120	82.16	60.95	83.98	81.82	65.21	88.12
10	-1	0	0	80	2.5	90	84.31	61.32	84.71	81.27	64.97	89.29
11C	0	0	0	85	2.5	90	82.85	62.43	86.63	81.15	67.37	90.59
12C	0	0	0	85	2.5	90	82.87	62.47	86.62	81.25	67.39	90.52
13C	0	0	0	85	2.5	90	82.88	62.46	86.59	81.16	67.29	90.57
14C	0	0	0	85	2.5	90	82.85	62.45	86.61	81.21	67.69	90.49
15C	0	0	0	85	2.5	90	82.89	62.48	86.64	81.13	67.35	90.46

A (X_T): Temperature (^oC), B ($X_{C\text{-}H2O2}$): H_2O_2 concentration (%), C (X_t): Time (min), Y_{PKA}: pulp yield of pulp-KA, Y_{PKB}: pulp yield of pulp-KB, Y_{BKA}: Brightness of pulp-KA, Y_{BKB}: Brightness of pulp-KB, Y_{WKA}: Whiteness of pulp-KA, Y_{WKB}: Whiteness of pulp-KB

Analysis of variance was used for examining the statistical significance of the bleaching parameters at the smaller the p-value and larger F-value (Myers et al., 2009; Anupam et al., 2018). The linear effects of bleaching temperature, H_2O_2 concentration and bleaching time, showed p-values less than $p<0.05$. In addition, the interaction effects of (temperature and H_2O_2 concentration, temperature, and time, and H_2O_2 concentration and time) and their quadratic effects were revealed a higher statistical significance for pulp yield, brightness, and whiteness ($p<0.05$). The optimal bleaching outputs were pulp yield of (84.28% and 82.99%), brightness of (62.59 and 68.35) and whiteness of (86.32 and 91.43) for pulp-KA and pulp-KB, respectively. Higher temperatures above the value mentioned were found to decrease the pulp yield, whereas an increase in the treatment time beyond 75 min resulted in an overcooked pulp. Furthermore, it led to the formation of grey spots, which might be because of the condensation of the residues.

Table 5.4 ANOVA table obtained for linear, quadratic and interaction effects of bleaching factors on pulp yield, brightness, and whiteness of pulp bleaching.

Source	Y_{PKA}		Y_{BKA}		Y_{WKA}		Y_{PKB}		Y_{BKB}		Y_{WKB}		
	F	P	F	P	F	P	F	P	F	P	F	P	
Model	1460.24	0.0001	2453.32	0.0001	2932.96	0.0001	438.12	0.0001	160.81	0.0001	690.14	0.0001	Significant
A	3544.67	0.0001	5083.94	0.0001	4135.44	0.0001	138.63	0.0001	259.75	0.0001	802.31	0.0001	
B	1910.93	0.0001	1760.60	0.0001	2577.49	0.0001	847.52	0.0001	394.84	0.0001	257.32	0.0001	
C	622.06	0.0001	3724.90	0.0001	4208.31	0.0001	536.40	0.0001	106.31	0.0001	321.13	0.0001	
AB	185.16	0.0001	167.28	0.0001	3282.61	0.0001	11.25	0.0202	97.39	0.0002	604.86	0.0001	
AC	17.86	0.0083	57.68	0.0006	197.13	0.0001	18.90	0.0074	568.15	0.0001	12.02	0.0179	
BC	7.90	0.0375	9423.01	0.0001	4609.75	0.0001	248.55	0.0001	17.34	0.0088	3685.73	0.0001	
A2	270.11	0.0001	12.33	0.0171	1892.63	0.0001	170.52	0.0001	65.03	0.0005	50.05	0.0009	
B2	107.70	0.0001	860.63	0.0001	1200.03	0.0001	612.45	0.0001	103.59	0.0002	276.38	0.0001	
C2	206.70	0.0001	1741.08	0.0064	10791.7	0.0001	284.60	0.0001	232.26	0.0001	756.79	0.0001	
Lack of fit	6.86	0.0588	3.85	0.1213	4.49	0.1014	2.22	0.2103	0.07	0.8046	0.085	0.7846	Not significant

F: F-value, P: p-value, A: Temperature (^oC), B: H_2O_2 concentration (%), C: time (min), Y_{PKA}: pulp yield of pulp-KA, Y_{PKB}: pulp yield of pulp-KB, Y_{BKA}: Brightness of pulp-KA, Y_{BKB}: Brightness of pulp-KB, Y_{WKA}: Whiteness of pulp-KA, Y_{WKB}: Whiteness of pulp-KB.

For the simulation of single stage HPB, the second order polynomial equation Eq. (4.2) was fitted to the experimental data. This gave six model equations describing the pulp yield, brightness, and whiteness, i.e. Eqs. ((5.3), (5.4), (5.5)) for pulp-KA and Eqs. ((5.6), (5.7), (5.8)) for pulp-KB. For the process modeling, only statistically significant regression coefficients were used. The quadratic equations representing the model in terms of the coded factors can be used to make estimate regarding the response for the given levels of each factors.

$$Y_{PKA} = 82.87 - 0.78X_T - 0.58X_{C-H_2O_2} - 0.33X_t + 0.25X_TX_{C-H_2O_2} - 0.08X_TX_t - 0.05X_{C-H_2O_2}X_t + 0.16X_T^2 + 0.09X_{C-H_2O_2}^2 - 0.14X_t^2 \quad (5.3)$$

$$Y_{BKA} = 62.46 + 0.86X_T + 0.51X_{C-H_2O_2} + 0.74X_t + 0.22X_TX_{C-H_2O_2} - 0.13X_TX_t + 1.65X_{C-H_2O_2}X_t + 0.03X_T^2 - 0.25X_{C-H_2O_2}^2 - 0.36X_t^2 \quad (5.4)$$

$$Y_{WKA} = 86.62 + 0.81X_T + 0.64X_{C-H_2O_2} + 0.81X_t + 1.02X_TX_{C-H_2O_2} + 0.25X_{Tt}X_t + 1.2X_{C-H_2O_2}X_t - 0.39X_T^2 - 0.31X_{C-H_2O_2}^2 - 0.94X_t^2 \quad (5.5)$$

$$Y_{PKB} = 81.19 + 0.32X_T - 0.8X_{C-H_2O_2} - 0.63X_t + 0.13X_TX_{C-H_2O_2} - 0.17X_TX_t + 0.61X_{C-H_2O_2}X_t + 0.26X_T^2 + 0.49X_{C-H_2O_2}^2 + 0.33X_t^2 \quad (5.6)$$

$$Y_{BKB} = 67.41 + 1.14X_T - 1.4X_{C-H_2O_2} + 0.73X_t + 0.99X_TX_{C-H_2O_2} - 2.38X_TX_t + 0.42X_{C-H_2O_2}X_t - 0.41X_T^2 - 0.52X_{C-H_2O_2}^2 - 0.78X_t^2 \quad (5.7)$$

$$Y_{WKB} = 90.52 + 0.69X_T + 0.39X_{C-H_2O_2} + 0.44X_t + 0.85X_TX_{C-H_2O_2} + 0.12X_TX_t + 2.1X_{C-H_2O_2}X_t - 0.12X_T^2 + 0.29X_{C-H_2O_2}^2 - 0.48X_t^2 \quad (5.8)$$

The determination and adjusted determination coefficients were found to be R^2=0.99 (R^2_{adj}=0.99) for pulp yield, brightness, and whiteness, pointing a high statistical significance. Furthermore, the higher adjusted determination coefficient of model, significant p-value and an insignificant lack of fit indicating the used independent process variables are significant which affect the responses

(Anupam et al., 2018). As far as the CCD is concerned, all the variables were aptly predicted, approving its adequacy. The simulated bleaching effects described by Eq. (5.3) to Eq (5.8), are illustrated by response surface plots in Figure 5.3 and Figure 5.4. These plots allow us to describe the optimum obtained levels of single stage HPB outputs, at the desirable regions of process variables.

Pulp yield

The bleached pulp yield obtained in the experiment is found to be in the range of 82.9-84.79% and 80.98-83.92% for pulp-KA and pulp-KB, respectively (Table 5.3). Regarding the regression coefficients shown by the response models (Table 5.4), pulp yield has significantly influenced by H_2O_2 concentration, temperature, time as well as the quadratic and an interaction effect. The decrease in pulp yield with increase in H_2O_2 concentration and temperature is because of the dissolution of hemicellulose and lignin in hydrogen peroxide bleaching in alkali media (Song et al., 2016; Sharma et al., 2018).

Brightness

The pulp brightness is found in the range of 60.71-63.81% and 64.28-68.35% for pulp-KA and pulp-KB, respectively (Table 5.3). This brightness variation between pulp-KA and pulp-KB can be attributed to the differences in the amount of lignin initially presented in the pulps (Song et al., 2016). As can be seen from Table 5.4, H_2O_2 concentration, bleaching temperature and time has a significant effect on the pulp brightness, followed by the quadratic and interaction effects of H_2O_2 concentration, temperature, and time. The interactions between H_2O_2 concentration and temperature and H_2O_2 concentration and time have positive effect, while that between temperature and time have negative effect on brightness as seen in equations Eq. (5.4) and Eq (5.7) and also follows from Figure 5.3d, e, f and Figure 5.4d, e, f. As it could be anticipated, the lignin-derived

chromophores have a leading role on the brightness of the chemical pulp. Hydrogen peroxide in alkali media could serve as a mild agent for solubilizing lignin derived chromophores, which led to the increase in brightness of pulp (Shatalov and Pereira, 2014; Song et al., 2016; Huang et al., 2019).

Whiteness

As follows from Table 5.3 and surface plots Figure 5.3g, h, i and Figure 5.4g, h, i, the pulp whiteness obtained was found in the range of 83.61-86.99% and 88.12-91.76% for pulp-KA and pulp-KB, respectively. H_2O_2 concentration, temperature and time had a significant effect on the pulp whiteness. Moreover, the quadratic variables (H_2O_2 concentration, temperature, and time) and their interaction had a significant influence on the pulp whiteness (Table 5.4). The single stage HPB has obviously lowered lignin content in the pulp and increased whiteness by degrading the residual lignin from the pulp (Song et al., 2016).

The fitted polynomial functions with respect to each independent process variables provided the optimum bleaching conditions at maximum points on the surface plots. The optimum values were obtained at H_2O_2 concentration of 2%, process temperature of 87.44 ^oC and 82.89 ^oC and 60 and 62.7 min for pulp-KA and pulp-KB, respectively. To approve these data, the replicated bleaching experiments were performed under optimized conditions. The bleached pulps having pulp yield of 84.58% and 84.26%, brightness of 60.89% and 67.05% and whiteness of 84.53% and 90.34% were obtained for pulp-KA and pulp-KB, respectively. This shows very good correlation between experimental values and model prediction.

The single stage HPB was selected among a group of potential stages of HPB. It has been confirmed to be very effective for the removal of the residual lignin. The single stage HPB for SCB Kraft pulp adopted in this study can decrease bleaching cost, environmental pollution, and

bleaching time (Kumar et al., 2013). Compared with number of treatment stages, the amount and type of chemicals used, the brightness and whiteness of the single stage HPB are brilliant, bearing in mind the use of chlorine free bleaching and the simplicity of the bleaching process employed.

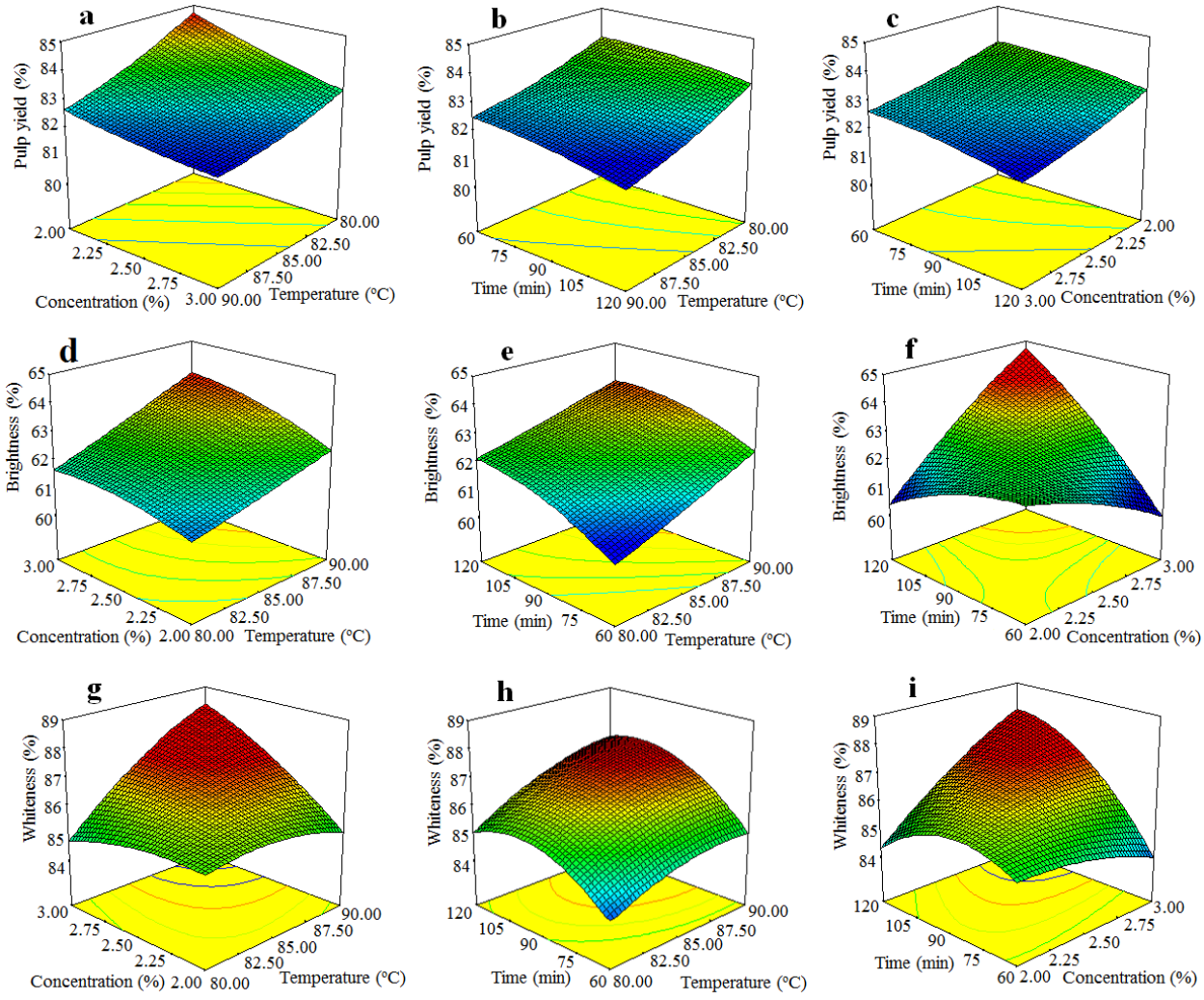


Figure 5.3 Pulp-KA response surface plots of pulp yield, brightness, and whiteness under variable condition of single stage hydrogen peroxide bleaching.

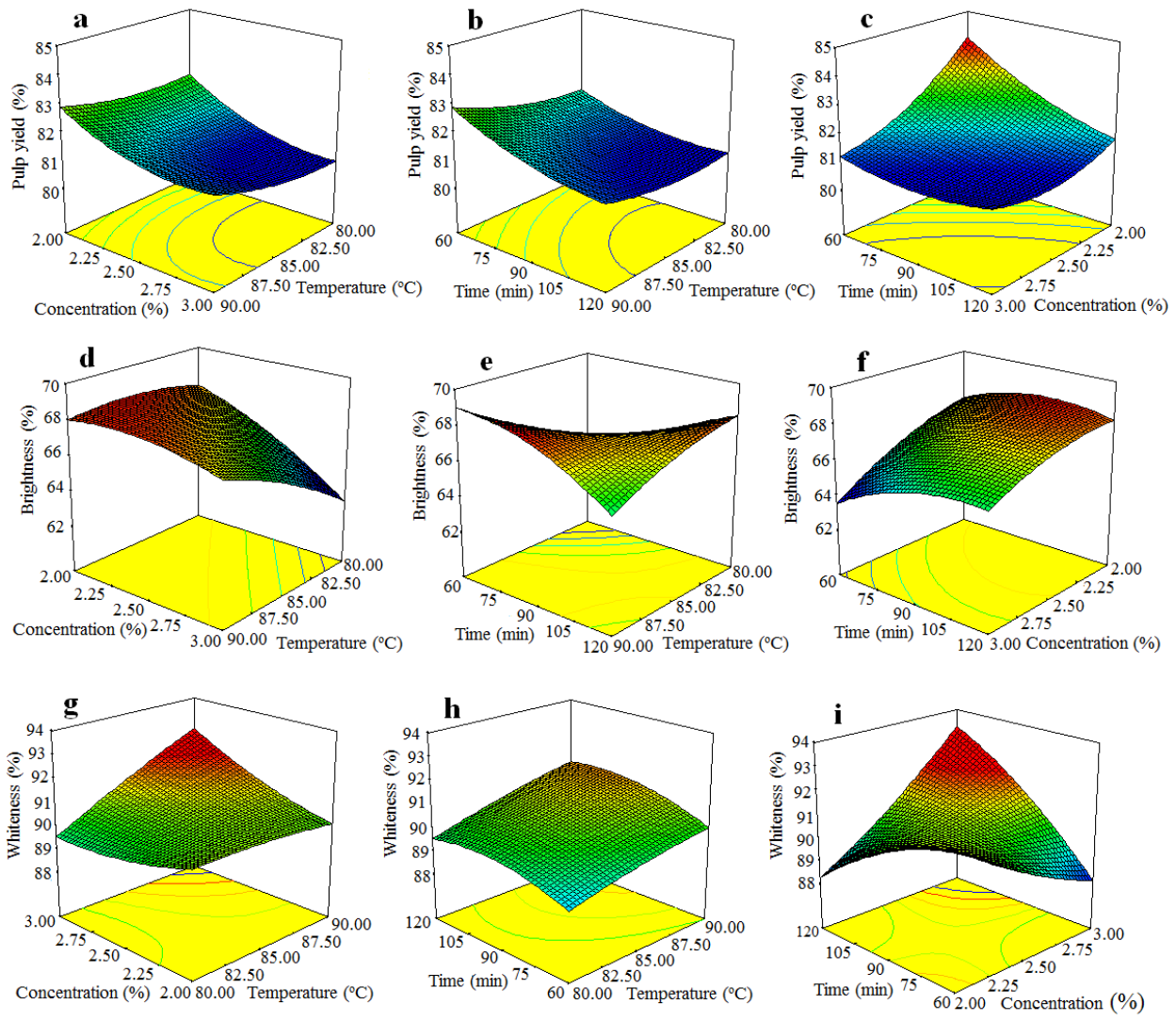


Figure 5.4 Pulp-KB Response surface plots of pulp yield, brightness, and whiteness under variable condition of single stage hydrogen peroxide bleaching.

5.3.3. Mechanical properties of paper from pulp-KA and pulp-KB

Conventional papers were prepared from ESCB Kraft pulp (pulp-KA and pulp-KB). Paper obtained from pulp-KA and pulp-KB had burst index (8.51 and 4.62 $kPam^2/g$), tensile index (48.22 and 44.40 Nm/g) and tear index (9.47 and 8.49 mNm^2/g), respectively. As reported by Mamaye et al. (2020), paper from soda pulp with kappa number of 16.73 and soda pulp with kappa number of

8.27 were burst index (6.53 and 3.13 $kPam^2/g$), tensile index (14.7 and 5.98 Nm/g) and tear index (5.22 and 3.92 mNm^2/g), respectively, which is lower than paper from pulp-KA and pulp-KB. This shows that paper mechanical properties are affected by sulphidity in addition to pulping conditions. The burst index, tensile index and tear index of paper made from pulp-KA was significantly higher than that of paper from pulp-KB. The decrease in the mechanical properties of paper from pulp-KB was due to decrease in amount and degree of polymerization of hemicellulose as result of higher temperature, chemical dose, and time of delignification. Hence, hemicellulose influences swelling behaviors of the fibers and acts as lubricating agent, which helps for the development of hydrogen bonding (Anupam et al., 2016; Sharma et al., 2018; Sharma et al., 2020). In terms of fiber morphology, ESCB has fiber length (1.86 mm), cell-wall thickness (2.53 µm), fiber diameter (30.02 µm), Runkel ratio (0.08) and flexibility coefficient (90.82), those characteristic of fibers results good mechanical properties of paper. Fibers with a high flexibility coefficient and length can complement a high mechanical property (tensile, burst, tear strength) (Mamaye et al., 2019; Sharma et al., 2020). Ethiopian sugarcane bagasse can be then viewed as a good candidate for making good papers that have a preferred mechanical strength. As seen from the results, the mechanical properties of SCB Kraft pulp paper are significantly affected by the pulping methods and pulping conditions in addition to the morphological and chemical characteristics of raw material (Fagbemi et al., 2017; Kassim et al., 2016; Anupam et al., 2016; Sharma et al., 2020).

5.4. Conclusion

High purity pulp with high brightness and whiteness were obtained by statistical optimization and modeling of Kraft pulping and single stage HPB using Design expert software. The pulping parameters investigated in this study were vital in that they strongly affected the mechanical properties of paper as well as their brightness and whiteness. The optimum pulp yield of 38.41%

with 17.68 kappa number was obtained at Kraft delignification conditions:130 °C temperature, 10% NaOH concentration at 60 min. The results have shown that the brightness and whiteness of pulp-KB were higher than those of pulp-KA. The studies carried out on the mechanical properties of the papers, clearly indicated the pulp-KA papers were higher in tensile, tear and burst index than the pulp-KB papers. The tensile, burst and tear strength of both papers prepared from pulp-KA and pulp-KB were affected by the pulping parameters. Based on the results, it can be concluded that the utilization of Ethiopian sugarcane bagasse using the adopted methods (Kraft delignification and single stage hydrogen peroxide bleaching) is a promising approach for the production of pulp and paper with allowable pulp yield, brightness, whiteness, and paper mechanical properties from sugarcane bagasse.

CHAPTER SIX

Characterization of soda and Kraft black liquor

6.1. Introduction

Pulp and paper industry consume large amount of fresh water in various processes including raw material preparation, pulp washing and paper manufacturing, pulp bleaching and fiber recycling, hence it is water intensive process (Merayo et al., 2013; Ashra et al., 2015). The amount of water used depends on the raw material and the pulping method used (Kesalkar et al., 2012). At the beginning of the 20th century 500 to1000 m^3 of water was consumed in the production of one ton of pulp (Kamali and Khodaparast, 2015; Toczylowska, 2017). In modern pulp mills the water consumption decreased 10 to 50 m^3 per ton of pulp. This is because modern pulp mills used wet process throughout the pulping and paper making processes (Toczylowska, 2017). The properties and volume of wastewater generated in each process depends on the raw material used, pulping method, bleaching method and number of bleaching stages, chemicals used, quantity and quality of pulp produced (Ashra et al., 2015; Kamali and Khodaparast, 2015). Kraft and soda pulping are the two major chemical pulping methods which produce unbleached dark pulp and wastewater (Cardoso et al., 2009). The generated large volume of wastewater has a significant impact on the environment (Ashra et al., 2015; Merayo et al., 2013).

The wastewater generated from pulp and paper industry with black or dark brown color is known as black liquor (Kamali and khodaparast, 2015; Zhu and Theliander, 2015; Domínguez et al., 2017; Irfan et al., 2017; Hidayati et al., 2018). The chemical composition and the physical properties of

black liquor depends on the nature of the raw materials (softwood like scot pine, hard wood like eucalyptus and non-wood such as bamboo and sugarcane bagasse), delignification conditions, dose of cooking chemicals used in pulping and bleaching (Cardoso et al., 2009; El-mekkawi et al., 2011; Bajpai, 2017). The black liquor generated by chemical pulping constitute a complex aqueous solution of organic materials from wood and non-wood resources (lignin, polysaccharides, and resins compounds) and inorganic compounds (mainly soluble salt ions such as sodium carbonate (Na_2CO_3), sodium sulfate (Na_2SO_4), sodium sulfide (Na_2S) and sodium thiosulfate ($Na_2S_2O_3$)). Due to those chemical compounds, the black liquor can cause environmental pollution (Andreuccetti et al., 2011; Kesalkar et al., 2012; Ashra et al., 2015; Kim et al., 2017; Hidayati et al., 2018).

The environmental pollution load of black liquor is evaluated by the amount of Biochemical Oxygen Demand (BOD), Chemical Oxygen Demand (COD), Total Dissolved Solid (TDS), organic (dissolved and suspended), and inorganic materials and color of effluent (Kamali et al., 2016; Kamali and Khodaparast, 2015). The pulp and paper industry effluent are characterized by high BOD load of 10-50 kg/ton of pulp and COD of about 20-200 kg/ton of pulp. The COD of black liquor varies from 10,000 to 120,000 mg/L and the pH range from 10 to 13 (Kaur et al., 2017; Hu et al., 2015). The high COD value of black liquor is due to dissolved inorganic and organic chemicals like dyes, heavy metals, detergents, starch and toxic substances (Zhu and Theliander, 2015). The BOD gives information about the readily biodegradable fraction of the organic load in the wastewater. It indicates the amount of oxygen taken up through the respiratory activity of microorganisms growing on the organic compounds present in the sample (Jouanneau et al., 2013). The biodegradability index (BI) is expressed as a ratio of BOD_5 to COD. This ratio

measures the extent to which a waste is amenable to biodegradation (Kamali and Khadaparast, 2015; Tembhekar et al., 2015).

In this chapter, the chemical composition, and physical properties of untreated and pretreated Ethiopian sugarcane bagasse (ESCB) soda and Kraft black liquor were determined. In addition, the colors of the black liquor were analyzed. Meanwhile, the effect of physical fractionation pretreatment and pulping methods on the properties of black liquor were investigated.

6.2. Materials and Methods

6.2.1. Materials

Black liquor was produced from untreated and pretreated Ethiopian sugarcane bagasse using Kraft and soda delignification, at a temperature of 130 ^{o}C, sodium hydroxide concentration of 10%, time of 60 min and a solid: liquid ratio of 1:10 kg/L. In addition, the Kraft delignification process has sodium sulfide concentration of 20% and sodium hydroxide to sodium sulfide ratio of 3:1. After reaction, the separation of black liquor (liquid) from the pulp (solid fractions) was carried out using 150 mesh stainless steel sieve and the obtained black liquor was then characterized. The black liquor samples are called as PSBL, USBL, PKBL and UKBL. PSBL and PKBL refer to pretreated soda and Kraft black liquor, respectively, and USBL and UKBL refer to untreated soda and Kraft black liquor, respectively.

6.2.2. Methods

6.2.2.1. Density and pH measurement

The pH of black liquor was determined by using pH meter (HI2020 edge ® Multiparameter pH meter). Density was determined following the pycnometer method (50 ml density bottle) by measuring the mass of black liquor of a known volume of black liquor at room temperature.

6.2.2.2. Biochemical oxygen demand determination

The black liquor Biochemical oxygen demand (BOD) measurement was performed in a closed bottle test following the American Public Health Association (APHA method 5210 B) method. The black liquor sample was pipetted into a BOD bottle containing aerated dilution water. The dissolved oxygen content was determined in a sealed bottle and incubated at 20 ^{o}C for five days in a dark room. After an incubation period of 5 days, the final dissolved oxygen was measured (Hang, 2010; Jouanneau et al., 2013). Then the BOD value was calculated using the following equation:

$$\mathrm{BOD} = \frac{100}{\mathrm{p}} * (\mathrm{DOB} - \mathrm{DOD}) \quad (6.1)$$

Where: DOB = initial oxygen in diluted sample (mg/L)

DOD = oxygen in diluted sample after 5-day incubation (mg/L)

P= ml sample*100/capacity of bottle

6.2.2.3. Chemical oxygen demand determination

The COD of the black liquor was assigned by dichromate open reflux technique, American Public Health Association (APHA method 5520 B) method. Fifty milliliters of black liquor sample were pipetted into refluxing flask, 1 g mercuric sulfate ($HgSO_4$) and 5 mL sulfuric acid (H_2SO_4) reagents were added to dissolve $HgSO_4$. Then 25 mL potassium dichromate ($K_2Cr_2O_7$) was added to the solution and finally adjusted by adding 70 mL H_2SO_4 reagent and refluxed for 2 h. At the end the mixture was cooled and diluted to about twice its volume with distilled water. The cooled mixture to room temperature was titrated for the excess of $K_2Cr_2O_7$ with ammonium ferrous sulfate ($(NH_4)_2Fe(SO_4)_2$) solution (Hang, 2010). Then the COD value was calculated using the following equation:

$$\mathrm{COD\ (mg/L)} = (\mathrm{A} - \mathrm{B}) * \mathrm{M} * 8000/\mathrm{D} \quad \text{(6.2)}$$

Where: A= Amount of ferrous ammonium sulfate, mL used for blank

B= Amount of ferrous ammonium sulfate used for sample, mL

M= Molarity of ferrous ammonium sulfate

D= Amount of sample used, mL

8000= milliequivalent weight of oxygen *1000 ml/L

6.2.2.4. Lignin content determination

The black liquor klason lignin (acid insoluble) was determined by hydrolysis treatment with 72% sulfuric acid (H_2SO_4). The short method is as follows: in 5 ml of black liquor 3 ml of 72% H_2SO_4 was added and incubated for 15 min at room temperature held in a thermostat condition of 30 ^oC in a water bath. Then the mixture was diluted to 3% by adding distilled water and autoclaved at 120 ^oC for an hour for hydrolysis of the polysaccharides. At the end of the hydrolysis the sample was cooled to room temperature filtrated by filter paper and the insoluble solid residue referred to Klason lignin was measured gravimetrically according to Technical Association of Pulp and Paper Industry (TAPPI) T222 cm-00 (Westman et al., 2014; Zhu and Theliander, 2015).

6.2.2.5. Total dissolved solid, inorganic, and organic matter determination

Total dissolved solid (TDS) was determined using TAPPI T264 cm-97. Inorganic matter was determined after combustion of the sample at 525 ^oC in a furnace for 2 h as per TAPPI T211 om-93 procedure. The organic matter was determined from the difference between total dissolved solids and inorganic matter (Costa et al., 2009; Garcia et al., 2009; Sharari et al., 2011). Each experimental run was done in triplicate.

6.2.2.6. Color measurement

The color of the black liquor was measured using spectrophotometer CM-600d (KONICA MINOLTA, INC., JAPAN) by placing black liquor in quartz cuvettes (Abuagela et al., 2018). The color of black liquor was recorded as lightness (L*), redness (a*) and yellowness (b*). Lightness (L*) was scaled from 0 (black) to 100 (white); redness (a*) from -60 (green) to 60 (red) and yellowness (b*) from -60 (blue) to 60 (yellow).

6.2.2.7. Statistical analysis

Statistical Package for Social Sciences (SPSS software, version 20) was used for statistical analysis, to determine the significant differences between the untreated and pretreated SCB Kraft and soda black liquor chemical composition, physical properties, and color. The mean value of each variables was compared at $p< 0.05$ level.

6.3. Results and Discussion

The results of the physicochemical characteristics of untreated and pretreated ESCB soda and Kraft black liquor are summarized in Table 6.1. In SCB soda and Kraft pulping around 900 mL concentrated black liquor was generated. It consumed an average of 14,970 mL fresh water for pulp washing where 50 g pulp was produced. After pulp washing, the totally amount of black liquor produced was reached around 15,870 mL.

Table 6.1 Physico-chemical properties of the black liquors derived from the soda and Kraft pulping of untreated and pretreated SCB.

Parameters	PSBL	USBL	PKBL	UKBL
pH	13.46	13.73	13.40	13.69
Density (g/mL)	1.05	1.12	1.06	1.13
Lignin (g/L)	28.45	40.53	23.29	36.51
TDS (g/L)	145.83	157.88	157.49	164.86
BOD (mg/L)	328	356	192	200
COD (mg/L)	50000	54300	74100	77400
BOD_5/COD	0.00656	0.00655	0.00259	0.00258
Inorganic material (g/L)	104.83	120.31	117.82	133.03
Organic material (g/L)	41.01	37.57	39.67	31.83

TDS: Total dissolved solid; BOD: Biochemical Oxygen Demand, COD: Chemical Oxygen Demand, PSBL: pretreated soda black liquor, USBL: untreated soda black liquor, PKBL: pretreated Kraft black liquor, UKBL: untreated Kraft black liquor

6.3.1. Density and pH

As shown in Table 6.1, the black liquor pH value indicates alkaline nature for both untreated and pretreated SCB soda and Kraft pulping processes. This may be attributed the sodium hydroxide (NaOH) solutions used for both pulping processes. However, the pH values of USBL and UKBL are significantly higher than those of PSBL and PKBL at p-value of 0.007 and 0.009, respectively (Table 6.2). The higher pH value of untreated black liquor indicates the higher amount of lignin and which absorbed more chemicals during pulping process. The density of USBL and UKBL are found to be higher than those of PSBL and PKBL, which is a statistically significant difference (p-

value of 0.006 and 0.008, respectively) (Table 6.2). This can be related to the higher amounts of inorganic components present in that USBL and UKBL. The density of most organic material in black liquor is close to that of water, whereas the inorganic component is nearly two times that of water (Cardoso et al., 2009). Because the untreated SCB is with its lignin and this indicate that the lignin of the bagasse highly holds the mineral components (inorganic) and these inorganic components have the strongest effect on the density of black liquor. Due to this the black liquor of untreated SCB have higher density than that of the pretreated SCB.

6.3.2. Lignin

The lignin content of (PSBL and USBL), and (PKBL and UKBL) were statistically significant different at (p-value of 0.003) and (p-value of 0.016), respectively (Table 6.2). The lignin contents of both untreated SCB soda and Kraft pulping black liquors were found to be higher than that of pretreated SCB. This indicates that considerable amount of lignin is present in untreated SCB. As a result, physical fractionation pretreatment of sugarcane bagasse has significantly decreased the lignin content of black liquor, which also decreased the pollution load of black liquor due to large amount chemical absorption of lignin presented in untreated SCB in pulp production process. In addition, the lignin contents of soda black liquor were higher than that of Kraft black liquor, which shows that more lignin was dissolved by soda pulping than the Kraft pulping of SCB.

6.3.3. Biochemical oxygen demand and Chemical oxygen demand analysis

The COD value between untreated and pretreated SCB of the soda and Kraft black liquor were show significant difference (Table 6.1). The Kraft black liquor has higher COD value than soda black liquor. The higher COD level means a greater amount of oxidizable substances in the Kraft black liquor than soda black liquor (Zhu and Theliander, 2015; Sathawong et al., 2018). The PFP reduces the amount of oxidizable organic material in the black liquor of soda and Kraft

delignification process. This can make PFP an attractive pretreatment method for the reduction of pollution load of pulp and paper production from sugarcane bagasse. On the other hand, low BOD_5: COD ratio was observed for both soda and Kraft black liquor. According to Bilin et al. (2016) and Abrevaya et al., (2015) the BOD_5: COD ratio less than 0.4 indicates the presence of a large amount of nonbiodegradable organic matter. The high level of BOD and COD indicate the presence of significant amount of lignin, suspended solids (mainly fibers), fatty acids, tannins, sulfur and sulfur compounds in soda and Kraft pulping black liquor of the ESCB (Kesalkar et al., 2012). The BOD and COD values of Kraft black liquors were higher than soda black liquors, this is because of sulfur and sulfur compounds developed in the Kraft delignification process as result of sodium sulfide pulping chemical. Furthermore, the pollution load of UKBL and USBL was higher that of PKBL and PSBL, due to its high content of organic and inorganic compounds (El-mekkawi et al., 2011).

6.3.4. Total dissolved solid, inorganic, and organic matter analysis

The inorganic material content of black liquor of PSBL and USBL was statistically significant difference at p-value 0.002. On the other hand, the TDS contents of black liquor of PSBL and USBL was statistically insignificant difference at p-value of 0.050 (Table 6.2). The inorganic material content between PKBL and UKBL was significant differences at p-value of 0.0001 (Table 6.2). The TDS and inorganic components of untreated SCB Kraft and soda black liquor were found to be higher than that of the pretreated SCB (Figure 6.1). The higher inorganic content in the untreated SCB soda and Kraft black liquor was due to the higher accumulation of non-fibrous materials in untreated SCB. The non-fibrous materials are center of the accumulation of the inorganic materials. The organic matters contents for both untreated and pretreated black liquor

were statically insignificant differences. As a result, untreated SCB absorb large amount of pulping chemical compared with the pretreated SCB.

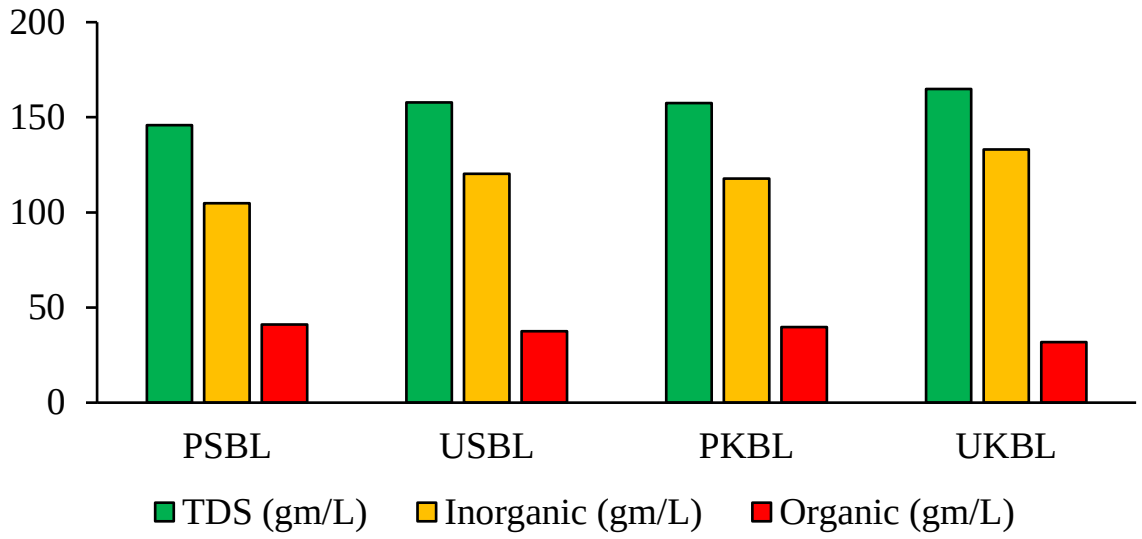


Figure 6.1 Total dissolved solid (TDS), inorganic and organic material of soda and Kraft black liquor.

Table 6.2 SPSS statistical significance tests of untreated and pretreated soda and Kraft black liquor.

Properties	p-values			
	PSBL-USBL	PKBL-UKBL	PSBL-PKBL	USBL-UKBL
pH	0.007	0.009	0.005	0.057
Density (g/mL)	0.107	0.008	0.635	0.368
Lignin (g/L)	0.003	0.016	0.064	0.018
TDS (g/L)	0.050	0.334	0.126	0.032
Inorganic material (g/L)	0.002	0.0001	0.005	0.0001
Organic material (g/L)	0.413	0.074	0.823	0.769

6.3.5. Color

The soda and Kraft pulping black liquor color measurement such as lightness (L*), redness (a*) and yellowness (b*) are summarized in Table 6.3.

Table 6.3 The lightness, redness, and yellowness value of untreated and pretreated SCB soda and Kraft black liquor.

Parameters	Lightness (L*)	Redness (a*)	Yellowness (b*)
PSBL	20.95	4.31	-1.06
USBL	21.11	3.21	-1.65
PKBL	25.55	13.33	6.35
UKBL	25.07	9.57	4.25

PSBL: pretreated soda black liquor, USBL: untreated soda black liquor, PKBL: pretreated Kraft black liquor, UKBL: untreated Kraft black liquor

The color is a primary quality parameter associated with the pollution load of black liquor. The tri-stimulus color parameters L*-a*-b* values were routinely used for describing the influence of delignification black liquor on the environment. The Kraft black liquor has the darkest color than that of soda black liquor. On the other hand, PFP has no significant effect on the lightness of the black liquor. The redness (a*-value) was found to be positive, which indicate the red color of the black liquor. The black liquor yellowness (b*-value) was found to be negative for soda black liquor (tending to blueness) and positive for Kraft black liquor to yellowness. The yellowness of Kraft black liquor which is associated with sodium sulfide (Na_2S) reagent used in the delignification process.

6.4. Conclusion

The Kraft black liquor has a higher content of inorganic materials and organic materials than the soda black liquor. On the other hand, pretreated SCB soda and Kraft black liquor had the lowest lignin, COD, BOD, TDS, organic and inorganic materials than the untreated SCB black liquor. The color of black liquor was significantly influenced by chemicals used in the pulping process and pretreatment. From the results, physical fractionation pretreatment of sugarcane bagasse decreases the lignin, COD, BOD, TDS, organic and inorganic materials of the black liquor. The black liquor physico-chemical properties were varied due to the pretreatment and pulping methods adopted. Based on the results, it can be concluded that the physical fractionation pretreatment adopted is a promising approach to reduce pollution load in pulp production from Ethiopian sugarcane bagasse.

CHAPTER SEVEN

General conclusion and recommendation

7.1. General conclusion

The aim of this PhD dissertation was to assess the possible ways for the utilization of Ethiopian sugarcane bagasse (*Saccharum officinarum L.*) as a raw material for pulp and paper making. Because of a sharp decline of the forest coverage in the world, some inexpensive and quality non-wood fibers like sugarcane bagasse will be required for pulp and paper manufacture. In this regard, the morphological properties, chemical composition, soda and Kraft delignification and hand sheet paper quality of Ethiopian sugarcane bagasse has been investigated.

The morphology and chemical composition characteristics of Ethiopian sugarcane bagasse results have shown that it owns the characteristics needed for paper pulp production. Sugarcane bagasse has an average fiber length, thin cell-wall thickness, and large lumen diameter, which are mandatory for the production of higher mechanical strength and quality paper. In addition, the chemical characteristics of sugarcane bagasse have revealed, the presence comparable cellulose, lignin and hemicellulose content with other wood and non-wood fiber sources conventionally used for paper pulp production. Furthermore, the physical fractionation pretreatment implemented for sugarcane bagasse has decreased the higher extractive substances, lignin, ash, and silica contents. The above results show that this biomass has a great potential source for the production of cellulose rich pulp. Therefore, it is evident that the use of sugarcane bagasse as paper pulp raw materials can bring both economic and environmental benefits.

A mathematical optimization and modeling were planned for soda and Kraft delignification of sugarcane bagasse and single stage hydrogen peroxide bleaching of the pulp. Multilevel categoric experimental design was employed to study the individual and interactive effects of the delignification process variables (temperature, sodium hydroxide concentration and time) on the pulp yield and kappa number. The optimum process condition was 130 ^{o}C temperature, 10% sodium hydroxide concentration at 60 min for both soda and Kraft pulping processes. At this point the pulp yield was found to be 35.99% with kappa number of 16.73 and 38.41% with kappa number of 17.68 for soda and Kraft pulping, respectively.

Single stage hydrogen peroxide bleaching for both soda and Kraft pulp optimization and modeling were done by using response surface methodology with central composite design, to study the individual and interaction effect of bleaching variables (temperature, H_2O_2 concentration and time) on the pulp yield, brightness, and whiteness. The optimum bleaching conditions for pulp-SA and pulp-SB were 80 and 90 ^{o}C temperature, 2.3% and 2% H_2O_2 concentration at 60 min, respectively. At this point, the pulp yield for pulp-SA and pulp-SB were 88.27% and 85.79%, respectively. The brightness for pulp-SA and pulp-SB were 61.96 and 71.16, respectively, whereas the corresponding whiteness were 84.14 and 90.17, respectively were obtained. Similarly, the optimum bleaching conditions for Kraft pulp were 87.44 and 82.89 ^{o}C temperature, 2% H_2O_2 concentration at 60 and 62.7 min for pulp-KA and pulp-KB, respectively. At this point, the pulp yield for pulp-KA and pulp-KB were 84.58% and 84.26%, respectively. The brightness for pulp-KA and pulp-KB were 60.89% and 67.05%, respectively, whereas the corresponding whiteness were 84.53% and 90.34%, respectively. The Soda and Kraft pulp single stage hydrogen peroxide bleaching results have comparable pulp yield, brightness, and whiteness.

Paper mechanical properties test results showed that paper made from pulp-SA and pulp-KA are higher in strength than pulp-SB and pulp-KB paper. In addition, the mechanical properties of paper from Kraft pulp are relatively higher than those of soda pulp paper. However, Kraft black liquor presents higher content of inorganic and non-biodegradable organic materials than soda black liquor even if the amount of these materials was reduced by the employed physical fractionation pretreatment method. In conclusion, the results in the optimum condition for both soda and Kraft pulping results comparable pulp yield and kappa number and paper mechanical properties. However, Kraft black liquor has a higher content of inorganic materials and non-biodegradable organic materials than the soda black liquor. As a result, Kraft pulping method can cause more environmental pollution than soda pulping. Due to this reason soda pulping method is more preferable for pulping Ethiopian sugarcane bagasse. The utilization of sugarcane bagasse in pulp and paper production is highly desirable since it can add value on the industrial byproducts and also reduce environmental issues caused by inappropriate disposal.

7.2. Recommendation

The research work in this dissertation has encountered its objectives stated in chapter one. However, further work might be necessary to utilize Ethiopian sugarcane bagasse for pulp and paper production in industrial scale. The following points are recommended for future work.

a) Pulping of sugarcane bagasse for large scale production

For large scale operation, the pulping of sugarcane bagasse needs to be assessed in sulfur free medium of pulping method (soda pulping). The researcher recommends that further research works need to be done for Pilot scale pulp production at optimum soda pulping process parameters.

b) Recovery technique

Due to environmental concerns of commercial delignification technologies, the relatively more environmentally friendly soda pulping was selected. In this study, soda pulp was found to be comparable to Kraft pulping regarding its pulp yield, pulp quality parameters. However, the chemical recovery issues of this process need to be solved. Thus, detailed study on the design of black liquor pretreatment and chemical recovery should be done.

c) Collection and storage of sugarcane bagasse

As it has been discussed in detail in chapter three higher moisture, hot water and 1% NaOH solubility of sugarcane bagasse due to the higher content of pith can cause decay of the sugarcane bagasse. Thus, collection, transportation, and storage of bagasse will be major issue. Thus, to overcome this problem further study should be done.

d) Utilization of pretreatment residue

As it has been discussed in detail in chapter three about the physical fractionation pretreatment of sugarcane bagasse, around 35% of residues is found after pretreatment. This residue is not suitable for pulp and paper production. Thus, detailed study on the characterization and utilization of this material should be done.

e) Economic assessment

Huge amount of sugarcane bagasse is produced in Ethiopian sugar factories. Some of this sugarcane bagasse can be used as energy source for sugar mills by direct burning. Large amount of sugarcane bagasse is surplus and dumped in the environment. Thus, comparison regarding technological, environmental, and economic feasibility should be studied specifically in Ethiopian scenario prior to implementing this study.

References

Abdullah, R., Ishak, C. F., Kadir, W. R., Bakar, R. A. (2015). Characterization and Feasibility Assessment of Recycled Paper Mill Sludges for Land Application in Relation to the Environment. *International Journal of Environmental Research and Public Health*, *12*, 9314–9329.

Abril, D., Medina, M., Abril, A. (2012). Sugarcane bagasse prehydrolysis using hot water. *Brazilian Journal of Chemical Engineering*, *29*, 31-38.

Abuagela, M. O., Iqdiam, B. M., Baker, G. L., Macintosh, A. J. (2018). Temperature-Controlled Pulsed Light Treatment : Impact on Aflatoxin Level and Quality Parameters of Peanut Oil. *Food and Bioprocess Technology*. https://doi.org/10.1007/s11947-018-2105-6

Adel, A. M., Abd, Z. H., Wahab, E., Ibrahim, A. A., Al, M. T. (2010). Characterization of microcrystalline cellulose prepared from lignocellulosic materials. Part I Acid catalyzed hydrolysis. *Bioresource Technology*, *101*, 4446–4455.

Agnihotri, S., Dutt, D., Tyagi, C. H. (2010). Complete characterization of bagasse of early species of *Saccharum officinerum*-CO 89003 for pulp and paper making. *BioResources*, *5*, 1197–1214.

Ai, J., Tschirner, U. (2010). Fiber length and pulping characteristics of switchgrass , alfalfa stems , hybrid poplar and willow biomasses. *Bioresource Technology*, *101*, 215–221.

Akgül, M., Tozluo, A. (2010). Alkaline-ethanol pulping of cotton stalks. *Scientific Research and Essays*, *5*, 1068–1074.

Alda, A. G. (2008). Feasibility of recycling pulp and paper mill sludge in the paper and board industries. *Resources, Conservation and Recycling*, *52*, 965–972.

Alila, S., Besbes, I., Rei, M., Mutjé, P., Boufi, S. (2013). Non-woody plants as raw materials for

production of microfibrillated cellulose (MFC): A comparative study. *Industrial Crops and Products*, *41*, 250–259.

Andrade, M. F., Colodette, J. L. (2014). Dissolving pulp production from sugar cane bagasse. *Industrial Crops and Products*, *52*, 58–64.

Andrés, F. N., Beltramini, L. B., Guilarducci, A. G., Romano, M. S., Ulibarrie, N. O. (2015). Lightweight Concrete : an Alternative for Recycling Cellulose Pulp. *Procedia Materials Science*, *8*, 831–838.

Anjos, O., Garcia-Gonzalo, E., Santos, A. J. A., Simoes, R., Martinez-Torres, J., Pereira, H., Garcia-Nieto, P. (2015). Using Apparent Density of Paper from Hardwood Kraft Pulps to Predict Sheet Properties, based on Unsupervised Classification and Multivariable. *BioResources*, *10*, 5920–5931.

Anuradha Jabasingh, S., and C.V. Nachiyar. (2011). Utilization of pretreated bagasse for the sustainable bioproduction of cellulase by *Aspergillus nidulans* MTCC344 using Response surface methodology. *Industrial crops and products* 34, 1564-1571.

Anuradha Jabasingh, S., and C.V. Nachiyar. (2012). Optimization of cellulase synthesis by RSM and evaluation of ethanol production from enzymatically hydrolyzed sugarcane bagasse using *Saccharomyces cerevisiae*. *Journal of Scientific and Industrial Research* 71, 353-359.

Anuradha Jabasingh, S. (2011). Response surface methodology for the evaluation and comparison of cellulase production by *Aspergillus nidulans* SU04 and *Aspergillus nidulans* MTCC344 cultivated on pretreated sugarcane bagasse. *Chemical and Biochemical Engineering Quarterly* 25, 501-511.

Anuradha Jabasingh, S., D. Lalith, M.A. Prabhu, Y. Abubekker, Z. Taye. (2016). Catalytic conversion of sugarcane bagasse to cellulosic ethanol: TiO_2 coupled nanocellulose as an

effective hydrolysis enhancer. *Carbohydrate Polymers* 136, 700-709.

Anupam, K., Deepika, Swaroop, V., Lal, P.S. (2018). Antagonistic, synergistic and interaction effects of process parameters during oxygen delignification of Melia dubia kraft pulp. *Journal of Cleaner Production* 199, 420-430.

Anupam, K., Kumar, A.S., Lal, P.S., Bist, V. (2016). Physicochemical, Morphological, and Anatomical Properties of Plant Fibers Used for Pulp and Papermaking; Fiber Plants. Biology, *Biotechnology and Applications*, 235-248.

Ashori, A. (2006). Nonwood Fibers A Potential Source of Raw Material in Papermaking. *Polymer-Plastics Technology and Engineering*, *45*, 1133–1136.

Ashra, O., Yerushalmi, L., Haghighat, F. (2015). Wastewater treatment in the pulp-and-paper industry : A review of treatment processes and the associated greenhouse gas emission. *Journal of Environmental Management*, *158*, 146–157.

Ayele, N., Dengia, A., Getaneh, A., Mengistu, L., Dilnesaw, Z. (2014). Effects of Bioactivators on Yield and Yield Components of Sugarcane at Wonji-Shoa Sugar Estate. *International Journal of Advanced Research*, *1*, 138–143.

Bajpai, P. (2010). Environmentally Friendly Production of Pulp and Paper. Canada: *John Wiley and Sons, Inc*, 8-61.

Bajpai, P. (2012). Biotechnology for Pulp and Paper Processing. Spain: *Springer*, 1-14.

Bajpai, P. (2017). The Pulp and Paper Industry. In *Emerging Waste Water Treatment Technologies*, Elsevier, 9–29.

Bassiouni, M., Ghazy, M. (2016). Effect of Temperature and Time on the Kraft Pulping of Egyptian Bagasse. *International Journal of Science and Research*, *5*, 179–184.

Berhanu, H., Kiflie, Z., Miranda, I., Lourenc, A., Ferreira, J., Feleke, S., Pereira, H. (2018).

Characterization of crop residues from false banana /*Ensete ventricosum*/ in Ethiopia in view of a full-resource valorization. *Plos One*, *13*, 1–21.

Berhanu, H., Kiflie, Z., Neiva, D., Gominho, J., Feleke, S., Yimam, A., Pereira, H. (2018). Optimization of ethanol-alkali deligni fi cation of false banana (*Ensete ventricosum*) fibers for pulp production using response surface methodology. *Industrial Crops and Products*, *126*, 426–433.

Bilin, L., Gmurek, M., Ledakowicz, S. (2016). Comparison between industrial and simulated textile wastewater treatment by AOPs Biodegradability, toxicity and cost assessment. *Chemical Engineering Journal*, *306*, 550–559.

Birhanu, A. (2014). Environmental degradation and management in Ethiopian highlands. *International Journal of Environmental Protection and Policy*, *2*, 24–34.

Birjandi, N., Younesi, H. (2016). Treatment of wastewater effluents from paper-recycling plants by coagulation process and optimization of treatment conditions with response surface methodology. *Applied Water Science*, *6*, 339–348.

Borges, F., Oliveira, D., Bras, J., Teresa, M., Pimenta, B., Aprigio, A., Naceur, M. (2016). Production of cellulose nanocrystals from sugarcane bagasse fibers and pith. *Industrial Crops and Products*, *93*, 48–57.

Brostow, W., Datashvili, T., Miller, H. (2010). Wood and Wood Derived Materials. *Journal of Materials Education*, *32*, 125–138.

Camarero, S., García, O., Vidal, T., Colom, J., Del Río, J. C., Gutiérrez, A., Martínez, Á. T. (2004). Efficient bleaching of non-wood high-quality paper pulp using laccase-mediator system. *Enzyme and Microbial Technology*, *35*, 113–120.

Cao, S., Lin, L., Huang, F., Huang, L., Chen, L. (2014). Morphological and Chemical Characterization of Green Bamboo (*Dendrocalamopsis oldhami (Munro) Keng f.*) for

Dissolving Pulp Production. *BioResources*, *9*, 4528–4539.

Caparrós, S., Díaz, M. J., Ariza, J., López, F., Jiménez, L. (2008). New perspectives for Paulownia fortunei L. valorisation of the autohydrolysis and pulping processes. *Bioresource Technology*, *99*, 741–749.

Cardoso, M., Domingos, É., Oliveira, D., Laura, M. (2009). Chemical composition and physical properties of black liquors and their effects on liquor recovery operation in Brazilian pulp mills. *Fuel*, *88*, 756–763.

Carvalho, D. M. De, Perez, A., Garcia, J. C., Colodette, J. L., Lopez, F., Diaz, M. J. (2014). Ethanol-Soda pulping of sugarcane bagasse and straw. *Cellulose Chemistry and Technology*, *48*, 355–364.

Cortesi, L., Smith, D., Miettenin, O., Axelrod, J., Porter, B., Noelle, M., Mark, M. van der. (2018). Environmental Paper Network, The state of the global paper industry.

Correa, L. J. (2012). Depithers for Efficient Preparation of Sugar Cane Bagasse Fibers in Pulp and Paper Industry. *Ingenieria Investigacion and Tecnologia*, *13*, 417–424.

Dillen, J. R., Dillén, S., Hamza, M. (2016). *Pulp and Paper : Wood Sources. Materials Science and Materials Engineering*.

Doherty, W.O.S., Rainey, T. J. (2006). Bagasse fractionation by the soda process. *Proceedings of the Australian Society of Sugar Cane Technologists*, *28*, 2–5.

Doherty, William O.S., Mousavioun, P., Fellows, C. M. (2011). Value-adding to cellulosic ethanol: Lignin polymers. *Industrial Crops and Products*, *33*, 259–276.

Domínguez-robles, J., Sánchez, R., Espinosa, E., Savy, D., Mazzei, P., Piccolo, A., Rodríguez, A. (2017). Isolation and Characterization of Gramineae and Fabaceae Soda Lignins. *International Journal of Molecular Sciences*, *18*, 1–17.

El-mekkawi, S. A., Ismail, I. M., El-attar, M. M., Fahmy, A. A., Mohammed, S. S. (2011). Utilization of black liquor as concrete admixture and set retarder aid. *Journal of Advanced Research*, *2*, 163–169.

Evangelina, M., Esteban, F., Kruyeniski, J., Cristina, M. (2015). Kinetic study of the extraction of hemicellulosic carbohydrates from sugarcane bagasse by hot water treatment. *Industrial Crops and Products*, *67*, 1–6.

Ezeudu, O. B., Agunwamba, J. C., Ezeasor, I. C., Madu, C. N. (2019). Sustainable Production and Consumption of Paper and Paper Products in Nigeria : A Review. *Resources*, *53*, 1–23.

Fagbemi, O. D., Fagbemigun, T. K., Mgbachiuzor, E., Igwe, C. C., Buhari, F. (2017). Investigation of Strength Properties of Paper Samples from Pulp Blends of *Hibiscus Cannabinus* and Pineapple Leaf Fibres. *International Journal of Science and Technology*, *6*, 714–718.

Fenta, D. T. (2010). *The Economicc significance of using bagasse as a source of raw material for pulp manufacturing: a case of Ethiopia*.

Fiserova, M., Gigac, J. (2011). Comparison of hardwood kraft pulp fibre characteristics and tensile strength. *Cellulose Chemicstry and Technology*, *45*, 627–631.

Galbe, M., Zacchi, G. (2012). Pretreatment : The key to efficient utilization of lignocellulosic materials. *Biomass and Bioenergy*, *46*, 70–78.

Hamzeh, Y., Ashori, A., Khorasani, Z., Abdulkhani, A., Abyaz, A. (2013). Pre-extraction of hemicelluloses from bagasse fibers: Effects of dry-strength additives on paper properties. *Industrial Crops and Products*, *43*, 365–371.

Hang, Y. D. (2010). Determination of Oxygen Demand. In Food Analysis. *USA: Springer,* 367–372.

Hemmasi, A. H., Samariha, A., Tabei, A., Nemati, M., Khakifirooz, A. (2011). Study of

Morphological and Chemical Composition of Fibers from Iranian Sugarcane Bagasse. *American-Eurasian Journal of Agricultural and Environmental Sciences*, *11*, 478–481.

Hidayati, S., Zuidar, A. S., Satyajaya, W., Murhadi, Retnowati, D. (2018). Isolation and characterization of formacell Lignins from oil empty fruits bunches. *Materials Science and Engineering*, *344*, 1–14.

Hu, G., Fu, S., Chu, F., Lin, M. (2017). Relationship between Paper Whiteness and Color Reproduction in Inkjet Printing. *BioResources*, *12*, 4854–4866.

Hu, Z., Que, Y., Gao, Y., Yin, Y., Zhao, Y. (2015). Using Black Liquor from the Soda Pulping Process for Protein Production by *Candida utilis*. *Bioresources*, *10*, 3908–3921.

Huang, C., Fang, G., Yu, L., Zhou, Y., Meng, X., Deng, Y., Ragauskas, A. (2019). Maximizing enzymatic hydrolysis efficiency of bamboo with a mild ethanol-assistant alkaline peroxide pretreatment. *Bioresource Technology*. https://doi.org/10.1016/j.biortech.2019.122568

Ibarra, D., Camarero, S., Romero, J., Martínez, M. J., Martínez, Á. T. (2006). Integrating laccase-mediator treatment into an industrial-type sequence for totally chlorine-free bleaching of eucalypt kraft pulp. *Journal of Chemical Technology and Biotechnology*, *81*, 1159–1165.

Jabasingh, S. A. (2011). Response Surface Methodology for the Evaluation and Comparison of Cellulase Production by *Aspergillus nidulans* SU04 and *Aspergillus nidulans* MTCC344 Cultivated on Pretreated Sugarcane Bagasse. *Biochemical Engineering Quarterly*, *25*, 501–511.

Jabasingh, S. A., Lalith, D., Prabhu, M. A., Yimam, A., Zewdu, T. (2016). Catalytic conversion of sugarcane bagasse to cellulosic ethanol : TiO_2 coupled nanocellulose as an effective hydrolysis enhancer. *Carbohydrate Polymers*, *136*, 700–709.

Jabasingh, S. A., Nachiyar, C. V. (2011). Utilization of pretreated bagasse for the sustainable

bioproduction of cellulase by *Aspergillus nidulans* MTCC344 using response surface methodology. *Industrial Crops and Products*, *34*, 1564–1571.

Jabasingh, S. A., Nachiyar, C. V. (2012). Optimization of cellulase synthesis by RSM and evaluation of ethanol production from enzymatically hydrolyzed sugarcane bagasse using Saccharomyces cerevisiae. *Journal of Scientific and Industrial Research*, *71*, 353–359.

Jimenez, L., Rodriguez, A., Antonio, P., Moral, A., Serrano, L. (2008). Alternative raw materials and pulping process using clean technologies. *Industrial Crops and Products*, *28*, 11–16.

Johar, N., Ahmad, I., Dufresne, A. (2012). Extraction , preparation and characterization of cellulose fibres and nanocrystals from rice husk. *Industrial Crops and Products*, *37*(1), 93–99.

Johnston, J. W. (2012). Modern Papermaking Modern Papermaking. New York, *Taylor and Francis,* 1-18.

Jouanneau, S., Recoules, L., Durand, M. J., Boukabache, A., Picot, V., Primault, Y., Thouand, G. (2013). Methods for assessing biochemical oxygen demand (BOD): A review. *Water Research*, *49*, 62–82.

Kamali, M., Gameiro, T., Elisabete, M., Costa, V., Capela, I. (2016). Anaerobic digestion of pulp and paper mill wastes – An overview of the developments and improvement opportunities. *Chemical Engineering Journal*, *298*, 162–182.

Kamali, M., Khodaparast, Z. (2015). Review on recent developments on pulp and paper mill wastewater treatment. *Ecotoxicology and Environmental Safety*, *114*, 326–342.

Karp, S. G., Woiciechowski, A. L., Soccol, V. T., Soccol, R. (2013). Pretreatment Strategies for Delignification of Sugarcane Bagasse: A Review. *Brazilian Archivies of Biology and Technology*, *56*, 679–689.

Kaur, D., Kant, N., Kumar, R. (2017). Prospects of rice straw as a raw material for paper making. *Waste Management*, *60*, 127–139.

Kesalkar, V. P., Khedikar, I. P., Sudame, A. M. (2012). Physico-chemical characteristics of wastewater from Paper Industry. *International Journal of Engineering Research and Application*, *2*, 137–143.

Khakifirooz, A., Ravanbakhsh, F., Samariha, A., Kiaei, M. (2013). Investigating the Possibility of Chemi-mechanical Pulping of Bagasse. *BioResources*, *8*, 21–30.

Khristova, P., Kordsachia, O., Patt, R., Karar, I., Khider, T. (2006). Environmentally friendly pulping and bleaching of bagasse. *Industrial Crops and Products*, *23*, 131–139.

Kiaei, M., Tajik, M., Vaysi, R. (2014). Chemical and biometrical properties of plum wood and its application in pulp and paper production. *Maderas. Science and Technology*, *16*, 313–322.

Kim, D., Cheon, J., Kim, J., Hwang, D., Hong, I., Kwon, O. H., Cho, D. (2017). Extraction and characterization of lignin from black liquor and preparation of biomass-based activated carbon there-from. *Carbon Letters*, *22*, 81–88.

Kumar, A., Sharma, A. K., Jain, R. K., Singh, B. P. (2013). The Use of Banana (*Musa sapientum*) and Ankara (*Calotropis procera*) in the Handmade Paper Industries. *Lignocellulose*, *2*, 269–280.

Kumar, V., Kumari, M. (2014). Processing and characterization of natural cellulose fibers thermoset polymer composites. *Carbohydrate Polymers*, *109*, 102–117.

Lei, Y., Liu, S., Li, J., Sun, R. (2010). Effect of hot-water extraction on alkaline pulping of bagasse. *Biotechnology Advances*, *28*, 609–612.

Li, L., Lee, S., Lee, H., Youn, H. (2011). Hydrogen peroxide bleaching of hardwood Kraft pulp with adsorbed birch xylan and its effect on paper properties. *BioResources*, *6*, 721–736.

Li, M. F., Sun, S. N., Xu, F., Sun, R. C. (2012). Formic acid based organosolv pulping of bamboo (*Phyllostachys acuta*): Comparative characterization of the dissolved lignins with milled wood lignin. *Chemical Engineering Journal*, *179*, 80–89.

Lin, B., He, B., Liu, Y., Ma, L. (2014). Correlation Analysis for Fiber Characteristics and Strength Properties of Softwood Kraft Pulps from Different Stages of a Bleaching Fiber Line. *BioResources*, *9*, 5024–5033.

Liu, Z., Ni, Y., Fatehi, P., Saeed, A. (2011). Isolation and cationization of hemicelluloses from pre-hydrolysis liquor of kraft-based dissolving pulp production process. *Biomass and Bioenergy*, *35*, 1789–1796.

Loureiro, P. E. G., Evtuguin, D. V, Grac, M., Carvalho, V. S. (2011). The final bleaching of eucalypt kraft pulps with hydrogen peroxide : relationship with industrial ECF bleaching history and cellulose degradation. *J Chem Technol Biotechnol*, *86*, 381–390.

Lwako, K. O., Joseph, B., Baptist, K. J. (2013). A Review on Pulp Manufacture from Non Wood Plant Materials. *Chemical Engineering and Applications*, *4*, 144–148.

Mamaye, M., Kiflie, Z., Yimam, A., Anuradha, S. (2019). Valorization of Ethiopian Sugarcane Bagasse to Assess its Suitability for Pulp and Paper Production. *Sugar Tech 21,* 995-1002.

Mamaye, M., Kiflie, Z., Feleke, S., Yimam, A. (2020). Evaluation of Soda Delignification and Single-Stage Hydrogen Peroxide Bleaching for the Ethiopian Sugarcane Bagasse for Paper Production. *Sugar Tech*. https://doi.org/10.1007/s12355-019-00793-y

Mansouri, S., Khiari, R., Bendouissa, N., Saadallah, S., Mhenni, F., Mauret, E. (2012). Chemical composition and pulp characterization of Tunisian vine stems. *Industrial Crops and Products*, *36*, 22–27.

Maryana, R., Nakagawa-izumi, A., Kajiyama, M., Ohi, H. (2017). Environment-Friendly Non-

Sulfur Cooking and Totally ChlorineFree Bleaching for Preparation of Sugarcane Bagasse Cellulose. *Journal of Fiber Science and Technology*, *73*, 182–191.

Mekonnen, T., Diro, M., Sharma, M., Negi, T. (2014). Protocol optimization for in vitro mass propagation of two sugarcane (*Saccharum officinarum L.*) clones grown in Ethiopia. *African Journal of Biotechnology*, *13*, 1358–1368.

Mercy, O. B., Adeola, F. J., Olajide, O. A., Babatunde, A., James, F. (2017). Evaluation of fiber characteristics of Ricinodedron Heudelotii (*Baill , Pierre Ex Pax*) for pulp and paper making. *Internagtional Journal of Science and Technology*, *6*, 634–641.

Miranda, I., Gominho, J., Pereira, H. (2012). Incorporation of bark and tops in Eucalyptus globulus wood pulping. *BioResources*, *7*, 4350–4361.

Mohammad, S., Mousavi, M., Ziaeddin, S., Resalati, H., Mahdavi, S., Rasooly, E. (2013). Papermaking potential of rapeseed straw, a new agricultural-based fi ber source. *Journal of Cleaner Production*, *52*, 420–424.

Mohieldin, S. D. (2014). Pretreatment Approaches in Non-wood Plants for Pulp and Paper Production : A Review. *Forest Products and Industries*, *3*, 84–88.

Moldes, D., Cadena, E. M., Vidal, T. (2010). Biobleaching of eucalypt kraft pulp with a two laccase-mediator stages sequence. *Bioresource Technology*, *101*, 6924–6929.

Monte, M. C., Fuente, E., Blanco, A., Negro, C. (2009). Waste management from pulp and paper production in the European Union. *Waste Management*, *29*, 293–308.

Moshkelani, M., Marinova, M., Perrier, M., Paris, J. (2013). The forest biorefinery and its implementation in the pulp and paper industry : Energy overview. *Applied Thermal Engineering*, *50*, 1427–1436.

Mousavioun, P., Doherty, W. O. S. (2010). Chemical and Thermal Properties of Bagasse Soda

Lignin. *Industrial Crops and Products*, *31*, 52–58.

Mussatto, S. I., Rocha, G. J. M., Roberto, I. C. (2008). Hydrogen peroxide bleaching of cellulose pulps obtained from brewer's spent grain. *Cellulose*, *15*, 641–649.

Myers, R. H., Montgomery, D. C., Anderson-Cook, C. M. (2009). *Response surface methodology, process and product optimization using designed experiments*. John Wiley and Sons.

Nagar, S., Vasanta, R. K. J., Thakur, V. (2013). Biobleaching application of cellulase poor and alkali stable xylanase from Bacillus pumilus SV-85S. *Biotech*, *3*, 277–285.

Peng, F., Peng, P., Xu, F., Sun, R. (2012). Fractional purification and bioconversion of hemicelluloses. *Biotechnology Advances*, *30*, 879–903.

Pereira, B. L. C., Carneiro, A. de C. O., Carvalho, A. M. M. L., Colodette, J. L., Oliveira, A. C., Fontes, M. P. F. (2013). Influence of Chemical Composition of Eucalyptus Wood on Gravimetric Yield and Charcoal Properties. *BioResources*, *8*, 4574–4592.

Pereira, P. H. F., Jacobus, C., Cioffi, M. O. H., Mulinari, R., Luz, M. Da, Silva, M. L. (2011). Sugarcane bagasse pulping and bleaching: thermal and chemical characterization. *BioResources*, *6*, 2471–2482.

Pokhrel, D., Viraraghavan, T. (2004). Treatment of pulp and paper mill wastewater -a review. *Science of the Total Environment*, *333*, 37–58.

Poletto, M., Zattera, A. J., Santana, R. M. C. (2012). Structural Differences Between Wood Species : Evidence from Chemical Composition, FTIR Spectroscopy, and Thermogravimetric Analysis. *Journal of Applied Polymer Science*, *126*, 336–343.

Przybysz, K., Malachowska, E., Martyniak, D., Boruszewski, P., Howska, J., Kalinowska, H., Przybysz, P. (2018). Yield of Pulp, Dimensional Properties of Fibers, and Properties of Paper Produced from Fast Growing Trees and Grasses. *Bioresources*, *13*, 1372–1387.

Requejo, A., Rodríguez, A., Colodette, J. L., Gomide, J. L., Jiménez, L. (2012). TCF bleaching sequence in kraft pulping of olive tree pruning residues. Bioresource Technology, *117*, 117–123.

Rodrıguez, A., Moral, A., Serrano, L., Labidi, J., Jimenez, L. (2008). Rice straw pulp obtained by using various methods. *Bioresource Technology*, *99*, 2881–2886.

Sable, I, Grinfelds, U., Jansons, A., Vikele, L., Irbe, I., Verovkins, A. (2012). Comparison of the properties of wood and pulp fibers from lodgepole pine (*Pinus contorta*) and Scots pine (*Pinus sylvestris*). *BioResources*, *7*, 1771–1783.

Sahin, H. T., Arslan, M. B. (2008). A study on physical and chemical properties of cellulose paper immersed in various solvent mixtures. *International Journal of Molecular Sciences*, *9* (1), 78–88.

Samariha, A., Khakifirooz, A. (2011). Application of NSSC pulping to sugarcane bagasse. *Bioresources*, *6*, 3313–3323.

Santos, R. B., Capanema, E. A., Balakshin, M. Y., Chang, H., Jameel, H. (2011). Effect of hardwoods characteristics on Kraft pulping process: Emphasis on lignin structure. *BioResources*, *6*, 3623–3637.

Sathawong, S., Sridach, W., Techato, K. (2018). Isolation and preparing the lignin based hydrogel. *Journal of Environmental Chemical Engineering*, *6*, 5879–5888.

Seyyedalipour, S. F., Kebria, D. Y., Ranjbar, N., Norouznejad, G. (2014). Study of Utilization of Pulp and Paper Industry Wastes in Production of Concrete. *International Journal of Engineering Research and Applications*, *4*, 115–122.

Sharari, M., Latibari, A. J., Guillet, A., Aurousseau, M., Mouhamadou, B., Mirshokraei, A., Parsapaghouh, D. (2011). Application of the white rot fungus Phanerochaete chrysosporium

in biotreatment of bagasse effluent. *Biodegradation*, *22*, 421–430.

Sharma, N., Bhawana, Godiyal, R., Thapliyal, B., Anupam, K. (2020). Morphological and anatomical characterization of bleached soda , soda-AQ and kraft pulps from essential oil isolated citronella grass. *Materials Today: Proceedings*. https://doi.org/10.1016/j.matpr.2020.01.373

Sharma, N., Godiyal, R. ., Bhawana, Thapliyal, B. P., Anupam, K. (2018). Pulping and Bleaching of Hydro Distillation Waste of Citronella Grass (*Cymbopogon winterianus Jowitt*) for Papermaking. *Waste and Biomass Valorization*, *9*, 409–419.

Shatalov, A A, Pereira, H. (2005). Arundo donax L . reed : new perspectives for pulping and bleaching. *Bioresource Technology*, *96*, 865–872.

Shatalov, Anatoly A., & Pereira, H. (2014). Dissolving grade eco-clean cellulose pulps by integrated fractionation of cardoon (*Cynara cardunculus L.*) stalk biomass. *Chemical Engineering Research and Design*, *92* (11).

Shendye, A., Aksoy, B., Fleming, P. D., Joyce, M. (2016). Psychophysical tests for Visual-numerical correlation of whiteness formulas. *TAPPI JOURNAL*, *15*, 339–345.

Sridach, W. (2010a). Environmentally benign pulping process of non-wood fibers. *Suranaree Journal of Science and Technology*, *17*, 105–123.

Sridach, W. (2010b). Pulping and paper properties of palmyra palm fruit fibers. *Songklanakarin Journal of Science and Technology*, *32*, 201–205.

Song, X., Jiang, Y., Rong, X., Wei, W., Wang, S., Nie, S. (2016). Surface characterization and chemical analysis of bamboo substrates pretreated by alkali hydrogen peroxide. *Bioresource Technology*, *216*, 1098–1101.

Sugesty, S., Kardiansyah, T., Hardiani, H. (2015). Bamboo as Raw Materials for Dissolving Pulp

with Environmental Friendly Technology for Rayon Fiber. *Procedia Chemistry*, *17*, 194–199.

Tadesse, F., Dilnesaw, Z., Mekonnenet, Y., Negi, T., Fetwi, M., Ayele, N., Getanh, A. (2014). Performance Evaluation of Sugarcane Varieties (*Cuban origin*) at Wonji-Shoa , Metahara and Finchaa Sugarcane Plantations of Ethiopia. *Global Advanced Research Journal of Physical and Applied Sciences*, *3*, *1-11*.

Tembhekar, P. D., Padoley, K. V, Mudliar, S. L., Mudliar, S. N. (2015). Kinetics of wet air oxidation pretreatment and biodegradability enhancement of a complex industrial wastewater. *Journal of Enviromental Chemical Engineering*, *3*, 339–348.

Toczylowska, R. (2017). Limits and perspectives of pulp and paper industry wastewater treatment – A review. *Renewable and Sustainable Energy Reviews*, *78*, 764–772.

Tolera, B., Diro, M., Belew, D. (2014). Response of sugarcane (*Saccharum officinarum L.*) varieties to BAP and kinetin on in vitro shoot multiplication. *Advances in Crop Science and Technology*, *3*, 694–697.

Udohitinah, J. S., Oluwadare, A. O. (2011). Pulping properties of kraft pulp of nigerian-grown kenaf (*Hibiscus cannabinus L.*). *BioResources*, *6*, 751–761.

Vena, P. F., Garcia-Aparicio, M. P., Brienzo, M., Gorgens, J. F., Rypstra, T. (2013). Impact of hemicelluloses pre-extraction on pulp properties of sugarcane bagasse. *Cellulose Chemicstry and Technology*, *47*, 425–441.

Ververis, C., Georghiou, K., Christodoulakis, N., Santas, P., Santas, R. (2004). Fiber dimensions , lignin and cellulose content of various plant materials and their suitability for paper production. *Industrial Crops and Products*, *19*, 245–254.

Ververis, C., Georghiou, K., Danielidis, D., Hatzinikolaou, D. G., Santas, P., Santas, R., Corleti, V. (2007). Cellulose , hemicelluloses , lignin and ash content of some organic materials and

their suitability for use as paper pulp supplements. *Bioresource Technology*, *98*, 296–301.

Vila, C., Romero, J., Francisco, J. L., Garrote, G., Parajó, J. C. (2011). Extracting value from Eucalyptus wood before kraft pulping: Effects of hemicelluloses solubilization on pulp properties. *Bioresource Technology*, *102*, 5251–5254.

Wang, J., Chen, Y., Wang, Y., Yuan, S., Yu, H. (2011). Optimization of the coagulation-flocculation process for pulp mill wastewater treatment using a combination of uniform design and response surface methodology. *Water Research*, *45*(17), 5633–5640.

Watkins, D., Hosur, M., Tcherbi-narteh, A., Jeelani, S. (2014). Extraction and characterization of lignin from different biomass resources. *Journal of Materials Research and Technology*, *4*, 26–32.

Wei, H., Chen, X., Shekiro, J., Kuhn, E., Wang, W., Ji, Y., Tucker, M. P. (2018). Kinetic Modelling and Experimental Studies for the Dilute-Acid Pretreatment and Subsequent Enzymatic Hydrolysis. *Catalysts*, *39*, 1–18.

Wong, L., Hoi, S., Martincigh, B. S. (2013). Sugar cane plant fibres : Separation and characterisation. *Industrial Crops and Products*, *47*, 1–12.

Wutisatwongkul, J., Thavarungkul, N., Tiansuwan, J., Termsuksawad, P. (2016). Influence of Soda Pulping Variables on Properties of Pineapple (*Ananas comosus Merr.*) Leaf Pulp and Paper Studied by Face-Centered Composite Experimental Design. *Advances in Materials Science and Engineering*, *2016*, 1–11.

Xu, F., Yu, J., Tesso, T., Dowell, F., Wang, D. (2013). Qualitative and quantitative analysis of lignocellulosic biomass using infrared techniques : A mine-review. *Applied Engery*, *104*, 801–809.

Yirefu, F., Tana, T., Tafesse, A., Zekarias, Y. (2013). Weed Interference in the sugarcane

(*Saccharum officinarum L.*) plantations of Ethiopia. *Agriculture, Forestry and Fisheries*, *2*, 239–247.

Yuan, Z., Kapu, N. S., Beatson, R., Feng, X., Martinez, D. M. (2016). Effect of alkaline pre-extraction of hemicelluloses and silica on kraft pulping of bamboo (*Neosinocalamus affinis Keng*). *Industrial Crops and Products*, *91*, 66–75.

Zhao, X., Liu, D. (2012). Fractionating pretreatment of sugarcane bagasse by aqueous formic acid with direct recycle of spent liquor to increase cellulose digestibility – the Formiline process. *Bioresource Technology*, *117*, 25–32.

Zhu, W., Theliander, H. (2015). Precipitation of Lignin from Softwood Black Liquor: An Investigation of the Equilibrium and Molecular Properties of Lignin. *Bioresources*, *10*, 1696–1714.

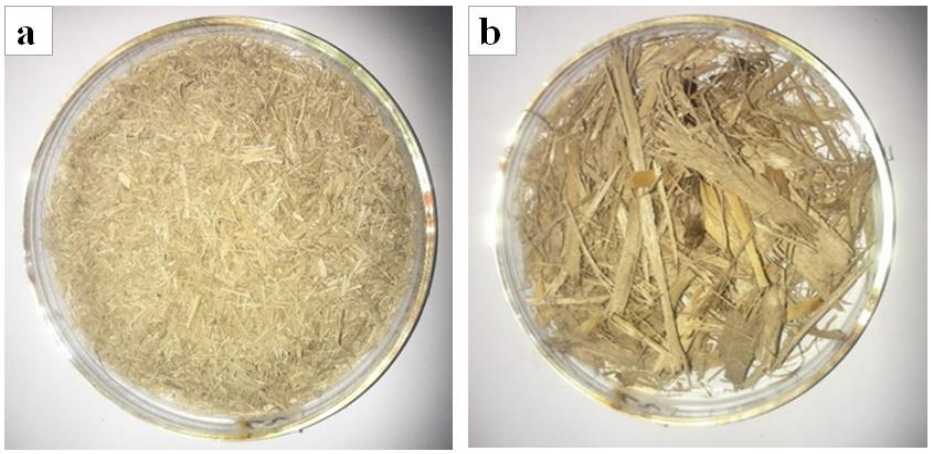
Zhu, W., Westman, G., Theliander, H. (2014). Characterization of Lignin Precipitation in the LignoBoost Process Investigation and Characterization of Lignin Precipitation in the LignoBoost Process. *Joutnal of Wood Chemisty and Thechnology*, *34*, 77–97.

APPENDICES

APPENDIX A: *List of publications in international journals*

1. **Medhanit M.,** Zebene K., Sisay F., Abubeker Y., Anuradha J. (2019). Valorization of Ethiopian Sugarcane Bagasse to Assess its Suitability for pulp and paper production, **Sugar Tech**, Volume 21, 995-1002. https://doi.org/10.1007/s12355-019-00724-x
2. **Medhanit M.**, Zebene K., Sisay F., and Abubeker Y. (2020). Evaluation of soda delignification and single stage hydrogen peroxide bleaching for the Ethiopian Sugarcane Bagasse for paper production, **Sugar Tech.** https://doi.org/10.1007/s12355-019-00793-y
3. **Medhanit M.,** Zebene K., Sisay F., Abubeker Y. (2019). Characterization of Soda and Kraft Black Liquor for Ethiopian Sugarcane Bagasse, **International Journals of Engineering and Industry**, Volume 2 (15-22).
4. **Medhanit M.**, Zebene K., Sisay F., Abubeker Y., (2020) Evaluation and optimization of the Kraft pulping and single stage hydrogen peroxide bleaching for Ethiopian Sugarcane Bagasse, **Journal of Natural Fibers.** https://doi.org/10.1080/15440478.2020.1764447

APPENDIX B: *Photographic image of sugarcane bagasse a) untreated and b) pretreated*



APPENDIX C: *Standard methods used for the determination of chemical composition of sugarcane bagasse*

a. Extractive content

6 g of oven dry milled sugarcane bagasse was weight and placed in a clean and dry soxhlet. Extractive solvent of 1:2 ratio of ethanol toluene was measured and add in the 500 ml round bottom flask. Connect the soxhlet, round bottom flask and condenser, switch on the heater and start water flow from the condenser. After 6 h extraction time remove the soxhlet with the extractive free sample and place it to oven to dry. Then weight the oven dry extractive free sugarcane bagasse sample. Finally, calculate the percentage extractive content as

$$Extractive\ (\%) = \frac{oven\ dry\ sample\ (Ws) - oven\ dry\ extractive\ free\ sample\ (Wf)}{oven\ dry\ sample(Ws)} * 100$$

b. Cellulose content

A gram of oven dry extractive free sugarcane bagasse was weight and placed in 250 ml flask, add 25 ml of 1:4 nitric acid to ethanol mixture. Boil four successive reflux and filter with filtering crucible and washed with distilled water. Dry by using an oven of 105±3 ^{o}C, weigh continue until the weight variation between two successive measurement was 0.005. Finally, the cellulose content was calculated as

$$Cellulose\ \% = \frac{residual\ mass\ of\ cellulose}{mass\ of sample} * 100$$

c. Lignin content

A gram of extractive free sugarcane bagasse weight and placed in 100 ml beaker, add 15 ml of 72% sulfuric acid and stirring and macerating the bagasse with a glass rod. Cover the beaker with

watch glass and keep it in a bath at 20±1 ^{o}C for 2 h. Transfer the solution from the beaker to flask and dilute to 3% concentration of sulfuric acid by adding 560 ml distilled water. Boil the solution for 4 h by connecting the reflex condenser. Then left the solution to overnight to settle and filter with filtering crucible, washed with hot distilled water to free of acid and dry the residue with crucible in an oven of 105±3 ^{o}C and weigh continue until the weight variation between two successive measurement is 0.005. Finally calculate the acid insoluble lignin as follow

$$lignin\ (\%) = \frac{weigth\ of\ lignin}{oven\ dry\ weigth\ of\ sample} * 100$$

d. Holocellulose content

Two and half gram's oven dried extractive free sample was weighted and placed in a flask, the solution of one-gram $NaClO_2$, 80 ml distilled water and 0.5ml glacial acetic acid was added and wall stirred for 1 h. Then the second solution of one-gram $NaClO_2$, 80 ml distilled water and 0.5 ml glacial acetic acid was added. After heating for 3 h in the water bath at 75 ^{o}C temperature the solution was transferred to filtering crucible and filtered, washed with 100 ml of 1% aqueous glacial acetic acid and then washed with 10 ml acetone. Filtering crucible containing the holocellulose was oven dried at 105±3 ^{o}C and placed in a desiccator to cool to room temperature. Weighed until the weight variation between two successive measurements was not greater than 0.005 (Hamzeh , et al. 2013). Finally, the holocellulose content was calculated as follow

$$Holocellulose, \% = \frac{oven\ dry\ weight\ of\ holocellulose}{oven\ dry\ \ extractive\ free\ weigth\ of\ intial\ sample} * 100$$

After getting the percentage holocellulose content, hemicellulose content was calculated by subtracting cellulose from holocellulose, because holocellulose contains both cellulose and hemicellulose.

$$Hemicellulose\ content, \% = holocellulose, \% - cellulose, \%$$

e. Ash content

The empty clean crucible was ignited in muffle furnace for 30 minutes at 525±25 ^{o}C after ignition, cool to room temperature by placing the crucible in a desiccator for 20 minutes, weigh the ignited crucible on the analytical balance. Then 2 g of moisture free bagasse was weighed and transferred to the crucible and placed in the muffle furnace at 525±25 ^{o}C for 1 h, after that place in a desiccator to cool to room temperature and weigh it. Finally, calculate the ash content as follows

$$Ash\ content\ \% = \frac{weight\ \ of\ ash}{weight\ of\ intial\ sample} * 100$$

f. Silica content

2 gram oven dry sugarcane bagasse place in the flask, add 100 ml of concentrated nitric acid and warm the bagasse becomes a thin paste, boil until a low viscosity solution and evaporate the solution to 40-50 ml, cool and add concentrated sulfuric acid. Heat the solution until white fumes of SO_3 were evolved. Clarify the solution by adding 15 ml of concentrated nitric acid without cooling the flask. Reheat the solution until white fume of SO_3 were again evolved, which does not darken on further heating. Then cool the solution and dilute by adding 250 ml of distilled water, boil it for few minutes and filter, washed with boiling distilled water of 125 ml. Place the filter paper containing the residue in crucible and ignited it in the muffle furnace at 525±25 ^{o}C until free from black carbon particles. Then transfer the crucible to desiccator for cooling and weight it. Finally, silica content was calculated as

$$X = \frac{a}{m} * 100$$

Where X= silicates and silica in parts per million (mg/kg) as SiO_2

a= weight of insoluble, mg

m =weight of oven dry sample, gm

g. 1% NaOH solubility

2 gram of oven dry sugarcane bagasse sample was placed in the flask and add 100 ml of 1% NaOH and stir with glass rod, place in the water bath for 60 minutes at temperature of 97 ^{o}C. Transfer to filter crucible and washed with 100 ml of hot distilled water. And 25 ml of 10% acetic acid and sake for 1 min, repeat the second 25 ml of 10% acetic acid. Then washed with hot distilled water until acid free. Finally, the percentage solubility was calculated as

$$S = \frac{A - B}{A} * 10$$

Where, A= Oven dry weight of sample before extraction, g

B= Oven dry weight of sample after extraction, g

h. Cold water solubility

2 gram of moisture free bagasse sample was placed in 500 ml beaker and add 300 ml of distilled water. Place in magnetic stirrer at room temperature for 48 h, transfer to the filtering crucible for filtration and washed with 200ml of cold distilled water, dry in an oven at 103±5 ^{o}C and place in a desiccator to cool, weigh continue until the weight variation between two successive measurement was 0.005. Cold water solubility was calculated as follows:

$$Cold\ water\ solubility, \% = \frac{initial\ weigth\ of\ sample - weigth\ after\ extraction}{initial\ weigth\ of\ sample} * 100$$

i. Hot water solubility

2 gram of oven dry sample was place in a 250 ml Erlenmeyer flask, add 100 ml of hot distilled water and place in a heat mantle. Attach the reflux condenser and digest for 3 h. The content of the flask was transfer to filter crucible and filter and washed with 200 ml hot distilled water and dry by an oven of 105±3 ºC, weigh continue until the weight variation between two successive measurement iwas 0.005. Finally, hot water solubility was calculated as

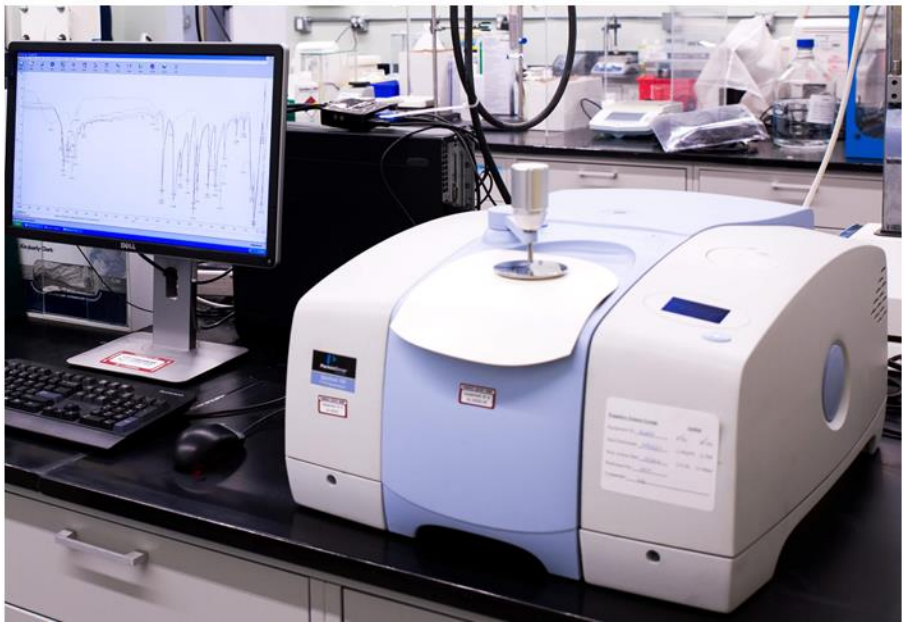
$$hot\ water\ solubility\ \% = \frac{intial\ weigth\ sample - weigth\ after\ extraction}{intial\ weigth\ of\ oven\ dry\ sample} * 100$$

APPENDIX D: *Photographic image of sugarcane bagasse morphological properties and chemical composition determination experimental setup.*

Motic Microscope

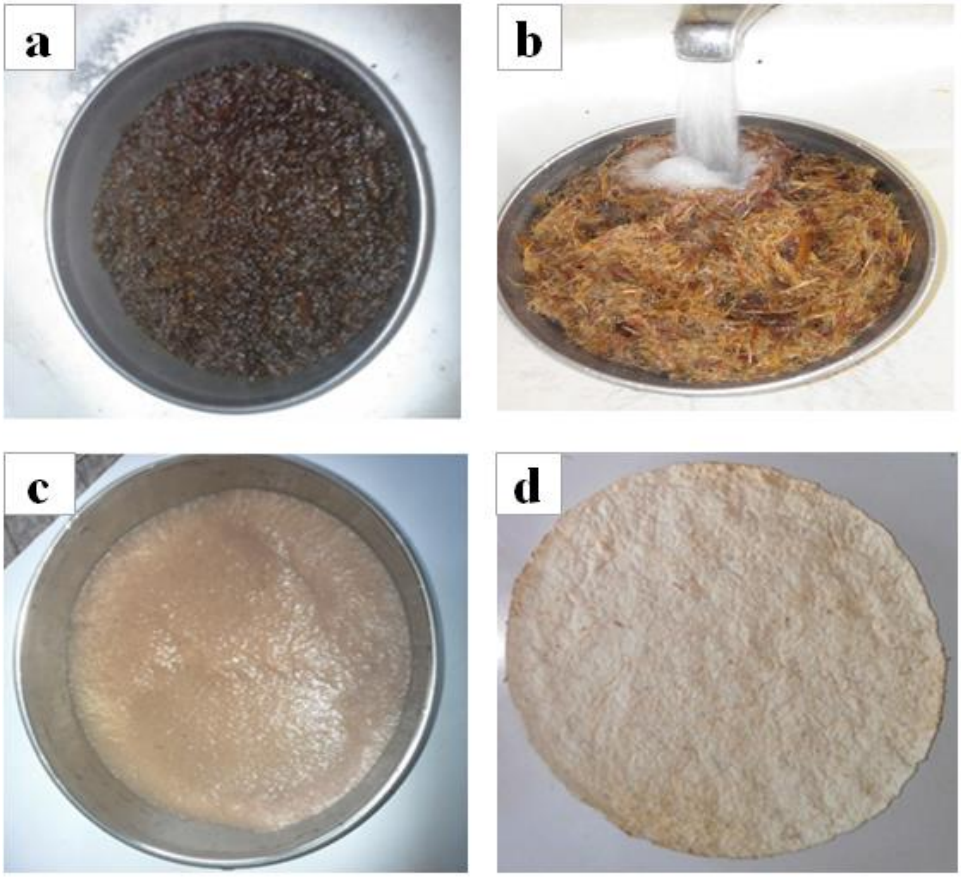
Extractive, cellulose, lignin, and hot water solubility contents

1% NaOH solubility and holocellulose contents



Fourier Transform Infrared Spectroscopy (FTIR)

APPENDIX E: *Photographic image of laboratory pulp production process a) pulp after cooking b) pulp washing c) pulp after washing d) dry pulp*



APPENDIX F: *Standard method used for Kappa number determination*

The kappa number is the volume in milliliter of 0.1 N potassium permanganate solution consumed by a gram of moisture free pulp. The results were corrected to 50% consumption of the permanganate added. It shows the degree of delignification of pulp and was proportional to the lignin content of pulp.

Ten grams of pulp (dry weight) was mixed and made into a pad by filtering on a Buchner funnel, avoiding any loss of fibers. The test specimen was disintegrated in 500 ml distilled water until free of fiber bundles. The disintegrated test specimen was transferred to a 2000 ml reaction beaker with properly rinsed by adding enough distilled water to bring the total volume to 795 ml. 100 ml potassium permanganate solution (0.1N) and 100 ml of the sulfuric acid solution (4N) was pipetted in a 250 ml beaker. The mixture was brought to 25°C quickly and was added immediately to the disintegrated test specimen, simultaneously started a stopwatch. The beaker was rinsed with 5 ml of distilled water and the total volume was made to 1000$\pm$5 mL.

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

$$K = \frac{pf}{W}$$

$$p = \frac{(b-a)N}{0.1}$$

Where,

K = kappa number

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

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

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

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

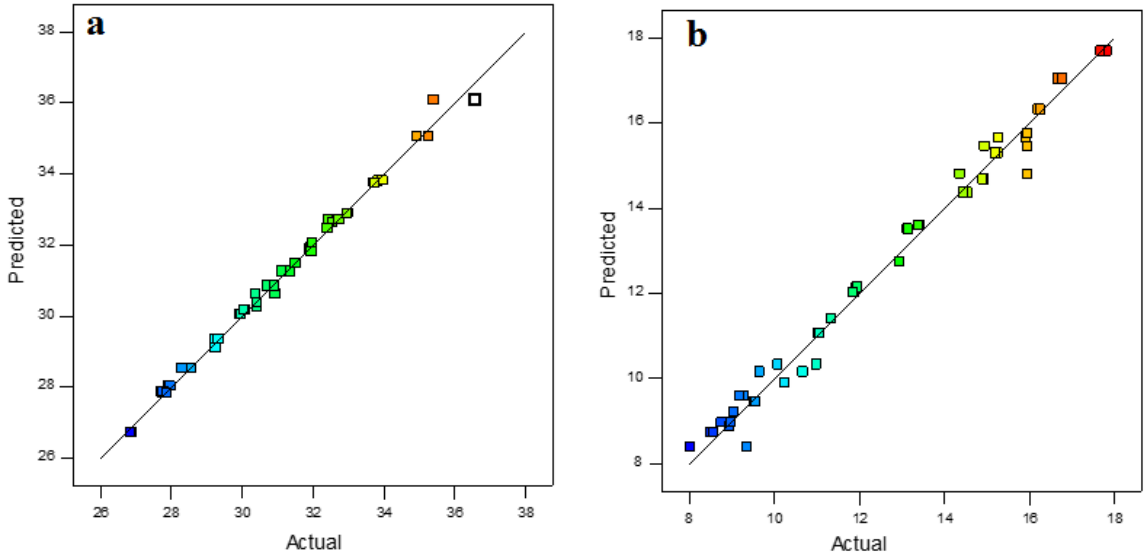
a = amount of the thiosulfate consumed by the test specimen, mL

N = normality of the thiosulfate solution.

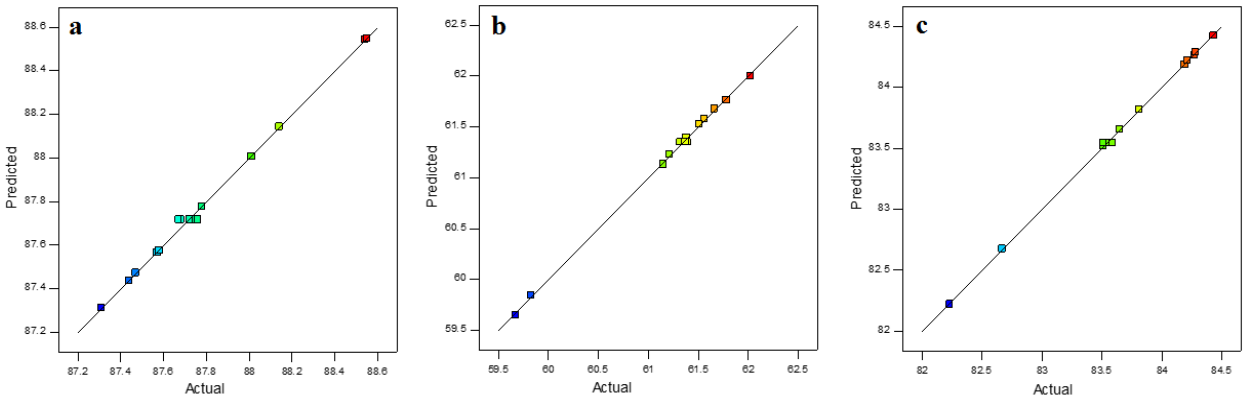
APPENDIX G: *Photographic image of kappa number determination*

APPENDIX H: *Photographic image of Color-Eye 3100 spectrophotometer used for brightness measurement of bleached pulp*

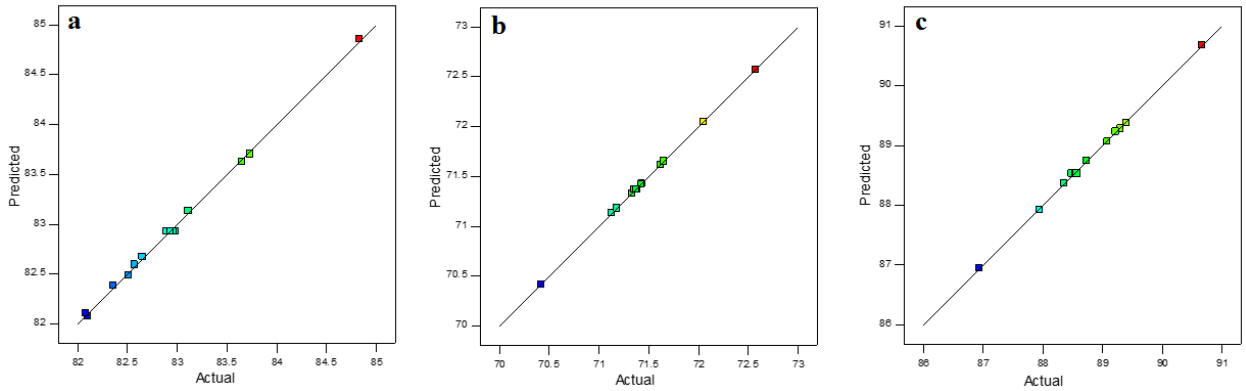
APPENDIX I: *Actual vs predicted graph of soda pulping a) pulp yield and b) kappa number*



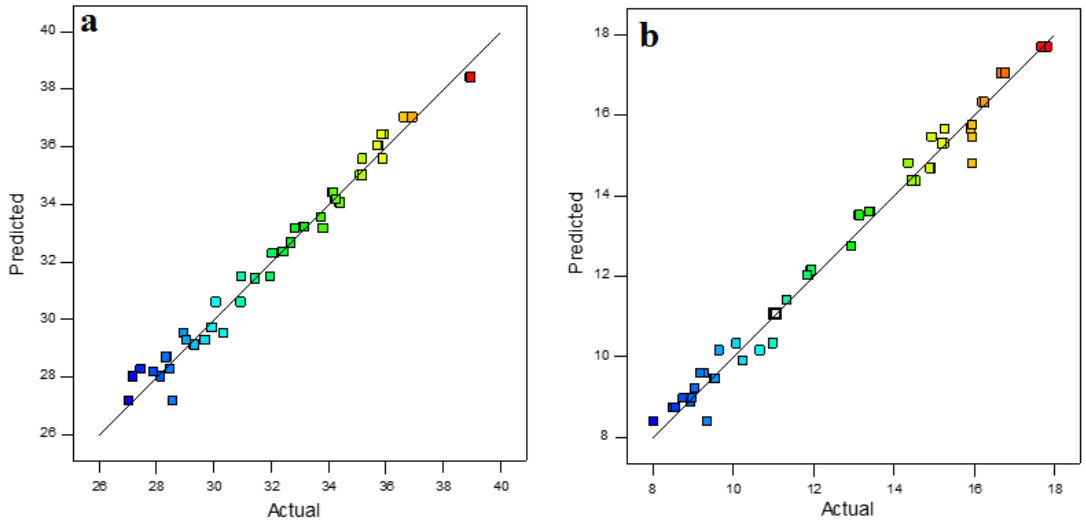
APPENDIX J: *Actual vs predicted graph of pulp-SA bleaching a) pulp yield, b) brightness and c) whiteness*



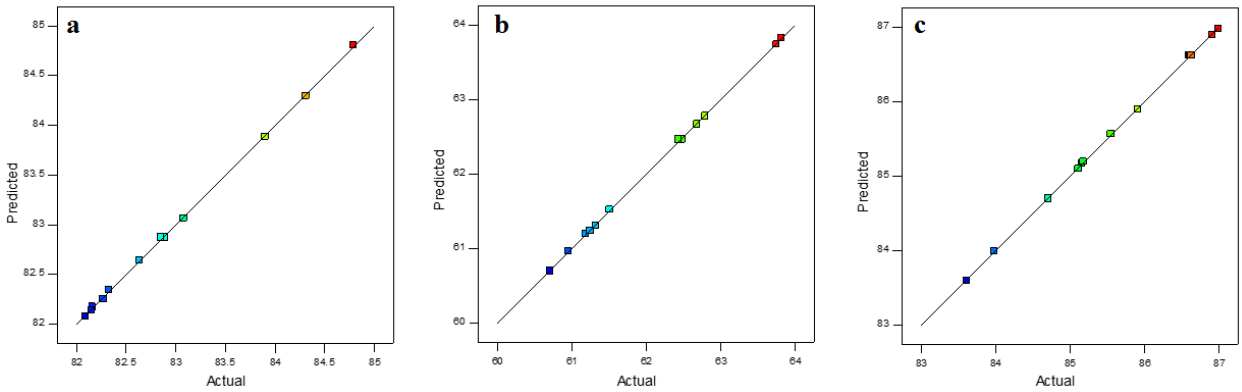
APPENDIX K: *Actual vs predicted graph of pulp-SB bleaching a) pulp yield, b) brightness and c) whiteness*



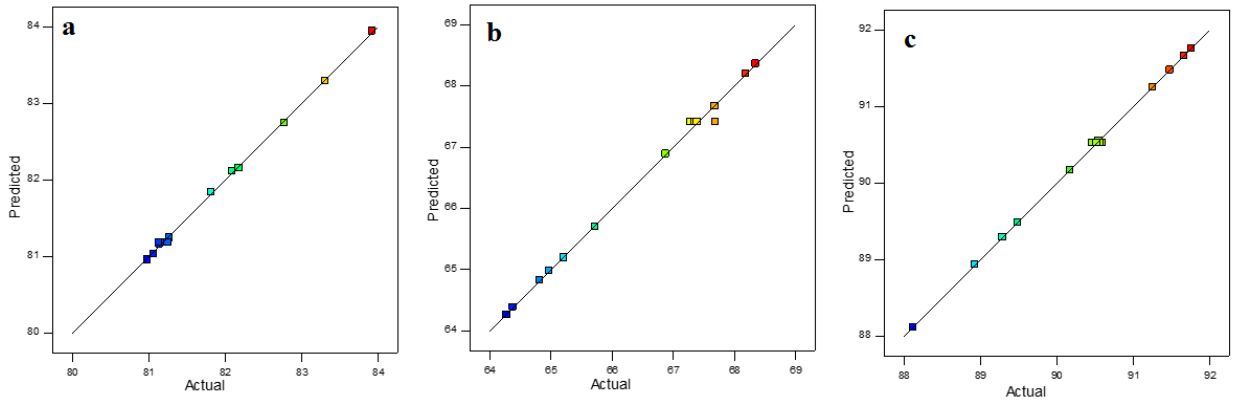
APPENDIX L: *Actual vs predicted graph of Kraft pulp a) pulp yield and b) kappa number*



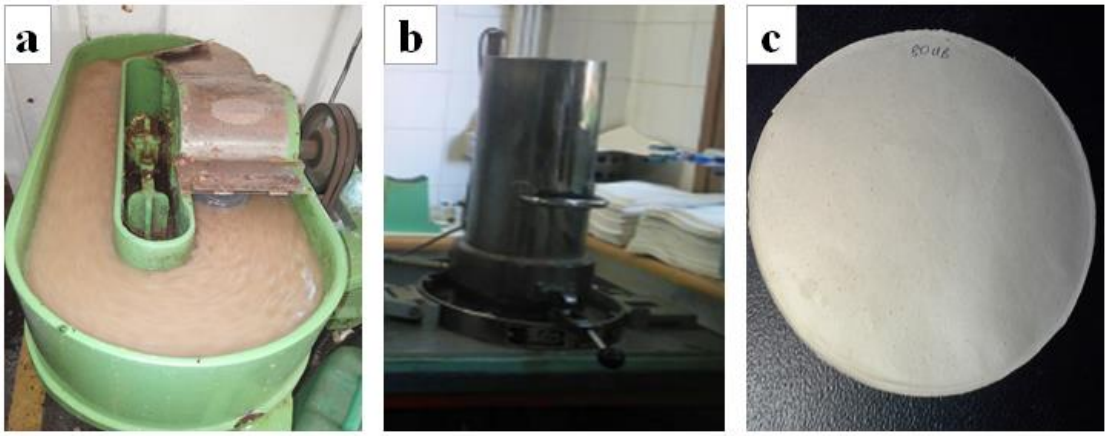
APPENDIX M: *Actual vs predicted graph of pulp-KA bleaching a) pulp yield, b) brightness and c) whiteness*



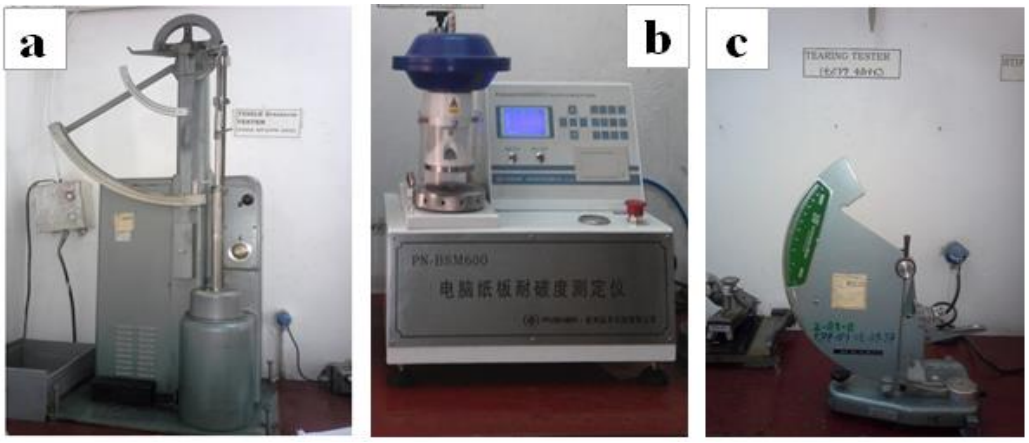
APPENDIX N: *Actual vs predicted graph of pulp-KB bleaching a) pulp yield, b) brightness and c) whiteness*



APPENDIX O: *Photographic image of papermaking a) pulp beating b) papermaking machine and c) paper*



APPENDIX P: *Photographic image of equipment's used for paper mechanical properties measurement a) Tensile strength tester b) Burst strength tester and c) Tear strength tester*



APPENDIX Q: *Formulas used for paper mechanical properties calculations*

$$\text{Grammage} = \text{Weight}\frac{\text{gm}}{\text{Area (m}^2\text{)}}$$

Tensile strength

$$X1 = \frac{a}{b}$$

Where, X1= tensile strength (KN/m)

a= maximum tensile force in (N), instrument reading in Kg to change into $N = Kg * 9.807$

b= Initial width of the sample, (mm)

Tensile index

$$X2 = 1000 * \frac{X1}{W}$$

Where, X2=Tensile index (NM/gm)

X1= Tensile strength (KN/m)

W= Mean Grammage (gm/m^2)

Burst strength

Instrument reading= Kg/cm^2

To change to Kg/cm^2 into kilo pascal $Kpa = \frac{Kg}{cm^2} * 98.0$

KPa= SI unit of bursting strength

$$bursting\ factor = \frac{bursting\ strength\ (Kg/cm^2)}{basis\ weigth\ (gm/m^2)} * 100$$

Burst index: bursting strength divided by basis weight

$$X = \frac{a}{W}$$

Where, X= burst index $KPam^2/Kg$

a= Burst strength in KPa

W= Basis weight gm/m^2

Tear strength

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

$$a = P * S$$

Where a = tearing strength in mN.

S= the average strength reading from the instrument

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

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

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

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

$$Tear\ factor = \frac{tear\ resistance\ (mN)}{basis\ weight\ (gm/m^2)}$$

$$Tear\ index = \frac{Tear\ factor}{10.2}$$

APPENDIX R: *Photographic image of a) black liquor and b) BOD determination experimental setup.*