Study of Pulp Characteristics after Cooking and Bleaching for Optimization of Process Parameters

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by

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CERTIFICATE

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innovate achieve lead

“I can do all things through GOD
who strengthens me”

This Thesis is dedicated to the memory of my Father

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ABSTRACT

Wood consists of 40-50 wt% cellulose, 25-30 wt% hemicellulose and 25-35 wt% lignin. Lignin is a complex chemical compound and the only aromatic polymer present in wood that is covalently linked to hemicellulose and cellulose. The cells in wood are joined together by middle lamella which is rich in lignin compared to cell walls. The cross-section of wood has two concentric regions called heartwood and sapwood and generally heartwood has high lignin content compared to sapwood. Heartwood is normally used for timber whereas sapwood is preferred as raw material in paper making, but entire wood log is being used in paper mills in recent years. A major focus of the kraft cooking is to obtain pulp having low lignin content. Elemental chlorine free bleaching is commonly used to increase brightness by removing residual lignin present in the cell walls. After bleaching, pulp fibers are refined to increase the flexibility and finally paper handsheets are made for mechanical testing. The properties (grammage, tensile strength etc) of paper are highly dependent on the properties (cellulose content, lignin content, water retention value-WRV) of pulp fibers. Hence, this research aims at the systematic study of pulp, papersheet and black liquor characteristics after cooking and bleaching to find the differences between heartwood and sapwood as well as depithed bagasse and whole bagasse.

In this work, effective removal of lignin from the selected species were performed by optimizing the kraft cooking process with respect to temperature, time and chip size. Eucalyptus citriodora (*Myrtaceae*), Subabul (*Leucaena leucocephala*) and Bagasse (*Saccharum officinarum*) were selected as raw materials. Characterization techniques such as Klason lignin, Cellulose content, WRV, Ash test, FTIR analysis, Thermogravimetric analysis (TGA), Microscopic analysis including SEM, Tensile test, Grammage and Fractography of sheets were used. The black liquor properties were analyzed using UV-Visible spectroscopy and fractional distillation.

To understand the influence of chip size during the cooking process, Eucalyptus citriodora that has ~ 60% heartwood was considered. Both heartwood and sapwood of different chip sizes (2000, 1000, 600, 425, 300, 150 µm) were subjected to kraft cooking. It was found that sapwood pulp has higher WRV and less residual lignin content compared to heartwood pulp. Also, as the sample size decreased from 2000 to 150 µm, a decrease of residual lignin content was observed. The influence of temperature (140ºC, 155ºC and 165ºC) during the kraft cooking process (3 hrs) was studied extensively by considering Subabul wood chips. The pulps cooked at 165ºC had loose pulp fibers with high cellulose content, high WRV, high inorganic content and low lignin

content compared to pulps obtained at 140°C and 155°C. Delignification process was modelled using MATLAB and a correlation between lignin content and cooking temperature was found. The tensile strength properties of unbleached sapwood sheets were 130 % higher than unbleached heartwood sheets due to higher amount of cellulose content.

The kraft pulping of whole and depithed bagasse was carried out at 165°C and 140°C with a cooking time of 1hr. The cellulose content, water absorption capacity, WRV were found to be higher and the klasons lignin was found to be lower for depithed bagasse pulp compared to whole bagasse pulp. TGA revealed better thermal stability for pulps processed at 140°C compared to 165°C because pulp fibers at 140°C are still intact due to lignin rich regions. The handsheets made from whole bagasse pulp (165°C) were much stiffer and stronger due to the presence of pith cells compared to depithed pulp (165°C) indicating its suitability as a packing material.

To understand the effect of cooking time, black liquor samples collected at different intervals of time were analyzed. The UV-Visible data of black liquor revealed significant lignin peaks (at wavelengths 195-200 nm) indicating the effectiveness of cooking temperature and time. Based on the absorbance, it can be concluded only 2 hrs of cooking time is required for effective lignin removal from heartwood where as total time of 3 hrs is required in case of sapwood, if cooking temperature is 165°C. From the bagasse black liquor analysis, it was confirmed that increase in temperature can reduce the cooking time. The fractional distillation of black liquor resulted in darker colored distillates at subsequent intervals of cooking time confirming higher extraction of chromophores.

The bleached pulps exhibited higher brightness, higher cellulose content, higher WRV with negligible residual lignin content compared to unbleached pulps. The tensile strength index of bleached sheets were 36% (depithed bagasse) and 176 % (sapwood) higher compared to unbleached handsheets due to better inter-fiber bonding (low lignin content). In this study, optimal process parameters such as chip size, cooking temperature and time, were identified for the kraft cooking process using heartwood and sapwood as well as whole bagasse and depithed bagasse separately. Based on pulp characteristics it is recommended to use sapwood (165°C, 3 hrs) and depithed bagasse (165°C, 1 hr) for making printing grade paper. Based on tensile strength index, it is recommended to use unbleached sapwood sheets (165°C, 3 hrs) and unbleached whole bagasse sheets (165°C, 1 hr) for packaging grade applications.

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LIST OF ABBREVIATIONS

SYMBOLS	**ABBREVIATIONS**
A	Absorbance at a particular wavelength (UV-Vis spectroscopy)
AQ	Anthraquinone
ASAQ	Sulfite-anthraquinone
B	Bleached
BB	Bleached bagasse
BD	Bulk delignification
BRW	Bleached rawwood
C	Concentration of soluble lignin in the filtrate
CED	Cupriethylene Diamine
CML	**Compound Middle lamella**
cP	Centipoise
CPPRI	Central Pulp and Paper Research Institute
CSF	Canadian standard freeness
D_0	First chlorine dioxide stage
D_1	Second chlorine dioxide stage
D_2	Third chlorine dioxide stage
DP	Degree of polymerization
DPB	**Depithed bagasse**
E. globulus	Eucalyptus globulus
ECF	Elemental Chlorine Free
Eop	First alkaline extraction stage reinforced with oxygen and hydrogen peroxide
Ep	First alkaline extraction stage reinforced with hydrogen peroxide

SYMBOLS	ABBREVIATIONS
EW	Earlywood
FTIR	Fourier Transform Infrared
G	Guaiacyl
HexA	Hexenuronic acid
HW	**Heartwood**
ID	Initial delignification
IPMA	Indian Paper Mills Association
ISO	International organization for standardization
ITC-PSPD	ITC Paperboards and Speciality Papers Division
KBr	Potassium bromide
LP	Lignin content in pulp
LW	Latewood
LW	Lignin content in wood
MC	Moisture content
MFA	Microfibril Angle
NTU	Nephelometric Turbidity Units
O	Oxygen stage
P	Primary cell wall
RD	Residual delignification
RH	Relative humidity
RW	Rawwood
S	Secondary cell wall
S	Syringyl
S1	Outer layer of the secondary cell wall
S2	Middle layer of the secondary cell wall

SYMBOLS	**ABBREVIATIONS**
S3	Inner layer of the secondary cell wall
SCB	Sugarcane bagasse
SEM	Scanning Electron Microscope
SW	**Sapwood**
TAPPI	Technical Association of the Pulp and Paper Industry
TCF	Total Chlorine Free
TGA	**Thermogravimetric analysis**
UB	Unbleached
UBRW	Unbleached rawwood
UV-Vis	**Ultraviolet-Visible**
VFA	Volatile Fatty Acids
WB	**Whole bagasse**
WRV	**Water Retention Value**
WRVP	Water Retention Value in pulp
WRVW	Water retention value in wood
WAC	Water absorption capacity
σ–ε	Stress-Strain (tensile testing)

CHAPTER 1: INTRODUCTION

1.1. Overview of pulp and paper

Paper is a nonwoven sheet in which approximately 0.25-4.5 mm length and 10 - 50 µm width pulp fibers are bonded together as a three-dimensional network. Paper is used in multiple applications including writing and printing. The consumption of paper and paperboard products are a yardstick of development of a society or a country and their use is absolutely indispensable in our daily life (Table 1.1). Pulp fibers are obtained from lignocellulosic materials such as softwoods, hardwoods, bagasse, bamboo, rice straw and wheat straw. Chemically these raw materials contain cellulose, hemicellulose and lignin. Physically this raw material consists of hollow cells or hollow pulp fibers joined together by middle lamella which is rich in lignin content. Each cell or pulp fiber resembles hollow pipe and consists of 2-5 µm thick cell wall 6-25 µm lumen (empty space in the middle). Unlike middle lamella, cell wall is rich in cellulose but it also contains lignin as continuous matrix. The challenge of the paper making is to remove lignin from middle lamella and separate pulp fibers as part of cooking and remove lignin from cell walls in multiple stages (due to nano-composite structure) as part of bleaching. In fact latter one is considered to be the biggest challenge faced by all paper industries. After bleaching, pulp fibers are slightly damaged because of lignin removal from cell walls and beating is carried out to induce further damage (kinks, compressions, etc.) to the individual pulp fibers, so that all pulp fibers become more flexible. Surprisingly lumen is almost collapsed (width becomes zero, cell walls join together) by the end of the process and this is the primary objective of bleaching and refining. Good paper can only be formed by pulp fibers which have collapsed lumen and poor in lignin content. So it is easy to make paper from bamboo because of its high cellulose content, but it is difficult to make paper from softwood because its cell wall contains lignin-cellulose nano-composite lamellas.

Table 1.1: Increase of net sales in Indian paper industry [Source: J K Paper Results – Dec 2016 -compiled by BS Research Bureau]

Name	Net sales (amount in crores)	
	Sep. 2015	Sep. 2016
TN Newsprint, (Tamil Nadu)	544.63	667.05
JK Paper, Rayagada (Orissa)	596.63	633.06
Ballarpur Industries, (Maharashtra)	985.62	419.63
Emami Paper, (West Bengal)	135.83	304.73
Seshasayee paper, Erode (Tamil Nadu)	228.42	264.01

Today, there are approximately 759 Pulp and Paper mills and the industry accounts for approximately 4% of the world's production of paper and ranks 15th largest paper industry in the world. The paper mills in India are distributed in the states of Andhra Pradesh, Telangana, Tamil Nadu, Maharashtra, Punjab, Madhya Pradesh and Gujarat. The paper mills use a variety of raw material based on their plant location (Andhra Pradesh mills uses Subabul wood, Karnataka mills uses seasonal bagasse, Punjab mills uses wheat straw) and recycled paper to make different grades of paper.

Most mills in the northern and western regions of India depend heavily on agricultural residues and waste paper as their raw material. Pulp and paper production in southern and eastern regions uses wood and bamboo as raw materials. The paper industry is classified into four segments, Printing and Writing (P and W), Packaging Paper and Board, Specialty Papers and Newsprint. Some of the most common classifications of printing papers are bond, coated, text, cover, book, offset, index, label, tag, newsprint, and writing. Paper may be defined in terms of its use and each grade serves a purpose, usually suggested by its grade name. The chart depicts the variation of the paper consumption across the segments in both global and Indian scenario (Fig 1.1). There are several challenges faced by the Indian paper industry such as high cost of energy and power, environmental concerns, technological obsolescence, raw material availability etc. Among these, the biggest challenge is the scarce availability of quality raw material. The wood supply to the industry is inadequate as it does not have access to the forest lands which are owned by the government due to which the supply of various wood species is met through social and agro farm forestry or plantation grown trees. The availability and supply of agro residues used as raw material by the paper industry is limited due to its use as an alternative fuel.

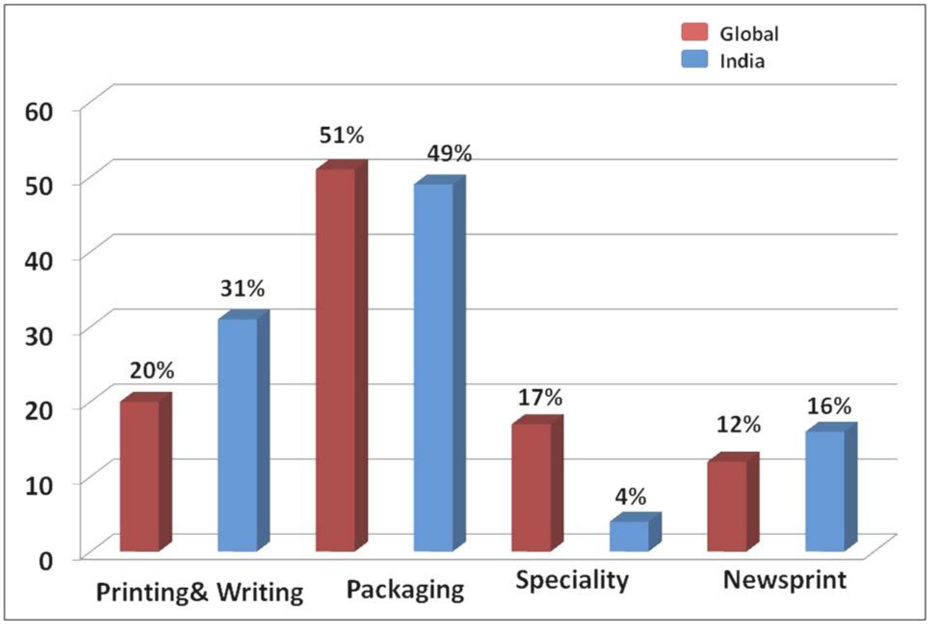


Fig 1.1: Segment wise consumption of paper in India and World. [Source: Industry, IPMA - Indian Paper Mills Association], 2018

The inadequate availability of indigenous waste paper for papermaking is limited and this is mainly attributed to the fact that although most of the consumed paper is collected, it is used for multiple purposes and not solely for paper production. For instance, note books and text books collected from the houses are used for wrapping and packing of various items sold by vendors of food products, envelop making, etc. In this regard ITC Paperboards and Speciality Papers Division (ITC-PSPD) has intensified its "recycling initiative" an activity involving domestic waste paper collection, which is aimed in meeting the requirement of the paper industry and also this waste paper collection would be helpful in reducing landfill requirements and also in protecting the environment.

Monoculture tree plantations are spreading throughout the tropical and sub-tropical regions, aimed at producing controlled and homogeneous structure of wood thus resulting in easy availability of wood, cost-effective process and higher yields. The industry is also trying to lower the plantation cycles from 54 to 42 months *(BS Research Bureau 2016)* to overcome the raw material availability. To counter the issue of wood deficit, Indian paper companies also started other initiatives like agro forestry which saw a rapid spread in few parts of India like Andhra Pradesh. According to industry experts, agricultural residue is more sustainable for paper manufacturing as compared to wood fiber because of loose structure of cell walls. The agricultural residue takes less time to process than wood for the same cooking parameters and same pulp characteristics indicating that paper produced from agro-biomass requires less water, fewer chemicals and energy. Bagasse is a sugarcane residue and it is considered to be the best alternative of wood for papermaking paper because of its low cost, loose network of cells and high amount of cellulose fibers. For a variety of reasons including brightness of the pulp, seasonal availability, problems with chemical recovery, non-wood fiber sources account for a small fraction of raw materials used in paper industry in India (*Indian Paper Industry report 2018)*. Still it is believed that agro-based paper manufacturing is highly environmental-friendly and extremely cost-competitive than wood pulp. Presently the pulp and paper industry is using woody and non woody plants to meet the fiber demand for making paper i.e. wood contributes towards 30-35%, agro residues 20-22% and recycled fibers 45-50% respectively (*Indian Paper Industry report 2018).*

During paper making, the pulp fibers are initially separated from wood chips by chemical or mechanical means, and then these fibers are brought into contact in the subsequent bleaching, beating, pressing and drying stages. In these stages, bonds between individual fibers is formed that gives the web network structure to the sheet which imparts not only mechanical strength but also contributes to the increase of different properties such as opacity and smoothness. In most cases, paper contains additives. Functional additives are dyes (metal complex pigments), sizing agents (rosin and alum), strength aids are polymers such as polyamines and fillers-(kaolin) or control additives such as aluminum sulfate, polyamines and polyethylene amine, retention aids such as silicic acid, starch which improves physical and chemical properties of the final paper. All these factors are of immense importance while considering the final use of the paper. Hence study of wood anatomy, fiber morphology, fiber testing and the processes such as kraft cooking, bleaching, beating and sheet making involved in paper production are utmost important to make a quality paper.

1.2. The chemical composition of wood

Wood consists of 40-50% cellulose, 25-30% hemicellulose and 25-35% lignin (approximate compositions and it differs between wood species). Paper is a thin material produced by pressing wet cellulose pulp derived from wood or non-wood materials and drying them to reduce the moisture content below 5-6%. It should be noticed that wood is stiff material, but paper is a flexible sheet and this is due to the fiber separation (cooking) and lumen collapsibility (bleaching and refining). The cellulose fibers are part of the cell wall of wood or non-wood biomass. Wood cell wall is a natural composite material in which cellulose is considered as reinforcement and lignin is considered as a matrix. Hemicellulose and extractives also present in the cell wall. The most abundant and major component of the wood cell wall is ***cellulose*** (appr.50%). It is a straight chain polymer with a chemical formula $(C_6H_{10}O_5)_n$, where n is the number of repeating sugar units or degree of polymerization (DP). It is a glucan polymer consisting of D-glucose linked by ß-1, 4-glycosidic bonds.

The presence of ß-D-linkages induces the chains to remain in extended forms. As a consequence, cellulose molecules fit snugly together over long segments, thus giving rise to powerful associative forces that eventually results in great strength of native cellulose materials and in products made from cellulose. Most paper making pulp fibers have a degree of polymerization values of 600-1500. Cellulose is a polysaccharide that gives strength for paper as its microfibrils are smaller in diameter (*5-30 nm wide*) and oriented in fiber direction (*slight deviation exist which is measured as microfibril angle-MFA*). Cellulose with degree of polymerization values (weight average) reaching up to 3500 *(native cellulose in-situ*) and requires a temperature of 320^{o}C and pressure of 25MPa to become amorphous in water (*Smook 1992*). It is hydrophilic due to OH groups and is considered as a thermoplastic polymer due to linear or branched structure. Cellulose is very important to paper properties because the attraction between cellulose molecules in different fiber surfaces is the principal source of fiber-to-fiber bonding in paper.

Hemicellulose, the second major component in wood fibers, generally has a branched structure (molecular chains of glucose and other monosaccharides) and is a non-crystalline polymer with shorter chain lengths. Hemicelluloses are important in papermaking because they promote the development of fiber-to fiber bonding through their influence on the ability of the fibers to take up water during processing. In contrast to cellulose which is crystalline, strong and resistant to hydrolysis, hemicellulose can be easily hydrolyzed by weak base or an acid due to which it has a random amorphous structure with little strength. It is associated with cellulose and lignin in cell wall lamella's as shown in Fig. 1.5b. Hemicellulose composition changes between the cell walls of stem, roots, and branches and is highly reactive than cellulose due to which the solubility and susceptibility towards hydrolysis is more. Retention of hemicellulose during the pulping process is important as it improves the pulp yield and contributes to the bonding strength of the fibers. ***Lignin***, a complex chemical compound and the only aromatic polymer present in wood is covalently linked to hemicelluloses and cellulose (Fig 1.2). It confers the mechanical strength to the wood cell wall. It is a thermoset polymer having three dimensional network structures but it is a non-crystalline and acts as a binding agent to hold the cellulose fibers together (*Bailey and Ollis 1986*). It consists of C_6-C_3 phenylpropanoid units arranged in irregular 3-D network which makes lignin highly resistant to degradation.

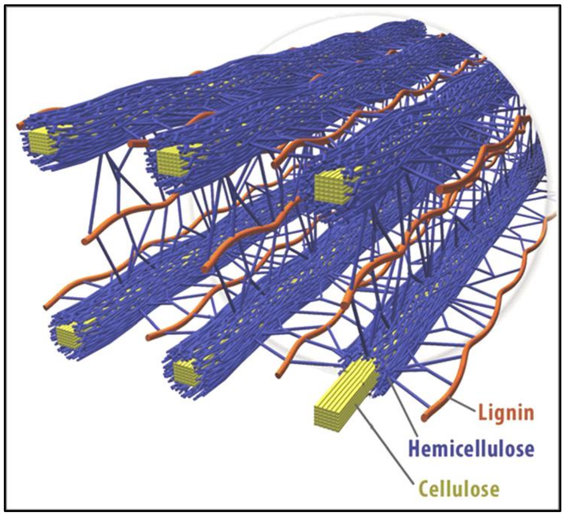


Fig 1.2: Spatial arrangement of cellulose, hemicellulose and lignin in the cell walls of wood *(Brandt et al. 2013)*

The low molecular weight substances in wood are classified as *organic and inorganic matter*. The organic matter is commonly referred as extractives and inorganic part is summarily obtained as ash. The ***extractives*** (extraneous components) comprising of aromatic compounds, terpenes, aliphatic acids and alcohols *(Meerts 2002; Fengel and Wegener 1989)* which interfere with the pulping process by causing foaming and corrosion. The ***ash content*** of the fibrous raw materials indicates the presence of inorganics (K, Ca, Mg and Si) in the range of ~ 0.5 to 1.0% in woods. Higher inorganic content is observed in non-woody fibrous raw materials due to the presence of silica.

The aim of paper manufacturing processes or viscose rayon production processes are to obtain the pulp having negligible lignin content but with high quality cellulose. For high quality paper or rayon grade pulp, lignin should be removed completely from middle lamella and cell walls, as it prevents the formation of fiber to fiber bonds in paper and thus reduces paper strength, also results in brightness decreases and causes yellowing of the paper due to its reaction with UV light *(Paulsson et al. 2012).*

1.3. The ultrastructure of wood cell

Wood consists of cells and these cells are bonded together by middle lamella which is rich in lignin. In the domain of wood and pulp, cells are called fibers and each cell consists of cell wall and lumen (Fig 1.3). Ultrastructure of the cell wall is the topic of study for several decades because it has a nano-composite structure. The concentric arrangement of the cell wall layers resulting high density, differences in the chemical composition and different orientations within each layer contributes in ultrastructural variations of the cell wall. Lumen is considered to be void and exists as a central canal in the fiber as shown in Fig. 1.6. Lumen diameter is around 10-20 µm and cell wall thickness varies between 2-10 µm. Cell wall is composed of two layers i.e relatively thin “primary wall” (P) and the thick “secondary wall” (S) as shown in Fig. 1.4.

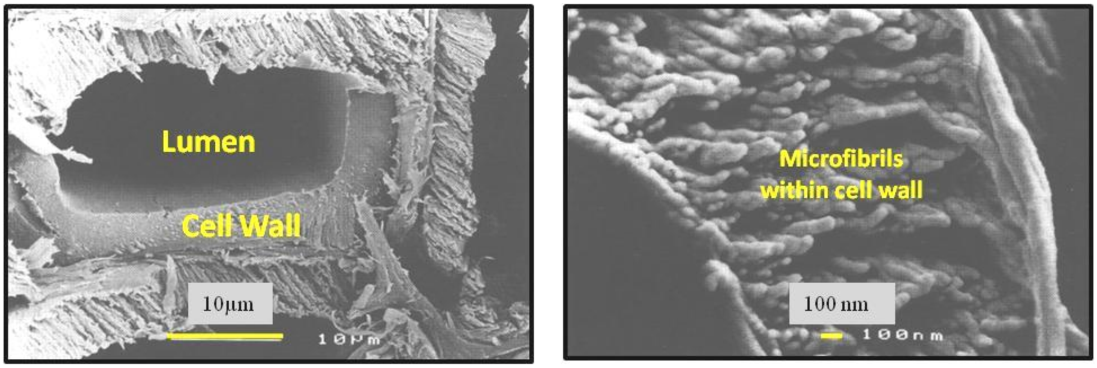


Fig 1.3: SEM image of wood cross-section *(Zimmermann et al. 1994)*

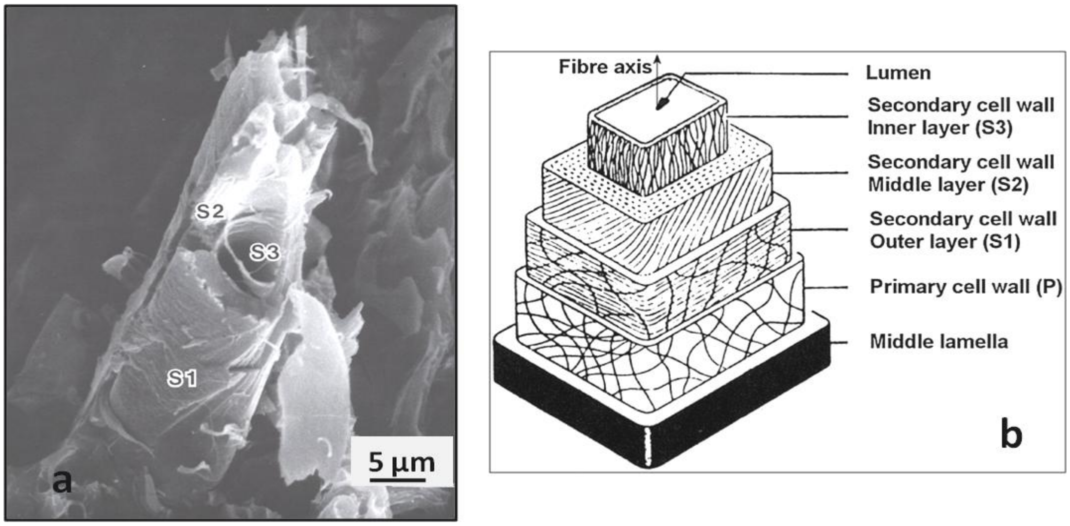


Fig 1.4: (a). Different layers in single cell wall *[Zimmermann et al. 1994];* (b). Microfibril arrangement within primary and secondary cell wall layers *[Karkkainen 2003]*

In the primary wall P (relatively impermeable with thickness of about 0.05µm) the cellulose fibrils are arranged in random structure as thin crossing layers and the amount of cellulose is very limited. Based on differences in the microfibrillar orientation, the secondary layer is divided into three sub layers S1, S2 and S3 that are termed as follows: the outer layer of the secondary wall (S1, 0.1-0.2 µm thickness) consisting microfibrils arranged in helical slope, the middle layer of the secondary wall (S2, main body of the fiber with 2-10 µm thickness) having fibrils run at a steep angle, and the inner layer of the secondary wall (S3, inner layer with 0.1 µm thickness) or tertiary wall (T) in which the fibrils are arranged under a gentle slope *(Fengel and Wegener 1989)* as shown in Fig 1.4. The S2 wall, thickest among all cell wall layers, consists of 50% crystalline cellulose microfibrils wound in a spiral fashion around the stem axis and embedded in a matrix of hemicellulose and lignin *(Adusumalli et al. 2010)*. Changes in the angle and differences in the packing of the fibrils result in lamellar structure of the S2. Lignin is an integral part of the secondary cell walls especially S2 layer that acts as a matrix and binds the cellulose fibrils and also it protects the wood from outside environment. The S3 layer has a higher concentration of non-structural substances, which gives the luminal surface a more or less as smooth appearance. Due to the steep running microfibrils, S2 layer provides tensile resistance to the cell wall, whereas S1 with its gentle fibrillar slope is responsible for compression resistance, both along the cell axes. The system of orienting microfibrils in combination with non-structural solidifying substances gives wood a sturdy construction which resists a wide range of forces acting on it. Wood cell is also considered as a complex anisotropic material due to the orientation of microfibrils. The composition of the cell wall is given in Table 1.2

Table 1.2: Distribution of chemical components in wood fiber cell wall *(Karlsson 2006)*

Wall Layer	**Lignin (%)**	**Cellulose (%)**	**Hemicellulose (%)**
Middle Lamella	90	0	10
Primary Wall (P)	70	10	20
Secondary Wall (S1)	40	35	25
Secondary Wall (S2)	15	55	30
Secondary Wall (S3)	10	55	35

The spiral angle of the cellulose fibrils is known as Micro Fibril Angle (MFA) and it is considered to be the most influential factor in wood and pulp fiber mechanical properties *(Courchene et al. 2006)*. Two main factors, cellulose microfibril angle (MFA) in S2 layer (thickest layer) and chemical composition govern the important functional and mechanical properties of the cell wall such as young's modulus, stiffness or flexibility *(Farber et al. 2001).*

Generally in the temperate regions, wood cells grow fast early in the growing season (spring), producing springwood or ***earlywood***. Later in the season, as winter approaches, growth slows down producing summerwood or ***latewood***. Earlywood is generally characterized by fibers with large cross-sectional area and thin cell walls with wide lumen (for water conduction). While the latewood fibers have a smaller cross-sectional area and thicker cell walls (for mechanical strength) with narrower lumen *(Bailey and Ollis 1986; Gullichsen J 2000)*. The earlywood fibers have a tendency to collapse in the pulping process especially in beating. The earlywood is the lighter part of the annular ring, while the latewood is the darker part. Latewood fibers in particular have to be beaten to induce strength and flexibility to the papersheet *(Karlsson 2006).* The cross-section of wood has two concentric regions called ***heartwood (HW) and sapwood (SW)*** (Fig 1.5). Initially the wood cells produced by the cambium become sapwood (consisting of fibers and vessels). With increase in age, the death of parenchyma cells and other controlled processes gradually transform the sapwood into heartwood. The sapwood is the outer region which constitutes the live parenchyma cells filled with starch grains and does the storage and conduction of water and mineral salts through vessels having large lumen.

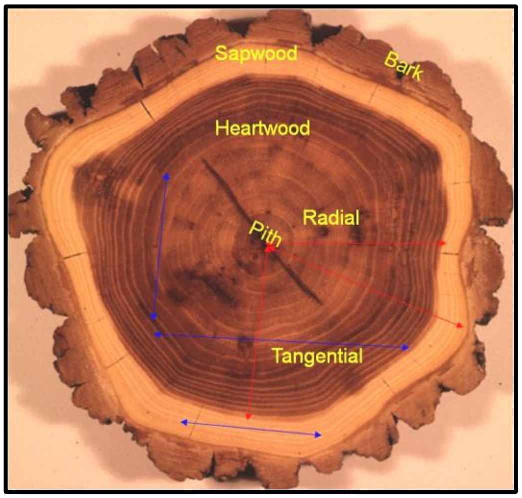


Fig 1.5: Cross-section of wood showing pith, heartwood, sapwood and bark.
[Note the heartwood and sapwood colour distinction]

In structural timber applications, sapwood is inferior to heartwood due to its pale colour and susceptibility to fungi/insects, but pulp mills require the wood species having only sapwood *(Bamber 1976).* Heartwood being the central part of the stem provides the structural support to the tree and consists of polyphenolics (tannins) is appears mostly darker in colour due to deposition of resinous organic compounds in the cell walls and cavities *(Fengel and Wegener 1989; Gominho and Pereira 2000; Gominho et al. 2001; Santiago et al. 2008; Rupert et al. 2008)*. Such depositions make liquor penetration very difficult during cooking; hence pulping process becomes difficult with heartwood *(Smook 1992)*. The acetyl content is higher in sapwood compared to heartwood, but heartwood has more lignin than sapwood. In pulp and paper manufacturing, the presence of heartwood in the wood logs causes problems such as pitch (tacky deposits or spots in the product caused mainly by extractives) formation, extractive deposition on equipment and pulp, higher chemical consumption and reduced pulp brightness *(Del Rıo et al. 1998)*.

1.4. Raw materials for paper making

1.4.1. Plantation grown wood species

Wood is classified into ***softwoods*** (coniferous trees such as pine, spruce etc) and ***hardwoods*** (deciduous trees such as eucalyptus, subabul etc). Both softwood and hardwood are used as a fiber source for paper and board (*Karlsson 2006)*. In India hardwoods with short rotation cycles (average fibre length of 0.2-4mm, cell wall thickness of 3-4 mm) are mostly used as a fibre source for paper and board manufacture. Hardwoods consist of libriform fibres, fibre tracheids (tubular structure; Fig 1.6) and conducting vessels (vessel and ray cells).

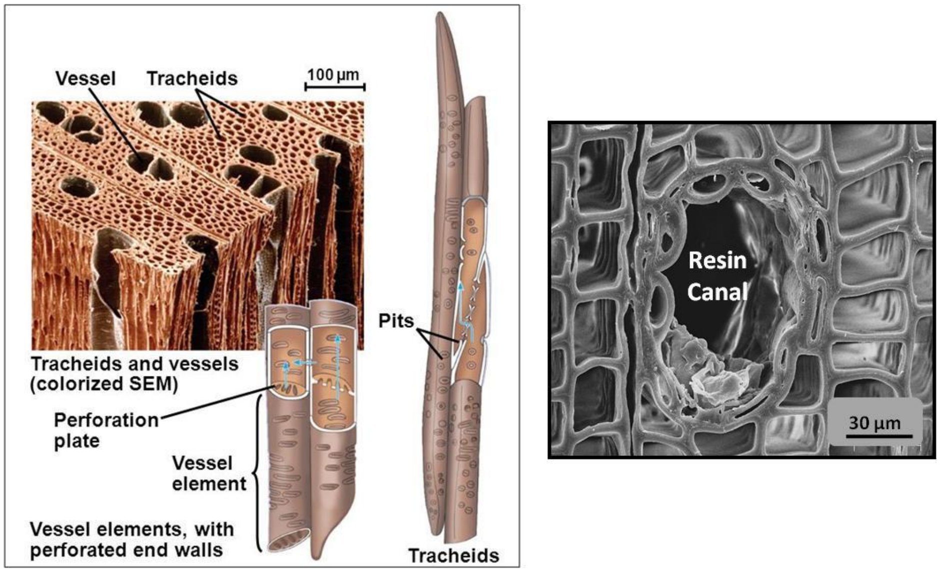


Fig 1.6: Cross-section of hardwood block revealing different cells *[Fengel and Wegener 1989]*

The vessels (200-400 µm in length and width upto 500 µm) are thin walled and have open or perforated ends for the conduction of fluids. Hardwood also has parenchyma cells which are short compact cells with stubby ends. Whereas, softwoods are composed 90% tracheid fibers, 10% ray cells and other fines *(fengel and Wegener 1989).* The fibers cells i.e. tracheids provide the combine functions of conduction and support and ray cells accomplish horizontal transport of liquids across the annular rings. Fibers from softwood are long (3-4 mm) and strong but have characteristic sausage shape with large number of fairly large, bordered pits *(Bamber 1976).* The biggest difference between the species is hardwood contains more cellulose, hemicelluloses and less lignin than softwood (Table 1.3).

Table 1.3: Chemical composition of Softwoods and Hardwoods ***(Smook 1992)***

Composition	**Softwoods (%)**	**Hardwoods (%)**
Cellulose (Skeletal polysaccharides)	42±2	45±2
Hemicelluloses (Matrix Polysaccharides)	27±2	30±5
Lignin (3 dimensional phenolic polymer network)	28±3	20±4
Extractives	3±2	5±3

The strongest papers are manufactured from chemical pulp made of softwood because of longer fiber lengths but hardwood fibers give paper a smooth printing surface and high opacity. High yield, less lignin content are necessary to attain a compromise between cost and quality. Because of less lignin content, it is easier to bleach hardwood pulp to high brightness. These numerous qualities make the hardwood fibers suitable for use in printing paper in India. Today, pulp from virgin fibers is produced mostly from wood fibers (more than 90%). In view of this, selection of wood based on fiber geometry (Table 1.4), its availability and cultivation in Indian conditions is of utmost importance. Due to the above reasons, Indian pulp and paper industries are mainly focusing on wood species having less lignin content and have faster growth rate.

Table 1.4: Geometry of fibers used in Indian pulp and paper industries ***(Karlsson 2006)***

Species	Fiber length (mm)	Fiber diameter (µm)	Fiber cell wall thickness (µm)
Eucalyptus	0.9-1.0	14-16	4-4.5
Pine	2.5-3.6	25-39	2.9-4.0
Subabul	0.25-4.6	9-49	2.2-5.4
Casuarina	0.2-4.0	7-45	3.2-5.84
Bamboo	2.8	15	6.2-7.4
Acacia	0.9-1	14	3.6-6.5
Bagasse	1.7	20	5.64

The wood fiber species widely used for paper making in India are ***Eucalyptus and Subabul*** and they are the first and second largest fast growing trees (raised in plantations). Greater opacity, absorbency and dimensional stability were observed in pulps made from these species. Chemically both Eucalyptus and Subabul wood species have, closer % of : (a). acid insoluble lignin (Eucalyptus 27.9; Subabul 24.3), (b). % of holocellulose (Eucalytus 70.3; Subabul 75.2) and (c). % of ash content (Eucalyptus 0.66; Subabul 0.65) as per the report published by CPPRI, India *(Subramanyam et al. 2004).*

The main differences between Eucalyptus and Subabul species are in terms of physical appearance (Fig 1.7), fiber properties as listed below (Table 1.5):

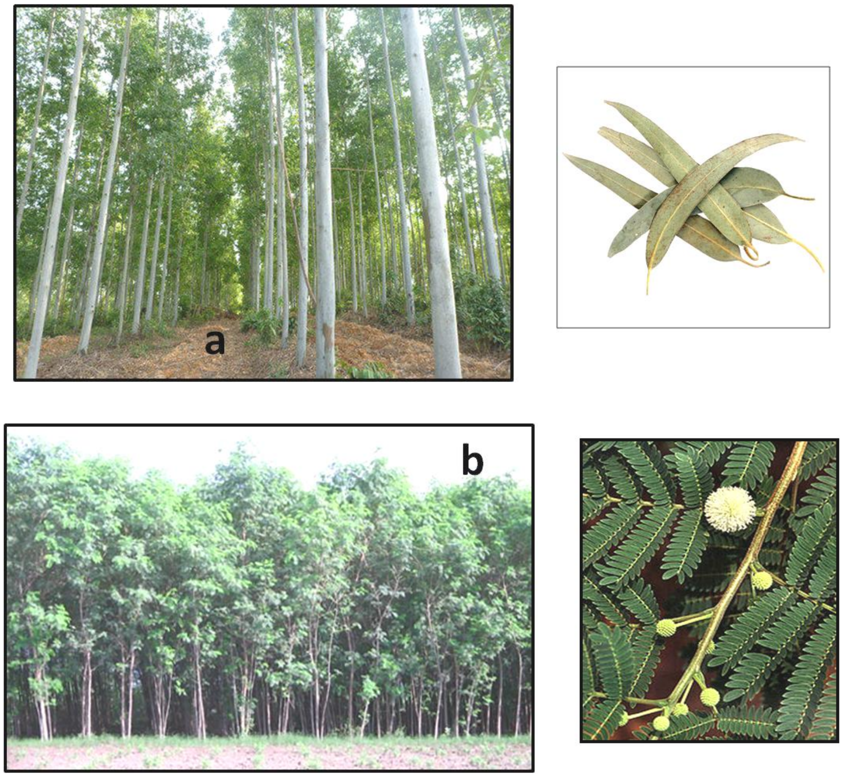


Fig 1.7: (a). Eucalyptus plantation at Uttar Pradesh, India; (b). Subabul plantation at Tamilnadu, India.

Table 1.5: Morphological characteristics of Eucalyptus and Subabul wood species ***(Subramanyam et al. 2004, CPPRI)***

Species	**Eucalyptus**	**Subabul**
Properties of fiber		
Fiber length	0.65 mm	1.02 mm
Mean fiber width	14.2 µm	20.1 µm
Lumen diameter	3.40 µm	9.18 µm
Cell wall thickness	5.4 µm	5.46 µm
Kinks per mm	0.98	0.76
Properties of non-fibrous tissue		
Length and Width of vessel	360 and 140 µm	297 and 31 µm
Length and Width of parenchyma	69 and 23 µm	122.4 and 25.5 µm

1.4.2 Agro based non-wood species (Bagasse)

The use of non-wood fibers for papermaking has been widespread in countries lacking an adequate supply of wood resources. There is a wide variety of non-wood plant fibers such as bagasse, rice straws, bamboo etc that can be used for paper making. The cellulose content of non-wood species (holocellulose: 77.8%) are comparable to wood species, but their lignin content (20.8%) is much lower and it is loosely packed within the cell walls than wood. Holocellulose is the term used to describe cellulose and hemicellulose content together. Due to this, the delignification of non-woods is relatively easy and consumes less chemicals. But the disadvantage of non-wood fibers is that they are high in volume, low in density and high in silica content (0.5-7%) etc in comparison with wood (silica<0.1%). In India, **Sugarcane bagasse** ***(Saccharum officinarum)*** is found to be the promising alternative for wood for papermaking because of its low cost, longer fiber, low refining energy consumption, good sheet formation and paper smoothness *(Pekka et al. 2002).* These features enable *S.officinarum* to meet the quality requirements for newsprint and fine paper manufacture, yet there are certain drawbacks like high storage cost and quality variation (pith), low brightness, low pulp yield and slow drainage which need special treatment (depithing etc.) *(Rajesh and Rao 1998).* Depithing can be conducted using moist/wet or dry conditions.

Bagasse contains 60-70% fiber and 30% pith. In both the processes, bagasse is mechanically abraded to break the clusters of pith away from the fibrous portion of the bagasse. Bagasse enters from the sugar factory and is feed into the depithers through a series of chutes. In depithers, a hammer mill is mounted on a vertical shaft. The rotor can be hanging with only an upper support or with upper and lower supports. The rotating assembly is mounted with straight hammers and operates at high speed (typically 1000–1800 rpm). The bagasse is fed into the top of the unit, and is hit by the hammers opening up clumps of bagasse. The pith is thrown through a screen while the longer bast material (i.e., the fiber bundles) falls down the center of the unit to a conveyor. The pith and bast fiber are conveyed away separately. The pith is separated from the bast fiber and conveyed away on communal conveyor belts. Pith consists of short length parenchyma cells which are rich in cellulose content.

Some of the important fiber properties of bagasse are given below.

Table 1.6: Morphological characteristics of Bagasse ***(Agnihotri et al. 2010)***

Fiber length	1.52 mm
Mean fiber width	21.8 µm
Lumen diameter	6.29 µm
Cell wall thickness	7.76 µm
Kinks per mm	1.06
Length and Width of vessel	151.6 and 27.8 µm
Length and Width of parenchyma	327.7 and 53.8 µm

Due to the rising global demand for fibrous material, worldwide shortage of trees in many areas, and increasing environmental awareness, non-woods fibers have become one of the important alternative sources of fibrous material for the 21st century. Therefore it is necessary to consider these alternatives 'fiber sources' to meet the possible shortfall of wood for papermaking (Table 1.7).

Table 1.7: Comparison of non-wood and wood resources for pulp and paper-making *(adopted from Rousu et al., 2002 and Kissinger et al., 2007)*

Description	Fiber Resources	
	Wood	Non-wood
Cycle growth	Long growth cycles [X]	Short cycle growth [✓]
Cellulose content	Higher cellulose content [✓]	Lower cellulose content depends on the types of non-wood [X]
Lignin content	Contain higher lignin content [X]	Contain lower lignin content [✓]
Chemical uses	Uses large volume of chemicals during pulping process [X]	Uses small amount of chemicals during pulping process [✓]
Pulping time	Need long time for pulping [X]	Shorten time for pulping process [✓]
Cost operation	Expensive due to the limited resources [X]	Cheaper because of the abundance and easily renewable resources [✓]
Environmental impact	Increase environmental problem such as global warming & soil erosion [X]	Reduces environmental impact which reduce the deforestration problem and improve sustainable forestry [✓]

Note: [✓] = advantages and [X] = disadvantages

1.5. Making pulp from wood

In pulping process wood is converted to fibers (Fig 1.8). In simple terms, the binding material lignin is removed from middle lamella and cells or fibers are separated. Manufacturing of pulp from wood starts with cutting wood logs *(Smook 1992; Biermann 1996)*, debarking (when wood is used as raw material), chipping, and other processes such as depithing (if bagasse is used as the raw material). During the pulping process, the chemical structure of cellulose is also changes. The degree of polymerization values (weight average) of cellulose decreases from 3500 to 600–1500 when wood is transformed into Pulp (*Smook 1992*). The pulp is manufactured from the wood or nonwood materials using *Chemical, Mechanical and Chemical Thermal mechanical pulping (CTMP) methods.*

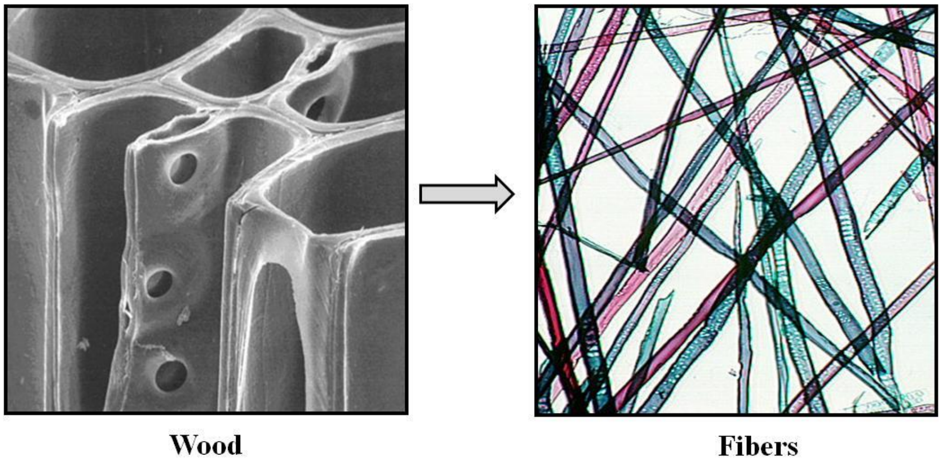


Fig 1.8: Micrograph of wood and pulp fibers

1.5.1 Chemical pulping or kraft cooking

In chemical pulping the objective is to degrade and dissolve away the lignin with minimal damage to cellulose and hemicelluloses (Fig 1.9 a and b).

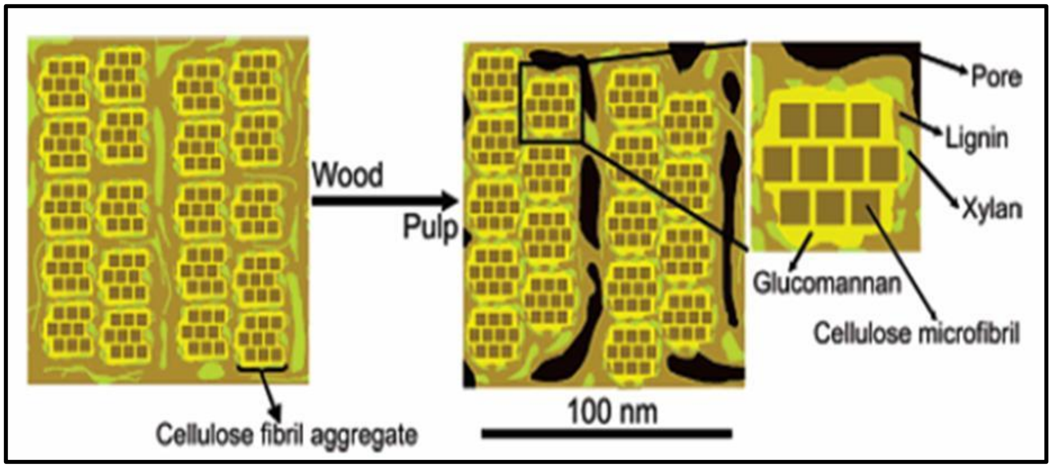
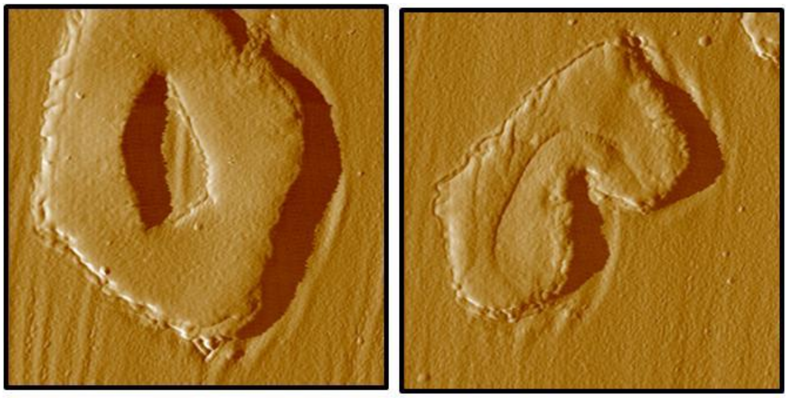


Fig 1.9 a: Schematic illustration showing the part of the S2 wall layer of spruce wood (left) and the corresponding layer in chemical pulp (right).
[Fahlen and Salmen 2005]

[Note: Magnification of a cellulose fibril aggregate with cellulose fibrils (dark brown) in close contact with hemicellulose glucomannan (yellow) and surrounded by a matrix consisting of lignin (brown) and hemicellulose xylan (green) and some of the glucomannan (yellow). In the pulp, pores (black) are also present within the matrix material]



WOOD Pulp

Fig 1.9 b: Singe fiber cross-section before (wood) and after (pulp) cooking. AFM picture was taken after smoothening the surface using diamond knife and cell wall thickness is around 5 µm. *[Note the collapse of lumen and cell wall damage due to cooking] (Adusumalli et al. 2010)*

The main procedures are the (alkaline) kraft process, (acidic) sulphite process and Soda process etc. Most of the world's chemical pulp is produced by ***kraft process***. The main reason for its dominance is its versatility in dealing with different raw materials coupled with superior pulp quality and the mature recovery of cooking chemicals *(Gullichsen 2000)*. Kraft process can even tolerate species with bark. Kraft process utilizes NaOH and Na_2S as active chemicals. The aqueous solution of these chemicals in required proportions is called white liquor. The delignification proceeds through the cleavage of β-aryl ether linkages that degrade and dissolves the lignin, thereby liberating the fibers *(Smook 1992; Britt 1970)*. The NaOH reacts with lignin and resins present in wood neutralizing organic acids. The general equation for reactions in Kraft process is shown in equation 1.

$$NaOH + Na_2S + \text{Wood} \rightarrow Na\text{-org.} + \text{S-org.} + NaHS \text{...........(1)}$$

To minimize the damage of cellulose by NaOH, instead of using high concentrations of NaOH, Na_2S is introduced which gives NaOH by reacting with water in white liquor slowly as shown in equations 2 and 3.

$$Na_2S + H_2O \leftrightarrow 2Na^+ + S^{2-} + H_2O \text{.............(2)}$$

$$S^{2-} + H_2O \leftrightarrow HS^- + OH^- \text{.................(3)}$$

The Na_2S produces sodium (Na^+), sulphide (S^{2-}), bisulphide (HS^-) ions in water. These Na^+ combine with OH^- ions to form NaOH. These ions react with lignin molecules and lead to ether scission i.e. breakage at ether bonds. These broken molecules or fragments dissolve in white liquor and ultimately leads to systematic degradation of lignin *(Smook 1992)*. The kraft delignification process is divided into three distinct phases i.e. the initial, bulk and residual delignification phases. The initial phase or impregnation stage takes place as the temperature rises to 140^oC and is controlled by diffusion which is affected only by the total cross-sectional area of accessible pores *(Sjostrom 1981)*. In this phase the selectivity is low and only 20% of total lignin (mainly from middle lamella; low molecular weight lignin) is removed. The bulk phase begins as the cooking temperature exceeds 140^oC. The increasing temperature accelerates the reactivity and leads to depolymerisation of lignin. The rate of lignin dissolution remains high and about 85-90% of the total lignin (from secondary cell wall layers; lignin fractions of higher molecular weight) is removed. The slow residual delignification phase is related to the removal of condensed lignin units and is affected by the alkali charge and the cooking temperature. The kraft pulping have an adverse effect on carbohydrates, causing a direct dissolution of the low-molecular polysaccharide fractions by the alkaline reaction solution under elevated temperatures (above 170^oC) and a substantial degradation and modification of the residual polysaccharides *(Shatalov et al. 2005)*. It is suggested that the poor selectivity in the residual delignification phase may be attributed to: (i) the low reactivity of the residual lignin towards the pulping chemicals results in more resistance to delignification; (ii) the residual lignin being chemically linked to carbohydrates is resistant to delignification *(Hamidi 2006)*. In a typical kraft cooking process, more than 90% of total lignin is removed with approximately 20-30% of carbohydrates loss. The final yield is normally within 45-65% depending on the extent of the cooking *(Nguyen et al. 2006)*.

1.6. Bleaching of chemical pulps

Brightness is the intrinsic luminous reflectance factor measured around 475nm. Unbleached pulps exhibit a wide range of brightness values (Table 1.8). The objective of bleaching of pulp is to increase its brightness by removal or modification of colored components in pulp (Fig 1.10). Cellulose and hemicelluloses are inherently white and do not contribute to the pulp colour. The chromophoric groups of lignin are principally responsible for colour. The oxidative mechanisms convert part of the phenolic groups (lignin) to quinine - like substances that are known to absorb light. Chemical pulps prior to bleaching contain almost 6% of residual lignin. The term residual lignin is used because it is mainly present in cell walls and it is difficult to remove during cooking.

Table 1.8: Approximate brightness ranges of unbleached pulps
(Smook 2002)

Type of Pulp	Brightness range
Kraft	15-30
Neutral sulphite semi chemical (NSSC), ammonium bisulphite	40-50
Groundwood, Sulphite, Bisulphite	50-60

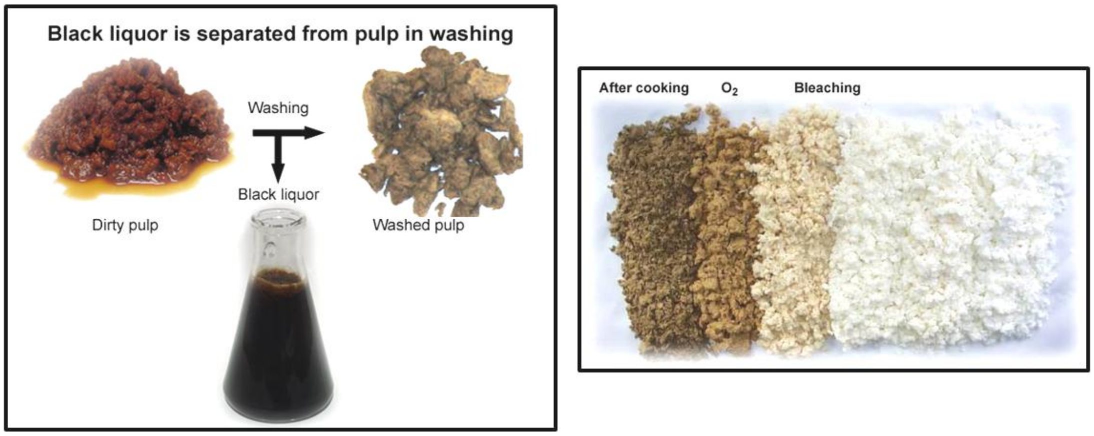


Fig 1.10: Pulp bleaching process
[The dark colour of the pulp is mainly due to residual lignin. This is removed gradually during bleaching]

The primary goal of bleaching is to remove the residual lignin (decrease in intrinsic viscosity) without degrading carbohydrates (cellulose) and also to increase the brightness of the pulp. The residual lignin generally contains less β-O-4 linkages, condensed carbon-carbon and lignin-carbohydrate linkages (*Britt K. W 1970)*. Removal of residual lignin during bleaching is regarded as a continuation of pulping process but it is done in a gentler, less destructive way, hence it is carried out in different stages. Bleaching process is carried at low temperature i.e. 50-80^{o}C, since high temperatures can increase the reaction rate and at above 80^{o}C, the strength of the fiber gets affected i.e. decrease of kappa number (indication of the lignin content or bleachability of pulp) and increase of pulp brightness. High temperatures in presence of chemical cause new lignin phenolic hydroxyl groups which gives rise to new chromophores. Two approaches are generally used for chemical bleaching of pulps. One approach utilizes selective chemicals that destroy some of the chromophoric group but do not attack lignin. The other approach is total removal of lignin. The first approach provides around 70% of the brightness and retain high pulp yield, while second approach provide 90% brightness but reduces pulp yield *(Smook 1992)*.

Due to global trends and environmental pressure for cleaner bleaching processes, **ECF** (Elemental chlorine free) and **TCF** (Total chlorine free) are being used more often to reduce the production of chlorinated organic compounds during pulp manufacturing *(Nie et al. 2016).* The distinguishing factor between the two processes is the use of chlorine dioxide, which is used in ECF but not in TCF. To compensate for the lack of chlorine dioxide, TCF will either add higher dosages of peroxide, or supplement the process with ozone. TCF's problems with lower brightness potential, weaker fiber strength, lower yield and higher energy requirements have eroded its promise as a successor to ECF. The ECF pulps constituted 93% of the world share of bleached chemical pulp market. Modern bleaching is achieved through a continuous sequence of process stages utilizing different chemicals and conditions in each stage. The commonly applied chemical treatments are: Chlorination (C), Alkaline extraction (E), Chlorine Dioxide (D), Oxygen (O), Hypochlorite (H), Peroxide (P), and Ozone (Z). Bleaching of chemical pulps is achieved either with an oxidizing agent or a reducing agent. In bleaching the main reaction mechanism is oxidation. The Bleaching agents C, P, O, and Z are important and commonly used oxidants which causes depolymerisation and create new hydrophilic groups.

Oxygen delignification is a process applied between cooking and bleaching sequences, where part of the residual lignin left in pulp after cooking is removed using oxygen and alkali *(Rapson 1979)*. The targeted reactions are the oxidation of lignin and breaking it down parts which dissolve in alkali, as well as destroying the coloured groups in lignin and removal of impurities, such as resin. Oxygen in its normal state is a weak oxidizing agent and is ineffective in delignification. Its oxidizing power can be promoted by raising the temperature and by alkaline conditions (Fig 1.11). The most essential factor in oxygen delignification is to bring oxygen gas into contact with the fibers under alkaline conditions. This means that the pulp suspension should have enough alkaline (OH ions) to neutralize and dissolve the organic acids, which are generated in oxygen-lignin reactions. 50% delignification, severe cellulose depolymerization takes place, causing deterioration of pulp viscosity and strength characteristics. This lack of selectivity is the main drawback of oxygen delignification, but the advantage is lower chemical requirements and higher brightness.

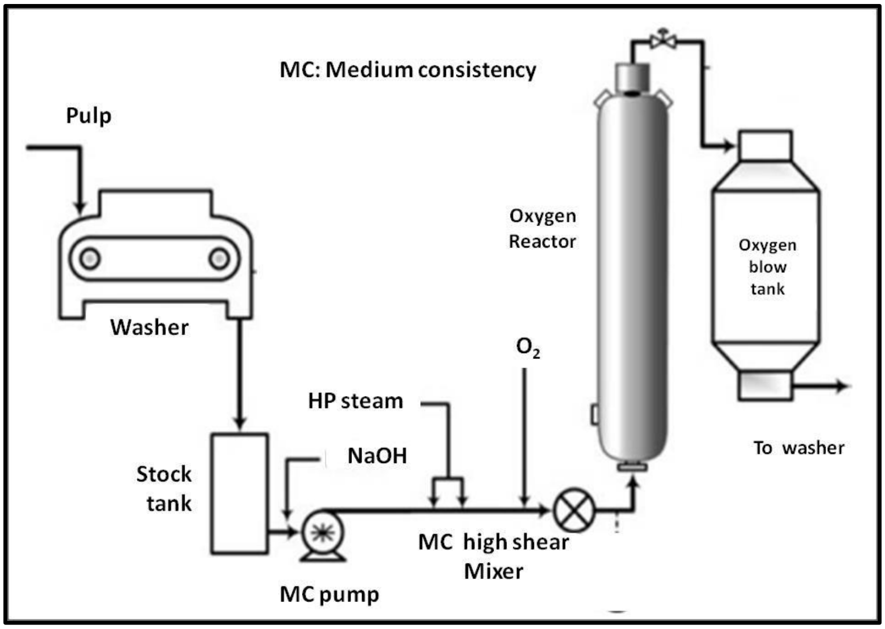


Fig 1.11: Flowchart of mini Oxygen delignification system showing system configuration and pulp sampling locations ***(Susilo and Bennington 2007)***

As chlorination causes environmental problems, it is replaced by chlorine dioxide, leading to more oxidative products than highly toxic chlorinated lignin fragments. The ***ClO_2*** *bleaching* is performed at low-to-medium consistency, with pH values ranging from 3-5 and at low temperature (appr. 70°C) in the first stage. ClO_2 oxidizes, solubilises the lignin and brightens the pulp. It is a radical reaction, which opens the aromatic rings, reacts with free phenolic groups and reduces their number. Lignin dissolution is caused by large number of carboxyl groups. The several advantages of ClO_2 include higher pulp brightness, improved strength properties, lower chemical consumption and a substantial decrease in the BOD of the effluents *(Germgard 1983).* ***Peroxide bleaching*** step enhances the delignification efficiency and improves the bleachability of the pulps at the final stages. Above pH 10.8, the formation of HO_2^- ions is so rapid that it decomposes to liberate O_2 gas which has no bleaching power. For it to act as an oxidizing beaching agent, the pH of H_2O_2 solution must be increased to basic range with the help of an alkali. The pH in H_2O_2 bleaching is maintained between 10.5-10.8. The most commonly used alkali in raising the pH of the bleach bath is sodium hydroxide (NaOH). Peroxide bleaching is usually performed at medium-to-high consistency at 60-80°C for 2-4 hrs *(Loras 1980).* This bleaching stage yields increased brightness values and stability. ***Ozone pulp bleaching*** has been extensively used as it offers a significant potential for environmental gains and it is most feasible in sequence with an oxygen stage. Given the current trend towards oxygen delignification, the advantages of ozone bleaching compared to other methods makes it a viable process alternative. Ozone bleaching involves efficient delignification of both hardwood and softwood pulps and all types of chemical pulps. It is a powerful oxidant at low temperatures. The bleaching process is carried out under acidic conditions and therefore the pulp is pre-treated with acid prior to bleaching process. Ozone requires very short contacting time with the pulp (10-15mins). The primary driving force for using ozone was to achieve maximum pulp brightness without using chlorine containing chemicals. Today ozone is used in both TCF and ECF bleaching processes. But the problems to be resolved in ozone bleaching are relative inefficiency of the ozone generating equipment and the non-selectivity of ozone towards lignin, which easily depolymerises the cellulose. As a new environmentally benign bleaching method, the use of enzymes has made an impact on the industrial bleaching of kraft pulp. The potential of incorporating oxidative enzymes for the development of chlorine free pulp bleaching processes are being intensively studied. The oxidative enzymes secreted by white rot fungi including laccase, lignin peroxidase are being commonly used *(Afrida et al. 2017).* Despite intensive investigations of oxidative enzymes for bio-bleaching, it is yet to be industrialized. The major challenges in using of oxidative enzymes for pulp bleaching are cost and environment. For example, Laccase is the most studied for biobleaching which require molecular oxygen and mediators such as ABTS (3-ethyl benzthiazoline-6-sulfonic acid) or HBT (1-hydroxybenzotriazole) *(Eugenio et al.2010).* However, utilization of ABTS or HBT as mediator, in industrial processes is hindered by their high cost and toxicity. In addition, using purified MnP in the mill is costly because this enzyme requires organic acid to stabilize Mn^{3+} and hydrogen peroxide as electron acceptor *(Moreira et al. 2001).*

1.7. Refining of chemical pulps

The objective of refining is to modify the pulp fiber cell walls in an optimal manner to meet the demands of a particular paper making furnish i.e. collapsibility. Refining involves a mechanical action which is aimed to induce the internal and external fibrillation as well as delamination of the cell wall (Fig 1.12).

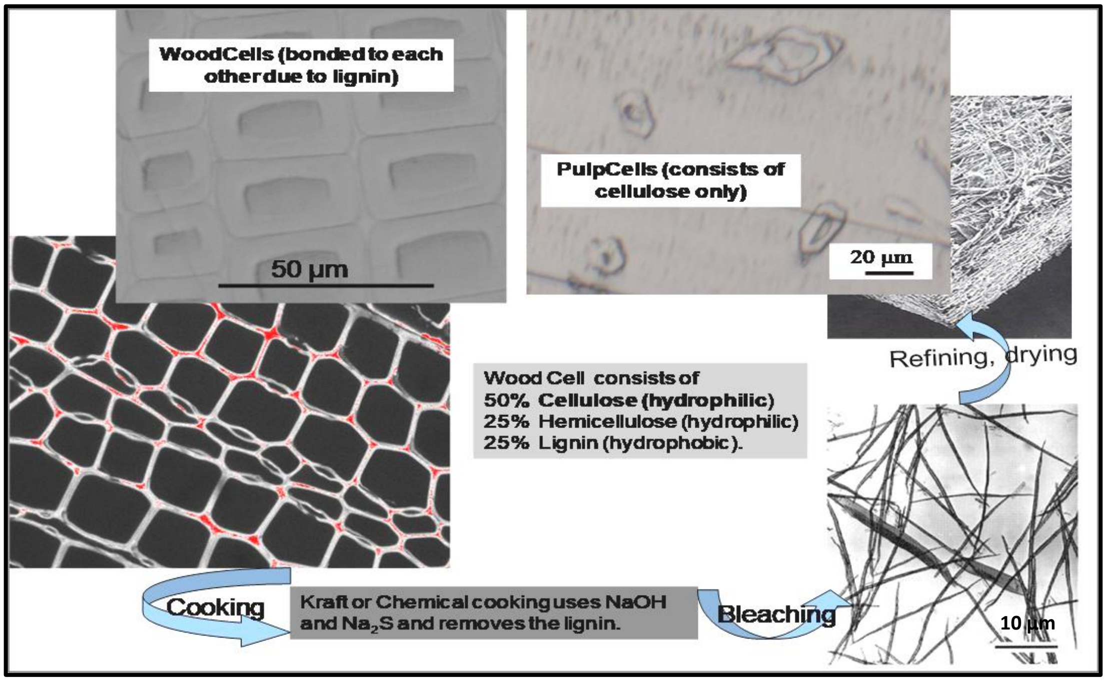


Fig 1.12: Making of papersheet after kraft cooking, bleaching and refining process. [Note the lignin rich areas (red marked) in the middle lamella. Note the pulp fibers with damaged cell wall].

In refining, both mechanical and hydraulic forces are employed to alter the fiber characteristics (*Karlsson 2006*). The initial action is to partially remove the primary wall. Removal of P-layer exposes the secondary wall and allows water to be absorbed into the molecular structure. The consequent loosening of the internal structure promotes fiber swelling and makes the fiber more soft and flexible. This “internal fibrillation” is regarded as the most important primary effect of refining. The further action of (external) fibrillation involves loosening of the fibrils and raising of finer microfibrils on the surface of the fibers, resulting in a very large increase in surface area for the beaten fibers (Fig 1.13). Fibers become more flexible by collapsing the lumens, thus creating ribbon like elements of great conformability *(Smook 1992)*. During beating and refining, fibers randomly and repeatedly undergo tensile, compressive, shear and bending forces *(Bajpai 2005).*

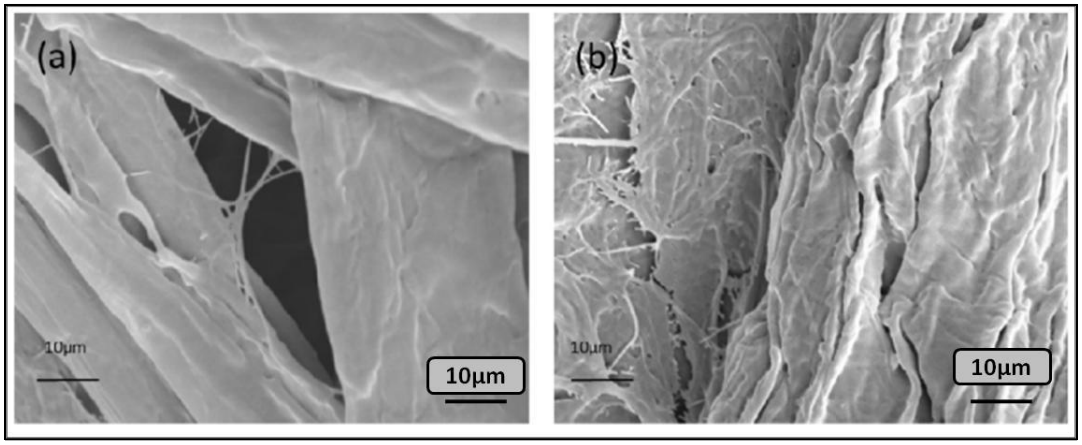


Fig 1.13: SEM images of softwood pulp fibers (a) before and (b) after refining *(Gao et al. 2015)*

Fiber shortening (or cutting) always occurs to some extent during refining which contributes to slower drainage and this reduces the production rate and increases energy consumption. Refining also produces fines consisting of fragments of broken fibers and particles that are removed from the fiber walls. Unbleached pulps are difficult to refine than the bleached pulps. The pulps with higher lignin content are less responsive to beating because the lignin does not absorb water, and therefore the fibers do not “swell” much. The common device used for beating in pulp industries is PFI mill. It utililizes a grooved roll eccentric to a smooth trough. The roll and the bedplate rotate at a high speed in the same direction but with different peripheral velocities. This induces friction, rubbing and crushing of the fibers to produce the beating effect (Fig 1.14).

PFI mill description/ working process: The cylindrical container generally turns at 720 ± 20 rpm and the beater roll with 33 bars turns at 1440 ± 30 rpm both in the same direction. The beater roll is pressed against the container wall with approximately 3.33 N/mm of bar length. The pulp is beaten due to the pressure between the wall and the bars. The beating time is between 2 and 10 minutes depending on the nature of pulp. A weighed and disintegrated pulp sample is put into the container and pulp sample is pressed evenly to the outside wall of the container by hand. The swivelling beating head is placed over the container and the beating procedure starts when the head is moved down into the container. By moving the hand lever, the beating head presses against the container wall. Due to the presence of pulp, there is no direct contact between the metal parts and the machine is subjected to beating after adjusting the number of revolutions. The head is moved again into the lateral position, the pulp is taken out of the mill and the shopper riegler (ºSR) value and/or the canadian standard freeness (CSF) value of the pulp is determined.

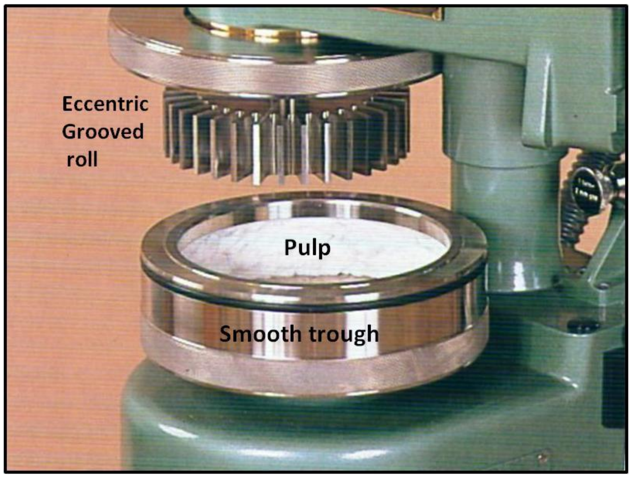


Fig 1.14: PFI Mill showing pulp inside the trough. ***(Popil 2018)***

The advantage of the PFI mill is that it only requires a small amount of pulp to carry out the complete refining in comparison to Lab-Valley beater. During refining, latewood fibers delaminate easily and cell wall thickness decreases considerably than earlywood *(Hickey and Rudie 1993).* In case of earlywood, the fibers preferentially split and become more flattened during refining. Hardwood pulps are quite easy to refine but sensitive to high loads involved in the refining process *(Chauhan et al. 2011).* Softwood fibers require coarser fillings and higher refining intensity than those required for short and thin hardwood fibers.

Pulps made from raw material with more compact fibers (high wall area to lumen area) can be refined easier and it also contains less shives. The effect of refining on paper properties is immense. Density and tensile strength increase due to improved fiber-to-fiber bonding, whereas the tear strength always decreases due to the strength attrition of individual fibers.

1.8. Paper making and testing

The pulp obtained from different raw materials (hardwood, softwoods, heartwood, sapwood, non-woods etc) are used to make different types/ grades of paper i.e. unbleached paper after kraft cooking, refined paper after cooking and beating process, bleached paper after cooking, beating and bleaching process etc. The quality of the finished stock essentially determines the properties of the paper produced. The furnish (pulp) can also be treated with few chemical additives. These include dyes, sizing agents, strength aids and fillers. The strength aids are polymers that bind to the fibers to improve strength. Kaolin clays and titanium dioxide are some of the examples of fillers used to improve optical qualities. Dyes and pigments are used to increase the brightness of the sheet. Resins are added to improve the wet strength of the paper. Drainage aids are used to increase the rate of water removal and retention aids helps to retain fines *(Karlsson 2006).*

For paper making, a slurry consisting of approx. 99.5% water and approx. 0.5% pulp fiber is pumped into the head box of the paper machine in which the slurry is evenly spread out onto the moving wire to form a web. The speed of the water jet relative to the speed of the wire orients the fibers (Fig 1.15).

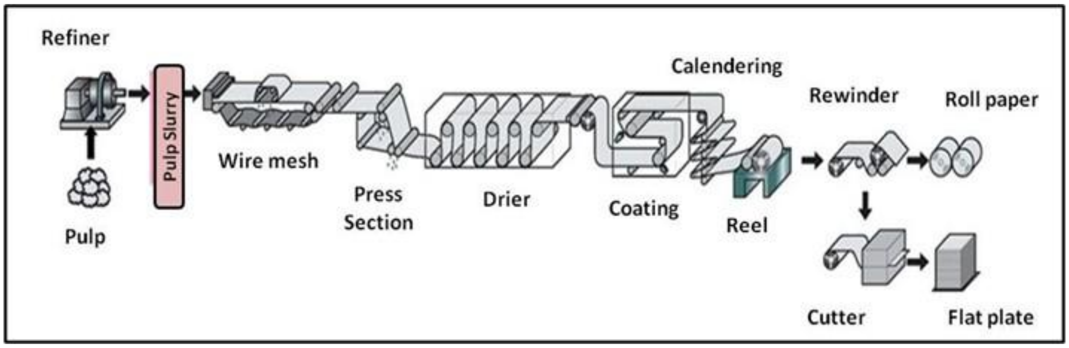


Fig 1.15: Schematic of paper making process

The wire allows the water to be drained and retains the fibers. Fines and fillers pass through the wire at the beginning, but later they are bonded to fibers. The next step is the pressing and drying section where additional dewatering occurs *(Smook 1992; Biermann 1996).* The paper web enters the press section in order to remove water that has not been removed on the wire. Pressing is an energy efficient procedure to get rid of unbound water and partly bound water from cell walls. As the paper enters the press section, it undergoes compression between two rotating rolls to squeeze out more water. When the paper leaves the press section, the sheet usually has about 65% moisture content. The remaining water is removed by drying the paper on steam heated dryers, which evaporates tons of water. The drying induces the uniformity in the web and better quality. Post drying treatment is calendaring (finishing operation) where the paper passes through a series of polished steel rolls to smooth the paper surface. Besides imparting smoothness, calendaring reduces sheet thickness to a desired level, reduces surface variations in the sheet and thereby creates a higher density paper sheet. The even surface for the paper can be achieved by applying a coating mixture. Various grades of paper, including paperboard, printing, writing and industrial or packaging grades sometimes have coatings. Three major coated paper categories exist i.e. glossy, dull, and mat. Most coated paper is ground with paper made from mechanical pulp. The term "coated free sheet" describes paper made from chemical pulp. People equate coated paper with the gloss stock of a magazine. Books and other products generally use dull coated paper. The nature of paper and papermaking has changed very little over the past 150 years; however the techniques and equipment necessary to make paper have changed dramatically. Because of this, we can rely on a consistent supply of high quality graded papers for almost any need we can imagine. The wide diversity of paper grades with different functional properties necessitates a multiplicity of test methods. Some of the important physical tests of paper are:

(a). *Grammage*: It is also called basis weight. It is defined as mass per unit area of the paper and board. It is expressed as g/m^2.

(b). *Thickness*: It determines how dense a paper is for a given grammage. A thickness gauge is used in which the paper is held under a given pressure between two parallel plates. Variations in thickness can affect basic properties such as strength and optical properties.

(c).Water absorption capacity: The moisture content in paper varies between 2-12%. Water has a negative effect on the paper; it plasticizes the cellulose fiber, relaxes and weakens the inter fiber bonding. Determination of the water absorption capacity of paper involves weighing a conditioned paper before and after drying.

(d).Tensile strength: It is determined by measuring the force required to break a narrow strip of paper when both the length of the test strip and the rate of loading are specified. The tensile strength of paper depends on the fiber properties such as cell wall damage, kinks and other weak spots along the length of the fiber. An increase in moisture content of the paper decreases the tensile strength.

(e). Tearing strength: It is the force required to tear a sheet of paper from an initial cut, under specified conditions. It is dependent on fiber orientation in the sheet. When a pulp is beaten, the tensile index increases and tears index decreases.

(f). Water absorbancy: It involves measuring the amount of water absorbed by the sample during a given time. This test is used as an indicator of degree of sizing, i.e. the water repellency of the paper.

(g). Brightness: It is the intrinsic luminous reflectance factor measured around 475nm. The function of the term brightness is to be able to measure the effect of bleaching and to measure the amount of colored substances in the pulp.

[Some of the other important physical tests of paper are Folding endurance, Roughness, Opacity, Gloss etc., are described in detail in literature (*Smook 1992)*]

1.9. Recovery of white liquor from black liquor in kraft cooking

After the kraft process, liquid is separated from solid pulp and this liquid is called weak black liquor. The weak black liquor is separated from the pulp by washing and is sent to the kraft recovery system, where the inorganic pulping chemicals are recovered for reuse, while the dissolved organics are used as a fuel to make steam and power as shown in Fig. 1.16. The recovery process in general has three main functions:

(a). Minimizing the environmental impact of waste material (black liquor) from the pulping process; (b). Recycling pulping chemicals NaOH and Na_2S; (c). Co-generating steam and power.

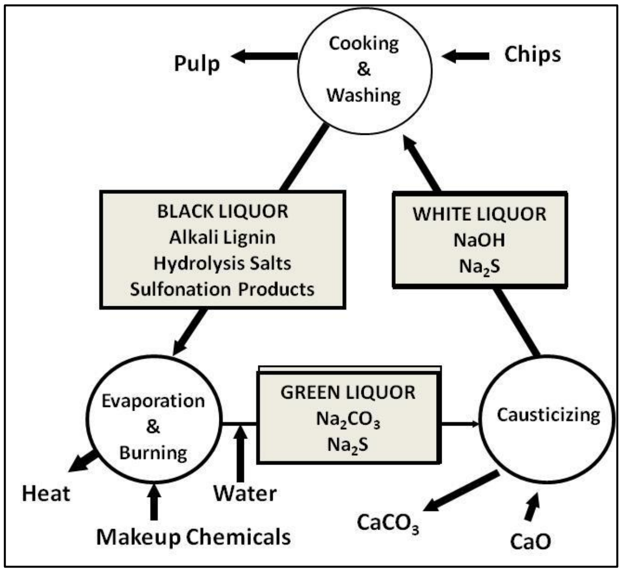


Fig 1.16: Recovery of white liquor in kraft pulping

- First the weak black liquor from brown stock washers is concentrated in multiple effect evaporators.
- It is concentrated to a point where it can be effectively burned in a recovery boiler, (usually at 65% solids or higher).
- The concentrated black liquor is sprayed into the lower part of the recovery boiler where it is burned in an oxygen deficient environment to form Na_2S.
- The extent of sulphide formation is measured by the reduction efficiency (Na_2S / (Na_2S + Na_2SO_4), typically over 90%.
- The inorganic sodium and sulphur are recovered as a molten smelt which consists mostly of Na_2S and sodium carbonate (Na_2CO_3).
- The molten smelt enters a dissolving tank where it is dissolved in water to form ***green liquor***.
- The green liquor is then sent to the causticizing plant, where it is reacted with lime (CaO) to convert Na_2CO_3 to NaOH.
- Conversion is measured by causticizing efficiency (NaOH / (NaOH + Na_2CO_3), typically 80 to 83%.
- The Na_2S passes through the causticizing step unchanged.
- The causticized green liquor is known as “white liquor” which contains mostly NaOH

and Na_2S.

- It is returned to the digester for reuse in kraft cooking.
- The precipitated $CaCO_3$ (lime mud) from the causticizing reaction is washed and sent to a lime kiln where it is heated to a high temperature to regenerate CaO for reuse.

<u>Recovery of heat from combustion of organics</u>

- The organic compounds in black liquor serve as a fuel for the production of steam which is used to generate electricity.
- The heat released as a result of black liquor combustion is recovered as high pressure/temperature superheated steam in the recovery boiler.
- The high pressure steam is passed through a steam turbine to generate electricity.

On an average, the kraft pulping process produces about 10 tons of weak black liquor or about 1.5 tons of black liquor dry solids that are processed through the chemical recovery process. The amount of steam produced is typically about 3.5 kg per kg black liquor solids. Kraft pulp mill can generate about 25 to 35 MW of electricity by burning 1500 t/d black liquor dry solids in its recovery boiler.

Table 1.9: Typical composition of the black liquor ***(Sjostrom 1993)***

Components	**% of dry solid content**	
	Kraft liquor	**Sulphite liquor**
Lignin	39-54	55
Degraded carbohydrates	25-35	28
Extractives	3-5	4
Inorganic compounds	18-25	13

1.10. Limitations of the existing research

The studies on pulping and bleaching of wood and non-woods materials and specifically the influence of heartwood (HW) and sapwood (SW) or bagasse pith on paper properties have been substantiated with the work done by various researchers. In line with this, the literature review on the above areas is presented below:

The extractives in heartwood promote higher chemical consumption, reducing pulp yield. Its low permeability makes the liquor circulation into the chips more difficult, reducing the lignin removal (*Del Rio et al. 1998*). Several authors used *Eucalyptus* to study heartwood influence in pulp production specially relating to extractives content *(Miranda et al. 2007; Morais and Pereira 2012)*. Similarly the presence of pith content in bagasse causes serious problems such as high chemical consumption during pulping and bleaching processes as reported by *Rainey and Covey* 2016 and numerous studies on morphological and chemical analysis of bagasse for pulp and paper production were carried out (*Sanguan et al. 2001, Monga 2017*). Whereas in bleaching, brightness stability is a key property of bleached chemical pulps and is primarily determined by wood species and bleaching process conditions. This fact was discussed by researchers through their studies *(Seco et al. 2008; Martino et al. 2013; Liu et al. 2010).*

Ana Lourenco et al. (2010) reported that E. globulus HW compared unfavourably to SW in kraft pulping at different pulping temperatures (i.e. 130ºC, 150ºC and 170ºC) owing to lower yields, mainly due to its higher content of extractives. Lignin removal was lower in HW in relation to SW (residual lignin of 2.0 and 1.1% after 180 min at 170ºC, respectively for HW and SW).

Similarly several authors *Miranda et al. (2007); Morais and Pereira (2012); Miranda et al. (2006)* concluded that a strong relation between extractives content and HW proportion exists and the potential loss of pulp yield (HW pulps presented lower yields compared to SW) and problems associated with accumulation of extractives are directly related to the HW proportion. Therefore presence of HW decreased the quality of raw material for pulping among the E. globulus trees that were investigated.

For softwoods (pine), *Esteves et al. (2005)* reported chemical differences between HW and SW in particular extractives content (19.7% for HW and 5.8 % for SW) and *Atac et* *al. (2012)* examined the differences in terms of chemical composition and fiber properties between HW and SW on kraft pulp properties with results indicating that HW had shorter fiber length, lower pulp viscosity and total pulp yield and more extractive content compared to SW. *Santiago et al. (2008)* presented a work to assess the effect of alkali and sulfide charges on the lignin and carbohydrates removal during the impregnation phase of E. globulus pulping process. It was concluded that as the effective alkali ($NaOH$+ Na_2S) charge at impregnation phase increased, the amount of dissolved wood also increased until it has reached a constant value.

Rupert et al. (2008) studied the effects of site on fibre, kraft pulp and handsheet properties of Eucalyptus globulus and concluded that the handsheets produced with pulp from the poor site resulted in comparatively higher bulkiness, lower burst, lower tear and tensile indices, lower zero span tensile strength, but higher opacity, higher light scattering and higher surface roughness. *Bertaud and Holmbom (2004)* focused on the distribution of wood components along a cross-section of a spruce stem. It was reported that heartwood contained significantly more lignin and less cellulose than sapwood. The transition zone between heartwood and sapwood had less lignin and lipophilic extractives than heartwood and sapwood. Also, the lipophilic extractives were less concentrated in the latewood.

With the purpose of simulating the cooking of wood chip mixtures, lot of work has been published by several researchers. *Mortha and Jain (2008)* developed a Kraft pulping model that allows predicting the effects of wood parameters and cooking variables on pulping results: mean kappa number, pulp yield and delignification homogeneity within chips. Similarly *Santos et al. (1997)* proposed a kinetic model for the kraft pulping delignification of Eucalyptus globulus to simulate typical kraft pulping experiments carried out at non-isothermal conditions using a temperature ramp.

Agnihotri S et al. (2010) discussed the complete characterization of depithed bagasse of early species of *saccharum officinerum* for pulp and paper making. Soda pulping process at different cooking conditions (130ºC and 160ºC) were performed. Physical strength properties such as tear index, tensile index, burst index etc were measured for handsheets. The study concluded that lignin content in bagasse is comparable to Eucalyptus globulus and Subabul, but α-cellulose and pentosans are slightly lower. 42.2% pulp yield, kappa number of 28.2 was obtained at optimum cooking conditions such as active alkali of 12%

(as Na_2O), temperature of 150ºC and time of 60 min. A homogeneous and strong paper was produced with less pitch problems. In a peer review article by *Rainey (2012),* the pulp properties of highly depithed bagasse pulp were tested and compared favourably with regular depithed bagasse pulp. In addition to better dewatering rates, the pulp yield, tear strength and water retention value seemingly improved. While a slight reduction in burst, tensile and short-span compression strengths (an edgewise test) occurred, the results were still comparable to the values reported for a regular bagasse pulp.

Sanjuan et al. (2001) discussed the morphological and chemical composition of pith and fibers from Mexican sugarcane bagasse. The studies indicated that the length of the fibers are higher than 1mm and high cell wall thickness and length of the parenchyma cells are very short with high diameter and a thin cell wall. Chemical analysis revealed that ash content and hot water extractives of pith fraction is much higher with lower holocellulose content. *Ghazy (2016)* studied the influence of temperature (160,165,170,175 and 180°C) and time (0, 30, 60, 90, 120 and 150 mins) on the kraft pulping of Egyptian bagasse (depithed) to verify the application of kinetics for the rate of delignification. The studied concluded that bagasse pulping is strongly affected by temperature and time of cooking. Over 175°C is not recommended for kraft pulping of Egyptian bagasse. The carbohydrate loss is almost equal to the dissolution of lignin at any cooking time (from 0 to 150 min) for temperature of 160-175°C whereas at 180°C the degradation of polysaccharides is higher than lignin dissolution.

Neto et al. (2002) investigated the effect of Eucalyptus globulus wood kraft pulping conditions on the chlorine dioxide consumption in ECF bleaching. The studies concluded that the pulping parameters namely: active alkali, sulfidity, temperature, and liquor-to-wood ratio, significantly affected the bleachability of pulps followed a conventional ECF bleaching sequence (DEDED - Alkaline extraction (E); Chlorine Dioxide (D)). The studies also concluded the extent of delignification of the unbleached pulp (kappa number) affected the bleaching response of the pulp, with the residual lignin and other oxidizable structures in the pulp becoming progressively more difficult to remove/bleach by ClO_2.

Seco et al. (2008) studied the strategies to reduce the brightness reversion of industrial ECF bleached Eucalyptus globulus kraft pulp. It is aimed to study the effect of bleaching parameters of a DEDD bleaching sequence and effect of a final Peroxide-P stage (DEPP instead of DEDD) in the brightness stability of bleached E. globulus kraft pulps. Brightness stability was increased with the increase in D_0 state temperature from 55°C to 90°C. Brightness stability was further improved significantly on increasing the ClO_2 charges from 2.8% to 3.2%. Substitution of the last D (ClO_2) stage in DEDD sequence by a P (H_2O_2) stage (DEPP) significantly reduced the brightness reversion. The results obtained from this study showed that brightness stability can be improved without any significant capital investment

Martino et al. (2013) presented a peer review article pertaining to factors affecting bleachability of Eucalyptus Pulp. Kraft pulping of pre-steamed *Eucalyptus* chips was carried at 156°C for 120mins. Quantitative chemical analysis of wood and pulp was performed aiming to find a correlation with bleaching performance. The unbleached pulps exhibited highest brightness of 4% (ISO) after oxygen pre-bleaching indicating the effect of cooking conditions. It was finally stated that the higher bleachability was due to its much higher HexA/lignin ratio. Here HexA stands for hexenuronic acid which is the main uronic acid group in chemical pulps. This acid does not exist in native wood but it is formed in chemical (alkaline) pulping through β-elimination of methoxyl groups.

Many TCF and ECF studies for bagasse pulp have been reported recently. For instance, *Mohta et al. (2001)* found that ECF bleaching of oxygen-delignified pulps gave higher brightness as compared to the $D_0E_1D_1$bleaching of soda and soda-AQ pulps. *Hedjazi et al. (2008)* used OQ(PO) bleaching sequence to delignify and bleach an alkaline sulfite-anthraquinone (ASAQ) bagasse pulp to a brightness value of 80% ISO. Totally chlorine-free (TCF) bleaching with the Q_1(OP)Q_2P sequence of the unbleached ASAQ (alkaline sulphite anthraquinone) bagasse pulps yielded bleached pulps with 76.9% ISO brightness, which is suitable for producing writing and printing grades of paper *(Khristova et al. 2006).*

Studies by the authors *Wang et al. 2009; Liu et al. 2010; Zeng et al. 2012* also found that the alkaline bagasse pulp can be bleached to a brightness of over 80% ISO using the (OP)Q(PO) bleaching sequence. *Fatriasari et al. (2015)* evaluated Sorghum as raw material using kraft pulping. The effects of alkali and sulphidity loading on kraft pulp and paper properties were investigated. The kraft pulping was carried out at alkali loadings 17, 19 and 22% by maintaining sulfidity at 20, 22 and 24% for 4 hours at 170°C and liquid to wood ratio of 10:1. Kraft pulping of Sorghum bicolor bagasse produced good pulp indicated by delignification selectivity at a low kappa number (< 10) and high screen yield. The unbleached pulp sheet was produced at a superior brightness level and high burst index. The increase of active alkali loading showed a negative effect on the pulp yield, kappa number and paper sheet properties.

1.11. Summary of gaps

The gaps between the existing literature and our objectives are categorized as three area's. In the first area, we found that the raw material used is typically whole wood log. Separating the whole wood log into heartwood and sapwood and performing the cooking process separately is currently not being practiced though it is known since 1970's. In the second area we found that only depithed bagasse is taken as raw material. Studies using whole bagasse (without depithing) and comparison of pulp characteristics obtained from whole bagasse and depithed bagasse were not carried out. In the third area we found that no systematic characterization was carried out for the papersheet obtained after kraft cooking i.e pulp characteristics after cooking, bleaching, paper sheet characteristics and black liquor characteristics. Although Eucalyptus and Subabul are commonly used raw material for pulping in India, limited information is available about the effect of using heartwood in kraft cooking and bleaching process.

1. There has been no report so far on a systematic study of lignin determination after cooking and bleaching by testing pulp, paper and black liquor properties simultaneously.
2. A detailed study on influence of raw material specifically heartwood and sapwood; whole bagasse and depithed bagasse with respect to pulping, bleaching and paper making was not conducted.
3. Researchers have concentrated on the cooking (digestion) process, but an elaborate study on pre-treatment (such as steaming the wood) and effect of chip size on pulp quality have not been reported.
4. Although several studies have focused on increasing pulp yield and paper sheet characteristics, pulp attributes such as Water retention value, Water absorption test (moisture content), Kappa number, Ash content, Cellulose content etc. have not been discussed together to draw a conclusion about % of lignin removal.

5. No correlations were drawn between chemical and mechanical analysis of pulp after cooking and bleaching, though it is known that lignin alters the mechanical properties.
6. Many studies discussed the use of non-wood resources in pulp and paper-based industries. But none have discussed the chemical behaviour of main constituent pith (from bagasse) in pulping and papermaking for optimization and further development of the process.

1.12. Objective of present research

Wood and bagasse are used as raw materials in Indian paper mills. The properties of nonwoven paper sheet are dependent on the properties of individual pulp fibers. Pulp fiber characteristics such as cellulose content, lignin content, length, cell wall collapsibility are influencing the final paper quality. Pulp characterization before paper making is important to improve the existing paper characteristics such as high ink absorption and also to develop new grades of paper such as packaging. But for many years, the pulp quality was determined after preparing handsheets and then performing paper testing in order to assess the suitability of pulp. The values reported in the literature are also highly variable between bleached and unbleached pulps, because the studies are limited to either cooking or bleaching or refining. There are only a few studies that have focused on systematic study of pulp fibers after cooking, bleaching and refining. Hence, this *Thesis* aims at the systematic study of pulp, paper handsheet and also black liquor characteristics after cooking and bleaching. An attempt has been made to understand the delignification kinetics during cooking, bleaching and refining by taking wood and bagasse. In both species cells are connected through middle lamella but cells are loosely connected in bagasse compared to wood. As a result of refining or beating, pulp fibers collapse (reduction in lumen size) and are flattened in shape compared to native wood fibers. Since cooking and bleaching affects the cell wall properties, these processes are to be optimized to preserve the intrinsic fiber strength and to avoid the formation of weak points in the fiber wall. Therefore studies using different raw materials (heartwood and sapwood; whole and depithed bagasse separately) were conducted to provide process parameters (temperature, time) required for Kraft process, in order to optimize the reactions, so as to avoid the wastage of valuable materials, chemicals and also their characterizations. In this sequence, effective removal of lignin from the selected wood and non-wood species (commonly grown and used in Indian paper mills) were performed by optimizing the kraft cooking processes with respect to pulp, paper and black liquor characteristics.

Therefore, the present research work "Study of Pulp Characteristics after Cooking and Bleaching for Optimization of Process Parameters" is based on the following hypothesis:

Process parameters such as chip size, cooking time and temperature and bleaching have a significant impact on pulp, black liquor and paper characteristics.

To test the above hypothesis, the following objectives are outlined….

1. To study the effect of chip size on Eucalyptus sapwood and heartwood pulp fibers.
2. To determine the effect of temperature on Subabul sapwood and heartwood pulp fibers.
3. To determine the effect of temperature on Kraft Pulping of whole and depithed Bagasse.
4. To study the effect of temperature and time on black liquor characteristics.
5. To differentiate between bleached and unbleached pulp and paper sheet characteristics.

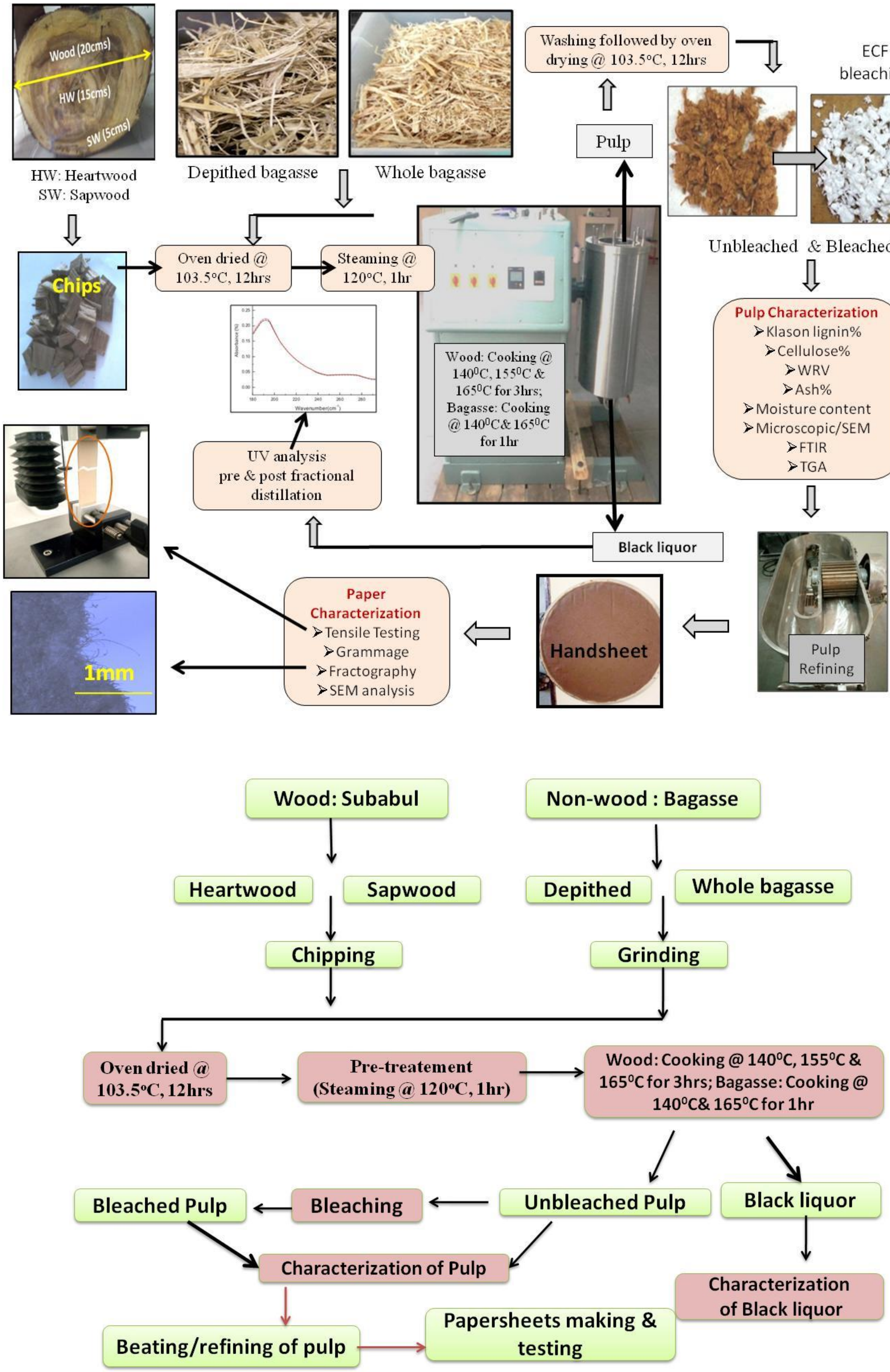


Fig. 1.17 Graphical Abstract of the Thesis

1.13. Summary of the Thesis

The studies carried out have been presented in the thesis under following chapters:

Chapter 2: Effect of chip size on Eucalyptus sapwood and heartwood pulp fibers

This chapter deals with experimental methods and analysis of “Kraft pulping of Eucalyptus heartwood and sapwood of different sizes”. In order to understand the negative correlation that exists between extractives content in heartwood and pulp yield, both heartwood and sapwood of different sizes i.e. 150, 300, 425, 600, 1000, 2000 µm were subjected to kraft cooking separately at 170°C, 2hrs, 1:4 ratio of wood: liquor in Parr reactor. The wood and pulps before and after kraft cooking were chemically characterized and analyzed for various properties using Klasons lignin test, FTIR data, Water retention value, Ash content value and SEM analysis.

Chapter 3: Effect of temperature on Subabul sapwood and heartwood pulp fibers

This chapter includes the key experimental results, observations and the statistical analysis of kraft cooking process of Subabul heartwood and sapwood chips separately at different temperatures. Subabul (*leucaena leucocephala*) wood chips of ~0.8-1 cm^3 are subjected to kraft cooking using rotary pulp digester at 140°C, 155°C and 165°C for 3hrs with 1:4-wood: liquor ratio. The wood and pulps obtained before and after cooking process are characterized using FTIR, Water retention value, Klasons lignin content, Cellulose content, Ash content @525°C, TGA and Optical microscopy tests. Delignification process was modelled using MATLAB and MINITAB through which a correlation between lignin content and cooking temperature was obtained.

Chapter 4: Effect of temperature on kraft pulping of Whole and Depithed Bagasse

This chapter involves a systematic study on the impact of pith on paper making process by kraft pulping of whole and depithed bagasse with respect to temperature and time. Screened sugarcane bagasse (whole and depithed separately) are subjected to Kraft cooking at 165°C and 140°C for 1hr with 1:7-wood: liquor ratio in Rotary Pulp digester. The bagasse and pulps are characterized using Klasons lignin test, %Cellulose content, Water retention value (WRV), Water absorption capacity (%), Ash content (525°C), Optical Microscopy, TGA and FTIR.

Chapter 5: Effect of temperature and time on black liquor characteristics

This chapter comprises of a detailed study of experimentation and result analysis of influence of temperature and time on black liquor properties. For the analysis, black liquor of approximately 15-20ml was collected from bottom of the digester (bottom valve) at different time intervals i.e. 1hr, 2hr and 3hr for wood samples and at 0.5 hr, 1hr for bagasse samples. After dilution, black liquor samples were subjected to UV-Vis spectrophotometer (to qualitatively confirm the presence of lignin fragments in the solution) prior and after fractional distillation. The absorption spectra are recorded from wavelength 190 to 400 nm. The fractional distillation process (used for separation of organic and inorganic content) is carried out at 110^{o}C for about 85mins with 25ml of black liquor sample (collected at different intervals of time).

Chapter 6: Effect of bleaching on pulp and papersheet characteristics

This chapter includes an elaborate study of pulp and paper sheet characteristics of wood (rawwood, heartwood and sapwood) and bagasse (whole and depithed bagasse) pulps before and after ECF (elemental chlorine free) bleaching process.The effect of bleaching on the pulp is evaluated by measuring Ash content, Water retention value and Cellulose content. The pulp results are then compared with unbleached pulps to understand the impact and effectiveness of the bleaching process. The Pulps (bleached and unbleached) are refined in lab valley beater prior to making paper sheets using hand pressing unit. The strength properties of paper sheets are evaluated using tensile testing. Fractography of sheets was characterised by using SEM and stereo microscopy.

Chapter 7: Conclusions and future studies

This chapter includes the conclusions of the main findings with respect to pulp characteristics, papersheet testing and black liquor characteristics and also the model developed in the study. Suggestions for further work are also presented. References and the details of the publications are presented at the end of the thesis.

CHAPTER -2

Effect of Chip Size on Sapwood and Heartwood Pulp Fibers

2.1. INTRODUCTION

Plantation grown hardwoods such as Eucalyptus and Subabul are used as raw materials in kraft pulping, especially in India. Most mills use whole wood as a raw material in pulping process with limited information on its (a) constituents such as bark, heartwood, sapwood and (b) chip morphology. The hardwood Eucalyptus citriodora (*Myrtaceae*) used as a raw material in paper industry has a substantial proportion of heartwood (HW). In addition to libriform fibers and fiber tracheids, heartwood has vessels blocked with tyloses and sapwood (SW) has ray and axial parenchyma cells filled with starch. During the pulping process, it is found that higher amount of heartwood fraction has a detrimental effect on the quality of pulp. This specific effect of heartwood on paper quality was studied by limited people (*Egas et al. 2002)* as most of the work was focused on the effect of heartwood in total delignification process rather than a separate investigation of heartwood and sapwood effects. Although there are a few studies which aim at understanding this correlation (*Miranda et al. 2007; Mariani et al. 2005)*, the emphasis was more on quantifying the end results of the pulping reaction. There is still a lack of comprehensive information regarding the causes behind different behaviour of heartwood and sapwood under identical conditions of kraft cooking.

Chipping of wood logs plays an important role in the overall quality of pulp. Efficiency of debarking, chip sizes (length, thickness), uniformity of chip sizes, removal of dust and fines are important factors that affect pulping process. As cooking of wood chips is a reaction-diffusion process (*Agarwal et al. 1994*), the effects of chip sizes or uneven chip surfaces in pulping leads to inadequate liquor impregnation, that gives birth to in homogeneous delignification, increased rejects, decreased screened yields; which in turn results in reduced strength and optical properties of the paper (*Brannvall 2017*). As non-uniform diffusion of white liquor leads to non-uniform pulping, it is important and necessary to have a detailed knowledge of influence of chip size (most importantly thickness) on pulping and pulp properties for getting high strength pulps. Therefore this study is aimed to gain both quantitative and qualitative understanding of:

(i). The differences between delignification of heartwood and sapwood immediately after

Kraft cooking.

(ii). The influence of chip sizes on heartwood and sapwood pulp fiber characteristic values.

Apart from the direct empirical evaluation of the lignin content before and after cooking in heartwood and sapwood, certain indirect experimental methods are used (Fourier Transform Infrared (FTIR) Analysis, water retention value, ash content and fiber morphology) to conclude the effects of heartwood in kraft cooking. The available information could be then used to study the possible advantages of various strategies like separation of heartwood and sapwood prior to pulping, optimization of wood chip sizes and rotation cycle of trees used as a raw material to reduce the heartwood content.

2.2. MATERIALS AND METHODS

2.2.1. Chipping of wood logs

The raw material used in this study was obtained from a first-rotation Eucalyptus citriodora (Myrtaceae) tree, 6-7 years of age, from a rain-fed eucalyptus clonal plantation grown under the supervision of Telangana Forest Development Corporation in Jawaharnagar, Hyderabad, India. The log selected was 8 mts in height and 10 cm in diameter (Fig 2.1).

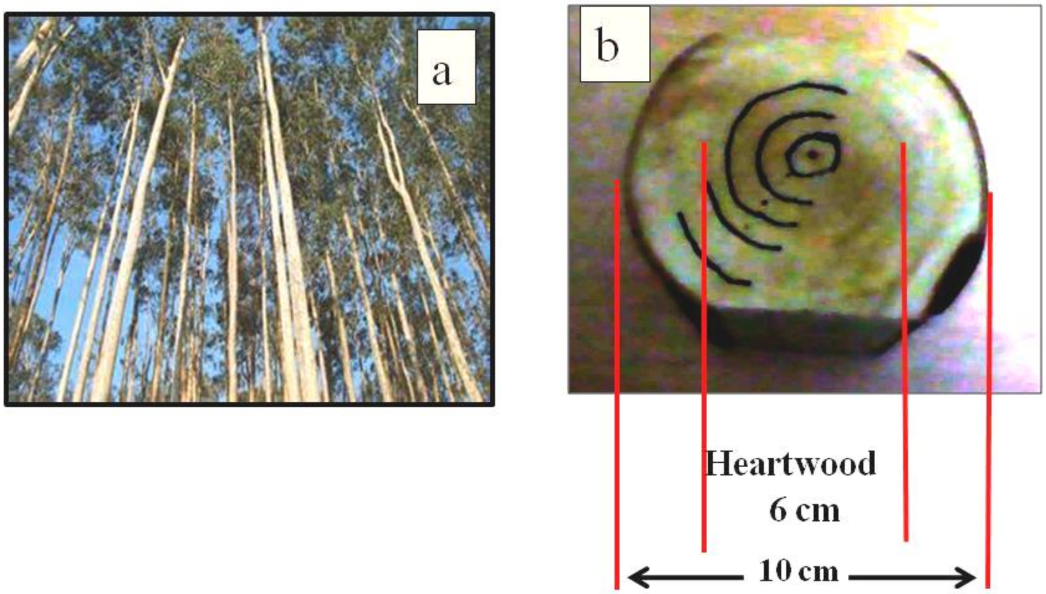


Fig 2.1: (a). Eucalyptus citriodora (*Myrtaceae*) trees of appr. 6-7yr age (b). Wood log that are considered for the pulping process *(collected from plantation in Jawaharnagar, Hyderabad, India 2014)*

Around 60% of the inner cross-sectional area at 4 mts of height from the root side was considered as heartwood (one such cross-section just above the root is shown in Fig 2.2). A 50 cm long section was taken at this height and sapwood and heartwood were separated using a wood turning machine. The radial cracks in heartwood (Fig 2.2) is due to the drying of the wood.

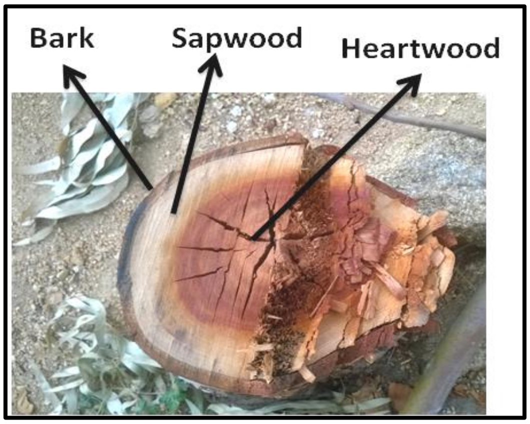


Fig 2.2: Cross-section of Eucalyptus citriodora (*Myrtaceae*) wood used for the study. ***[Note the heartwood and sapwood distincion]***

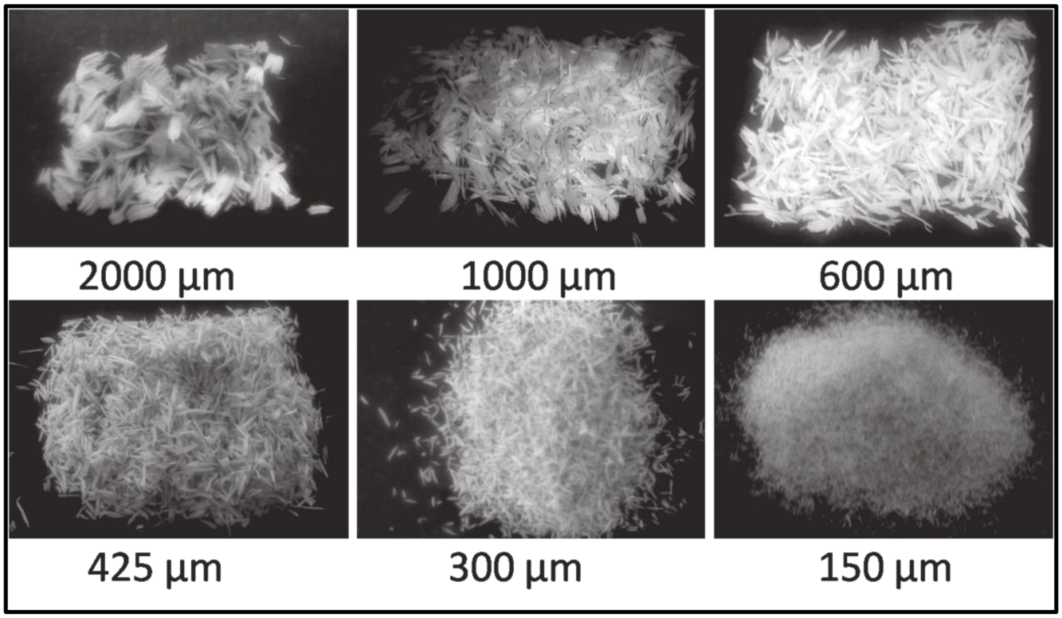


Fig 2.3: Different sizes of Eucalyptus wood chips (before cooking) separated by sieve analysis

The sapwood and heartwood chips were sieved and distributed into 6 sizes ranging from 2000 to 150 µm as shown in Fig 2.3. The sieved heartwood and sapwood thin chips were used instead of thick chips in order to reduce impregnation difficulties that lead to experimental errors. Since Kraft process can tolerate high amount of extractives and for better accuracy in ash content measurement, all samples were used without removing extractives.

2.2.2. Kraft cooking of sapwood and heartwood chips

Delignification is carried out in a high pressure reactor (*Anton Parr Model 4848;* Fig 2.4). The reaction mixture of white liquor and sieved wood chips were loaded in 600 ml SS reactor equipped with temperature controller and stirrer. The conditions for cooking of 5gms of oven dry weight wood are: liquor-to-wood ratio (ml/g) 4:1; sulfidity 30% (both Na_2S and NaOH expressed as Na_2O); active alkali 20% (as Na_2O). Based on the optimal ratio, 20 ml of the white liquor i.e. solution of water + NaOH + Na_2S was used for delignification. The pulping was carried out under isothermal conditions in two stages i.e. at 130°C for 30 min and at 170°C for 90 min, with heating time of 10 min for both the temperatures and at 160 rpm of stirrer rotation. The delignified pulp samples were separated from the black liquor using a funnel and a whatman filter paper. The pulp was dried in a hot air oven (OSWORLD OOG-90) at a temperature of 103.5°C until a constant weight was observed and stored for further analysis. It should be noted that both heartwood and sapwood were delignified under same cooking conditions.

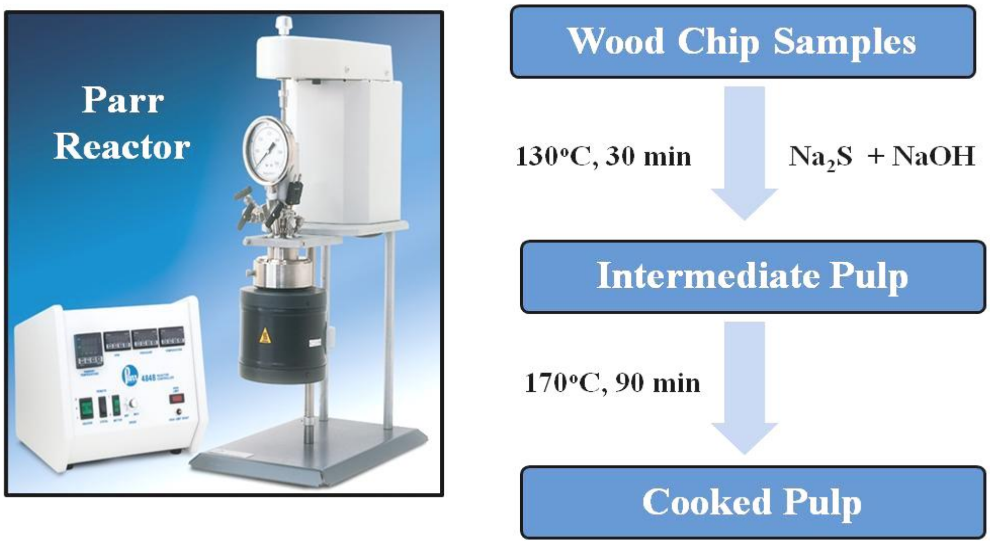


Fig. 2.4: Parr Reactor equipped with heating mantel and stirrer used for kraft cooking of thin wood chips

2.2.3. *Analysis of pulp using Klasons lignin estimation, Water retention value and Ash test*

Heartwood and sapwood characteristics were analyzed before delignification (raw) and later milled and sieved fractions were analyzed after the Kraft pulping process.

(i). Klasons lignin estimation *(TAPPI T222 and TAPPI UM250):*

0.15 g of oven dry sample was taken (uniform size). The weighed sample was added to 3 ml of 72% H_2SO_4 in a 50 ml conical flask, stirred thoroughly for uniform mixing and kept at 25^{o}C for 1 hr. After which, 84 ml of demineralized water was added to the sample and is kept in the autoclave at 120°C for 1hr. After 1hr, filtration was carried out to separate the solids from the liquid. The separated solids were dried overnight and weighed to give the klason lignin content. The liquid was used to assess the amount of acid soluble lignin using UV-Vis Spectrophotometer. 5 ml of 3% sulphuric acid was added to the filtrate and its absorbance at 205 nm was recorded. Both soluble and insoluble lignin content was calculated as per the equations given below.

$$Total\ Lignin = Insoluble\ lignin + Soluble\ lignin$$

$$Insoluble\ lignin\ content\ (\%) = (W_{lignin} / W_{fiber})*100$$

$$Soluble\ lignin\ content\ (\%) = [CV/(1000* W_{fiber})]*100$$

$$Where\ C = (A/110)*(V_{final}/V_{initial})$$

W_{lignin} = oven-dry weight of the insoluble lignin or Klason lignin (g); W_{fiber} = oven-dry weight of pulp fiber (g); C = concentration of soluble lignin in the filtrate (g/l); V= total volume of the filtrate (ml); A = absorbance at a wavelength of 205 nm; V_{final} = final volume of the solution (ml); $V_{initial}$ = initial volume of the solution (ml).

(ii). Estimation of water retention value *(WRV, TAPPI standard - UM 256):*

Both the heartwood and sapwood samples of the six sizes were analyzed for their WRV before and after delignification. The samples of 5gms each were taken in plastic vials and analyzed for their WRV using a refrigerated centrifuge (*Rota 4R-V/FM*; 2600 rpm, 25^{o}C for 30mins) by adding 15ml of deionized water. The wet pulp samples after centrifuge process are separated from the liquid using whatman filter paper and then oven dried at 103.5 °C till constant weight is attained. The WRV is calculated using the following equation:

$$WRV = (weight\ after\ centrifuge/\ weight\ after\ drying) - 1$$

(iii). Estimation of ash content *(TAPPI standard-T211):*

Ash represents the inorganic matter in the sample. Ash content for both the wood and pulp fractions was determined by incinerating 5 g of oven dried samples in a muffle furnace (Tempo TI-58HTB) at 525°C for ~3hrs (until constant weight is attained). The % ash is calculated using the following equation:

*% Ash= (weight of ash/ weight of oven dried sample) * 100*

2.2.4. Analysis of pulp using FTIR and Microscopy

(i). Fourier Transform Infrared (FTIR) Analysis:

The pulp samples were analyzed using FTIR spectroscopy (JASCO 4200, transmittance mode) in order to detect the various functional groups especially aromatic skeleton vibrations. To attain the spectral data, pulp samples were dried, ground to fine size using emery paper and mixed with potassium bromide (KBr) and grinded using motor and pestle and is then compressed to form thin uniform pellets.

(ii). Analysis using optical microscopy and scanning electron microscopy:

This analysis gives structural and morphological differences of both wood (heartwood and sapwood) samples and the corresponding pulp samples. The wood or pulp fibers of ~1g are taken in a clean plastic vial and 2ml of water is added to the sample and given a swirling action so that the pulp is thoroughly spread. The wet pulp sample is poured on a clean glass slide and the excess water is removed using a blotting paper. The sample is dried in atmospheric air, so that loose fibers are adhered to glass slide. Imaging of individual dried pulp fibers is carried out using optical microscopy *(METAVIS U400)*.The detailed structural characteristics of sapwood and heartwood pulps (chip size: 2000 µm) are further analyzed using scanning electron microscopy (SEM) after gold sputtering because these pulp fibers are non-conductive.

2.3. RESULTS AND DISCUSSIONS

2.3.1. Comparison between wood and pulp characteristics

Fig 2.5 represents the **images** of the wood and pulp samples of heartwood and sapwood (2000, 1000 and 600 µm sizes). In chemical pulping, the main objective of the cooking stage is to separate the fibers (or) cells. During pulping, the cooking liquor penetrates through the cell interfaces and capillaries. In hardwoods, these capillaries are mainly the vessel elements, libriform cells and ray cell channels that makes radial liquid penetration within the wood chips. Therefore this diffusion process chemically degrades and dissolves the lignin components in the middle lamellae (i.e. the interface between fibers) and secondary layers, due to which the wood fibers are separated from the lignin matrix *(Saka et al. 1982).* In line with the above hypothesis, a greater porosity with highly developed specific surface area, high degree of fiber dissociation such as longitudinal breakage or splitting of fibers, external fibrillation, separation of individual fibers etc., from the wood structure are observed in both the heartwood and sapwood pulps (for all sizes). These qualitative observations confirm the effectiveness of the selected process conditions.

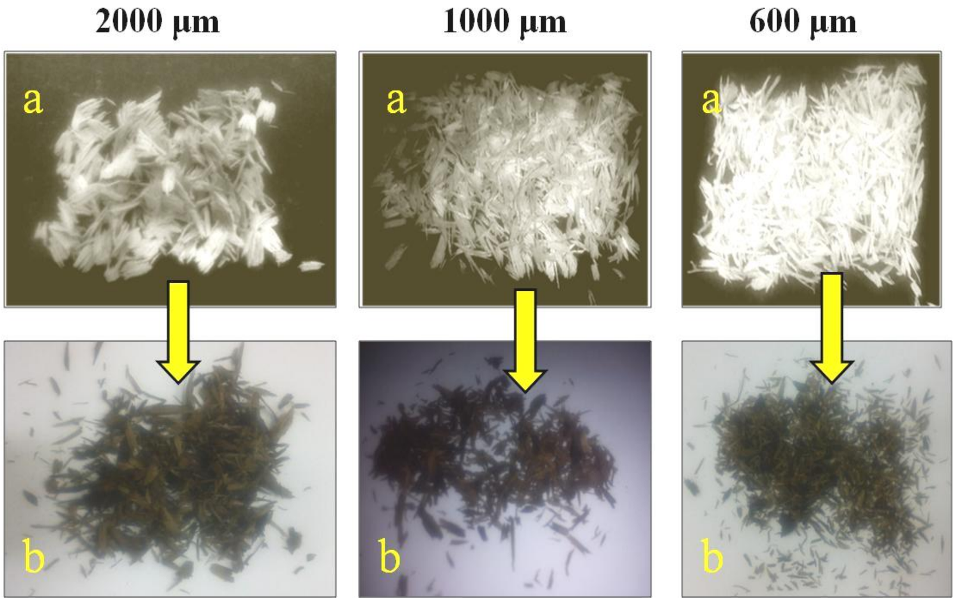


Fig 2.5: (a). Images of different sizes of thin wood chips
(b). Corresponding pulps obtained after kraft cooking

Characterization of wood and pulp is carried out using klasons lignin estimation, water retention value, ash content, FTIR spectroscopy and microscopic analysis. The results (Table 2.1) are presented to understand the impact of the kraft cooking with respect to raw material i.e sapwood/heartwood and material chip size.

Table 2.1: Wood and pulp characterization data

(kraft cooking at 130^oC for 30mins and at 170^oC for 90 mins with 1:4 wood: liquor)

Sample (2000µm)	**Lignin %**	**Kappa number**	**Water retention value**	**Ash %**
Heartwood	25.4± 1.27	170±8.5	0.811±0.06	0.169±0.007
Sapwood	26.8± 1.06	182±7.1	0.826±0.07	0.439±0.008
Heartwood Pulp	3.8± 0.12	25±1.3	2.241±0.05	0.165±0.002
Sapwood Pulp	1.5± 0.02	10±0.13	2.881±0.03	0.403±0.009

(i). Klasons lignin estimation:

From the attained results, it was found that the amount of lignin content is quite low for both the pulps (heartwood and sapwood) when compared to their corresponding wood chips as shown in Table 2.1. The main chemical bond that builds the lignin network structure in wood is phenolic and non-phenolic ether, covalent carbon-carbon bonds (also called condensed bonds) and lignin carbohydrate linkages. The lignin network consists mostly of aromatic phenols. In kraft cooking process, with the active chemical species hydroxide and hydrogen sulphide ions, the environment is highly alkaline with pH levels ranging from 11 to 14. At these high pH levels, diffusion rates of pulping chemicals into wood is quite high and similar in both longitudinal and radial directions *(Brannvall 2017).* The major fragmentation reaction in kraft pulping is the cleavage of the phenolic β-O-4 structures by a nucleophilic attack of the hydrogen sulphide ion. For the applied process conditions, the wood chips are heated and delignification reaction begins in which the lignin network structure is broken down and solubilized into the alkaline solution i.e. 10% of induced alkali is consumed during the initial period of cooking (130^{o}C) for the neutralization of acids deriving from the polysaccharides (acidic and uronic acids) and 25–30% of the alkali is consumed for neutralizing lignin degradation products during the heating period (170°C). These conditions thus lead to cleavage of the β-O-4 structural linkages of lignin and also the cleavage of ether and ester bonds between lignin and hemicellulose (*Norgren and Lindstrom 2000*), thus resulting in less residual lignin content in the obtained pulp fibers (decrease of around 90% lignin content). Thus it can be stated that charge of hydroxide ions, hydrogen sulphide ions, sodium ions followed by cooking temperature and cooking time are important parameter which decide the properties of the final pulp.

(ii). Water retention value (WRV):

Lignin is hydrophobic in nature due to the presence of aromatic groups in network structure (*Hon and Shiraishi 1991*). WRV of the samples (wood and pulp) was measured to assess the approximate removal of the lignin during kraft cooking. The more is the removal of lignin, higher the cellulose% and thereby higher the WRV of the sample. Since the amount of lignin% is almost similar in heartwood and sapwood, the WRV of both the wood samples are almost equal as shown in Table 2.1. However an increase in WRV for both heartwood and sapwood pulps is observed because during the pulping process, lignin degradation (cleavage of linkages between phenyl propane units) or fragments of the lignin network structure is commonly seen with a constant generation of free hydroxyl groups that increases the hydrophilicity. Due to the above reasons, the pulp fibers having negligible residual lignin content due to effective removal of lignin constituents from wood cell interfaces exhibited greater porosity resulting in higher WRV. Water retention value of unbleached pulp was reported in the range of 0.877 to 1.276 *(Mayr 2017)* or 1.77 ± 0.053 to 1.84 ± 0.031 *(SCAN-C 62:00).*

(iii). Ash test:

Ash is an indication of amount of inorganics present in the sample. The ash % in wood is in the range of 0.5 to 3.1% *(Fengel and Wegener 1989).* The elements in the wood ash are calcium, potassium, magnesium and silicon based on the species. Sulphur, phosphorus and manganese are also present in few species (*Hon and Shiraishi 1991*). The ash content value of heartwood and sapwood before and after delignification remained almost same as shown in Table 2.1. The initial mass loss of wood (during the ash test) is generally observed at temperatures lower than 200°C, which is due to the evaporation of water and organic solvents. The mass loss observed at temperatures over 500^{o}C is due to the decomposition of carbonates of both calcium and potassium.

At 500-600^{o}C, wood ash mainly consists of $CaCO_3$ and $K_2Ca(CO_3)_2$ *(Misra 1993).* With increase in temperature; the mass of sulphur, sodium and potassium decreases. The nitrogen content in wood ash is normally insignificant due to the conversion of most of the wood nitrogen to NH_3, NO_x and N_2. After the ash test, it is observed that the pulp ash colour (white appearance) is similar to wood ash *[It is stated that the amount and type of minerals left in ash account for its colour i.e. in white ash, all the carbon has converted to CO, CO_2 leaving only inorganics]*. This phenomenon could be due heavy deposition of inorganic constituents on the fiber surfaces causing differences in lignin reactivity during the incineration process thereby resulting in white colour appearance (if surface oxidation happens then ash colour turns to black colour). Although pulp contains slightly more inorganics than wood due to the formation of lignosulfonates its lower residual lignin content resulted lower ash values (closer to wood ash values) as shown in Table 2.1. Since wood and pulp are of the same sizes (around 2 mm) incineration rate would remain same assuming pores size distribution has negligible effect in incineration.

(iv). FTIR analysis:

In the fingerprint region (Fig 2.6) the spectrum containing many bands assigned to main wood components is observed. The bands at 1595 cm^{-1} and 1507 cm^{-1} are assigned to characteristic stretching or occurrence of aromatic structures of lignin. The bands centred at 1426 cm^{-1}, 1375 cm^{-1} and 1160 cm^{-1} are assigned to characteristic bending or stretching vibrations of different functional groups for lignin and cellulose. The presence of the peak at 1735 cm^{-1} in the FTIR spectrum of raw wood is due to characteristic of carbonyl stretching of unconjugated ketone and carboxyl groups of hemicellulose and lignin. Such peak is not observed in FTIR spectra of pulp samples, except as a low intense peak for 2000 µm heartwood pulp (Fig 2.7). The relative intensity of peaks between wood and pulp are also quite different i.e. the band intensities have considerably reduced in pulps. Therefore these observations qualitatively summarize that, wood has higher residual lignin than pulp, but cooking after size reduction has decreased the residual lignin content.

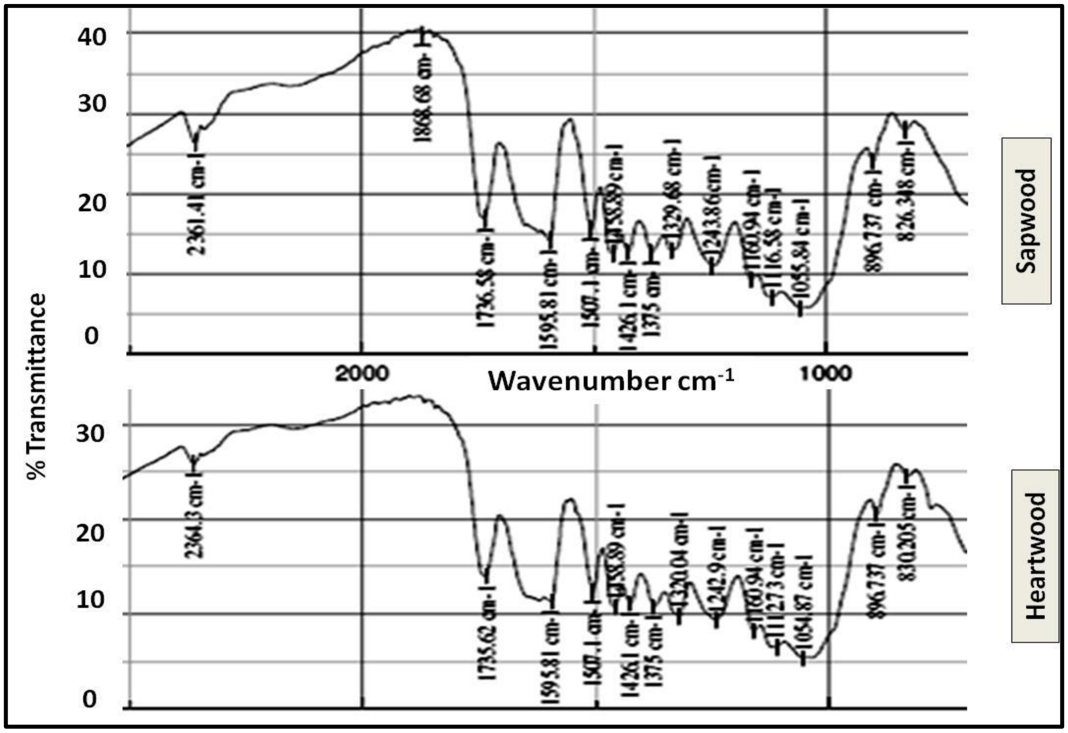


Fig 2.6: FTIR Spectrum of heartwood and sapwood samples

[Note: Peaks in the region 900-1800 cm^{-1} are characteristic of lignin]

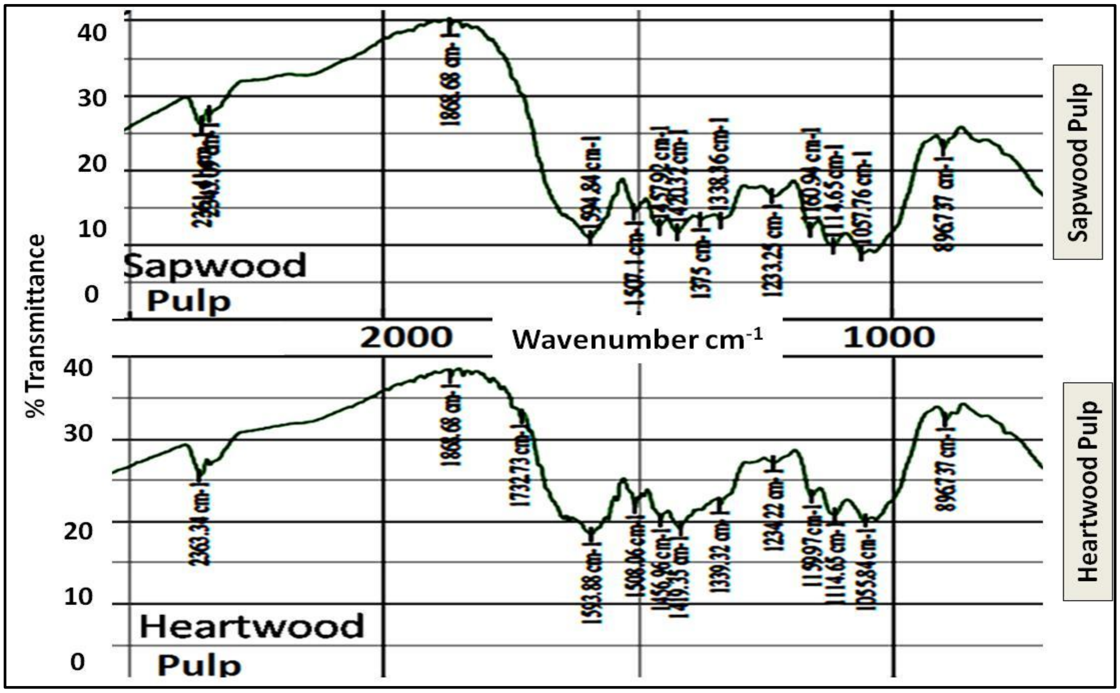


Fig 2.7: FTIR Spectrum of heartwood and sapwood pulp samples

(iv). Microscopic analysis:

The pulping process opens up the lignin rich cell interfaces (middle lamella) which enables the separation of wood fibers and also it loosens up the cell wall structures. Cleavage of the glycosidic bond is promoted under high alkalinity conditions which leads to a decrease in the degree of polymerization of cellulose (3500 to 600-1500) and also reduces the length of resulting fibers *(Shinoda et al. 2012)*. In this regard, the pulp images (Fig 2.8) give the impression of middle lamella degradation and in few cases, cells are fragmented to cell wall dimensions (appr. 30-40 µm). Higher flexibility, fiber deformation/splits, fibrillation on the fiber surface, tapered ends etc are also observed from the obtained pulps. Also 45^{o} shear fracture can be seen in few sapwood pulps. Fiber deformation is beneficial to some of the paper properties i.e. curly fibers develop a paper of low tensile index, but may lead to high tear index due to uneven distribution of stresses along the length of a curled fiber in a fracture-zone *(Page et al. 1985)*. Also, a clear visibility of ray parenchyma cells that act as a bridge between the phloem and the xylem, where water and metabolites pass through the meristematic cells *(Pfautsch et al. 2015)* of the vascular cambium can be observed on the surface of the sapwood pulp fibers.

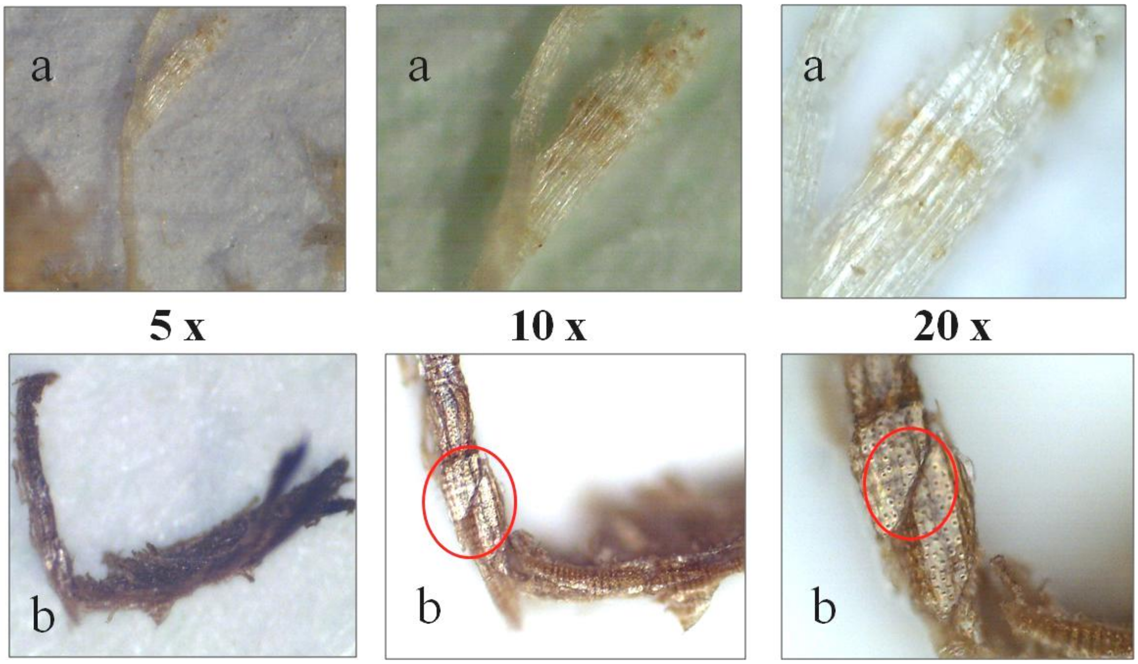


Fig 2.8: Optical microscopic images of (a). sapwood and (b). sapwood pulp fibers
[Note: chip size 425µm; the red circle indicates fracture in the pulp fibers]

2.3.2. *Influence of chip size on sapwood pulp and heartwood pulp characteristics*

By maintaining the reasonable sulfidity level (30%) and varying the wood chip size, the characteristics of heartwood pulp and sapwood pulp were studied separately after kraft pulping. More specifically, the aim is to observe a possible amplification or a clearer pronouncement of the differences in delignification of heartwood and sapwood of a particular species given that the delignification was carried out at exactly the same reaction conditions for both. In line with the hypothesis, such differences were more clearly observed for a smaller size of wood sample, owing to improved chemical impregnation and availability of a larger surface area for the delignification reaction to occur. This difference was observed in all the test results i.e. klasons lignin content, water retention value, ash content, FTIR spectroscopy, microscopy and SEM analysis.

(i). Klasons lignin estimation:

From the test, it was found that the amount of total lignin present in heartwood (25.4 %) and sapwood (26.8 %) is almost equal as shown in Table 2.1. For the same Kraft cooking conditions, the amount of residual lignin decreased with increase in size in both heartwood and sapwood pulps (Table 2.2).

Table 2.2: Total residual lignin content of pulp measured through Klason lignin technique

Sample Size (µm)	Sapwood pulp (%)	Heartwood pulp (%)
2000	1.487± 0.04	3.785± 0.04
1000	1.364± 0.06	2.930± 0.02
600	1.133± 0.04	2.865± 0.02
425	0.931± 0.02	2.768± 0.04
300	0.652± 0.01	2.522± 0.03
150	0.529± 0.03	2.373± 0.01

This is an indication of better delignification due to increased surface area which is leading to better chemical impregnation through the CML (compound middle lamella) and cell walls. When the residual lignin was estimated in the delignified pulp samples, it was clearly seen that the amount of residual lignin was overall higher for heartwood pulps (2.4–3.8%) when compared with sapwood pulps (0.5–1.5%) indicating better delignification in sapwood than in heartwood across all sizes. This can be due to the blockage of vessels with tyloses in heartwood, because vessels with large lumen are known to improve the diffusion of the white liquor during cooking. It can also be due to the ray parenchyma cells present in the heartwood which may have much amount of phenolic extractives. Tyloses are balloon like structures formed due to the growth of adjacent parenchyma cells through the pit (*Bamber 1976*). Sapwood contains high amounts of mono and disaccharides along with polysaccharides and almost free from tyloses and phenolic extractives. It is also assumed that bonding is relatively stronger between cellulose fibrils and continuous phase of lignin (matrix) in heartwood compared to sapwood, causing the decrease in the delignification rate of heartwood. *[Generally, the residual lignin (0.5-4%) is removed in series of bleaching stages because lignin is strongly interlinked with cellulose fibrils as a continuous phase in the cell wall resembling a matrix phase in unidirectional composite.]*

(ii). Water retention value (WRV):

Since the amount of lignin is similar in heartwood and sapwood, the WRV of the raw heartwood and sapwood are also same across all sizes as shown in Table 2.3. However, it observed that though the WRV increases for both heartwood and sapwood pulps due to the removal of lignin, the percentage increase for sapwood is higher than heartwood (for all chip sizes). This could be due to the differences in their residual lignin content of the pulp. Among the wood samples, the increase in WRV is much higher for sapwood (0.84 –3.06) than heartwood (0.85–2.33) in the case of 150 µm size particles. When the WRV results are compared with residual lignin (%) values shown in Table 2.1, it can be concluded that the difference is WRV is due to the difference in residual lignin content. In general, higher lignin removal from the wood results in increase of cellulose percentage of the pulp, which in turn results in higher WRV.

Table 2.3: Water retention value (WRV) of wood and pulp measured by using centrifugal method

Sample (μm)	WRV (Wood)		WRV (Pulp)	
	Sapwood	Heartwood	Sapwood	Heartwood
2000	0.826±0.01	0.811±0.02	2.881±0.01	2.241±0.07
1000	0.829±0.03	0.807±0.02	2.906±0.02	2.262±0.01
600	0.822±0.02	0.813±0.03	2.954±0.04	2.279±0.02
425	0.827±0.02	0.820±0.04	2.998±0.03	2.290±0.03
300	0.829±0.01	0.832±0.05	3.033±0.02	2.304±0.04
150	0.840±0.05	0.849±0.05	3.061±0.02	2.333±0.05

Hence, after the pulping process, sapwood has exhibited higher degree of surface fibrillation and greater porosity due to removal of lignin from cell interfaces and thereby resulted in higher water retention values. Therefore the results indicate that the differences observed could be a direct or indirect reason for the relative difficulty in the delignification of heartwood portion of the log.

(iii). Ash test:

The percentage of ash content is higher in sapwood pulp than in heartwood pulp irrespective of size (Table 2.4). This is consistent with earlier studies for similar species (*Mariani et al. 2005).* Since heartwood contains less living matter than sapwood, the ash content is an indication of the amount of inorganic substances, which is expected to be higher for sapwood pulp than for heartwood pulp. The lower lignin content and high amounts of inorganics enable SW pulp to incinerate better than HW pulp resulting in high ash content. During the conversion of sapwood into heartwood, extensive translocation of chemical compounds occurs, while sugars and macronutrients (N, P, K, Ca and Mg) are removed from senescing sapwood rings (*Meerts 2002*).

Table 2.4: Ash content of pulp measured by keeping samples in muffle furnace at 525°C (~3hrs)

Ash Content of Pulp (%)		
Sample Size (μm)	Sapwood pulp	Heartwood pulp
2000	0.403± 0.009	0.165± 0.001
1000	0.419± 0.009	0.162± 0.002
600	0.425± 0.004	0.165± 0.001
425	0.430± 0.002	0.168± 0.002
300	0.438±0.001	0.171± 0.002
150	0.443± 0.002	0.173± 0.006

(iv). FTIR analysis:

From the FTIR spectra of wood and delignified heartwood and sapwood pulps of sizes 425 μm (Fig 2.6 and 2.9) and 2000 μm (Fig 2.7), the absorption peak at 3400 cm^{-1} due to the OH stretching and peak at 2920 cm^{-1} due to the C–H stretching in methyl and methylene group of lignin and extractives were observed in all FTIR spectra's (not shown). The absorption peak at 2360 cm^{-1} corresponds to the lignin is observed in 2000 μm pulp, but no such peak is observed in 425 μm pulp samples indicating that size reduction has improved the delignification process. In the fingerprint region of 900-1800 cm^{-1} many absorption bands related to various functional groups of lignin are observed. The band around 1593 cm^{-1} and 1420 cm^{-1} representative of aromatic skeletal vibrations is present in all FTIR spectra's. The bands for aromatic skeleton vibrations assigned at 1508 cm^{-1} are very prominent in all spectra except for sapwood pulp (sharp peak is not evident) of size 425 μm which have 0.9% residual lignin.

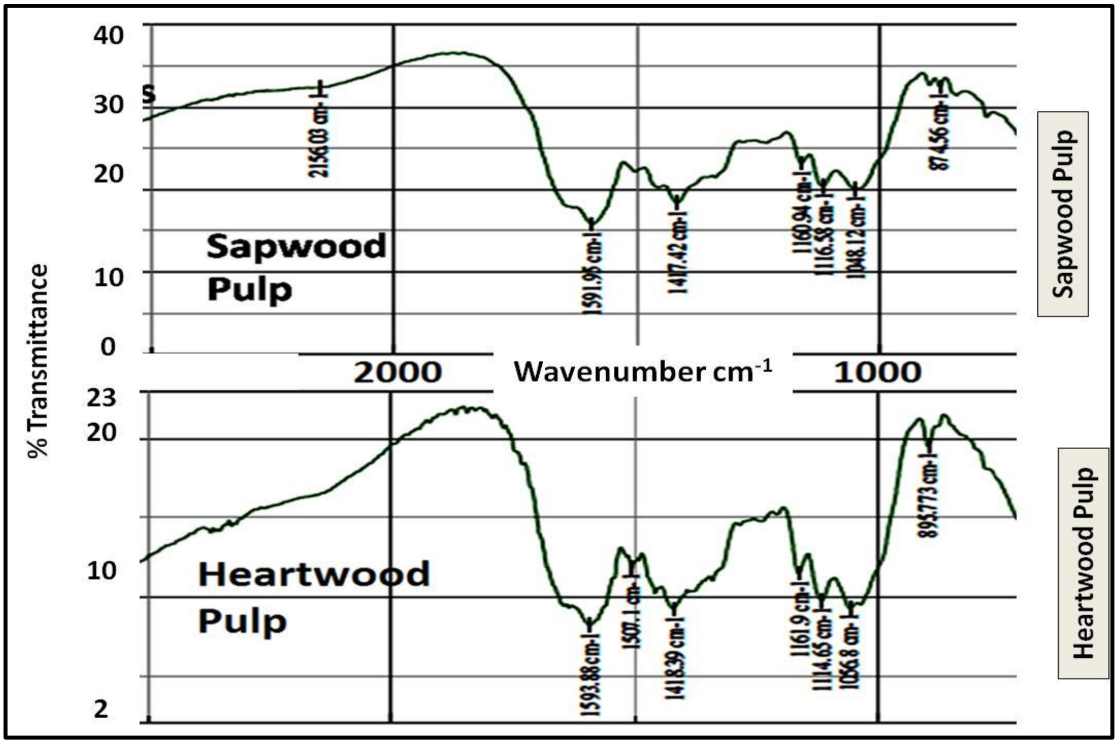
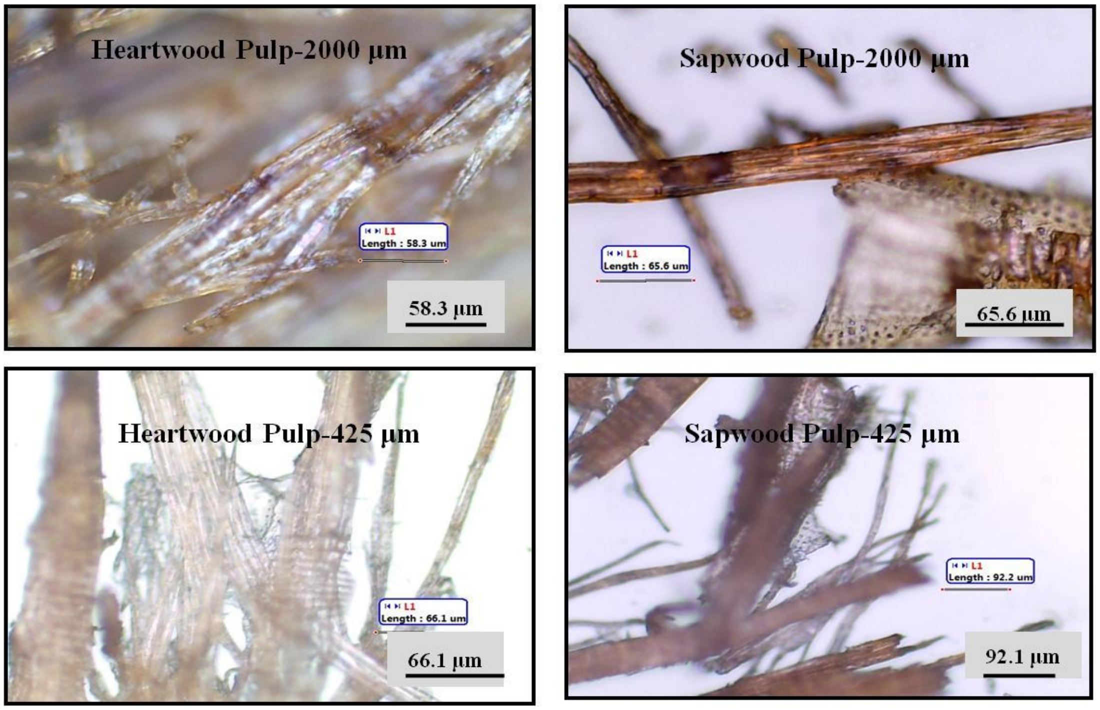


Fig 2.9: FTIR spectrum of the residual lignin in pulp samples of size 425 µm

The band around 1460 cm^{-1} representative of C–H deformations (asymmetric) is absent again in sample size of 425 µm (for both heartwood and sapwood). The band around 1339 cm^{-1} and 1234 cm^{-1} representative of syringyl ring breathing with CO stretching is also absent in sample size of 425 µm (for both heartwood pulp and sapwood pulp). This confirms the fact, that the size reduction improves the delignification capacity of the wood, because lignin is removed not only from CML (compound middle lamella) but also from the cell wall. The band around 1160 cm^{-1}, 1114 cm^{-1} and 1055 cm^{-1} representative of aromatic C–H in-plane deformation is present in all spectra's shown in Figs. 2.6, 2.7 and 2.9. The band around 890 cm^{-1} representative of aromatic C–H out-of-plane deformation is present in all FTIR spectra's, but intensity is low for sapwood pulp indicating the easier removal of lignin in smaller size (425 µm) sapwood samples.

(v). Microscopic analysis (optical and scanning electron microscopy):

The flexibility coefficient is directly governed by fiber diameter. The fiber flexibility enhances the area for bonding among fibers due to better fiber collapsing and improves all the mechanical properties like burst index, tensile index etc. A better separation of fibers and tracheids, revealing higher delignification rate are evident in sapwood pulps (Fig 2.10) compared to heartwood pulps.


Heartwood Pulp-2000 µm

Sapwood Pulp-2000 µm

Heartwood Pulp-425 µm

Sapwood Pulp-425 µm

Fig 2.10: Optical images of heartwood and sapwood pulps of different sizes

Also, vessels of 60-65 µm width which mainly consist of starch deposits or minute quantities of guaiacyl residues of lignin, libriform fibers of appr.15-18 µm width are observed in sapwood pulps. In heartwood pulps, the network looks denser i.e. libriform fibers (appr. 58 µm) are not well separated compared to sapwood pulp. Cluster of fiber bundles, kinks followed by slight fiber peeling on surface area is prominent in heartwood pulps. Fiber kink is described as an abrupt change in the fiber curvature. Kink affects the wet strength of the paper and these dislocations reduce the bending stiffness of fibers significantly. The images also confirm better separation of cells (fibers) in 425 µm pulp fibers than 2000 µm. For visual characterization of the fiber surface structures and to confirm the information obtained with optical microscopy the pulp fibers were also studied by SEM. Figure 2.11 represents the SEM analysis of heartwood and sapwood pulps in which the microfibrils, layering the surface structure measuring with an average fiber diameters ranging from appr. 32-40 µm is observed. In sapwood pulp, the fibers tend to be more flexible and conformable *(Geneo 1999)* due to both external and internal fibrillation. Also, due to degradation of middle lamella, longitudinal de-adhesions of microfibrils has occurred that resulted in a clear visibility of conducting vessels and parenchyma cells. Whereas in heartwood pulp, clustered aggregates of fibers and fines were observed along with the re-oriented fiber axis direction forming kinks.

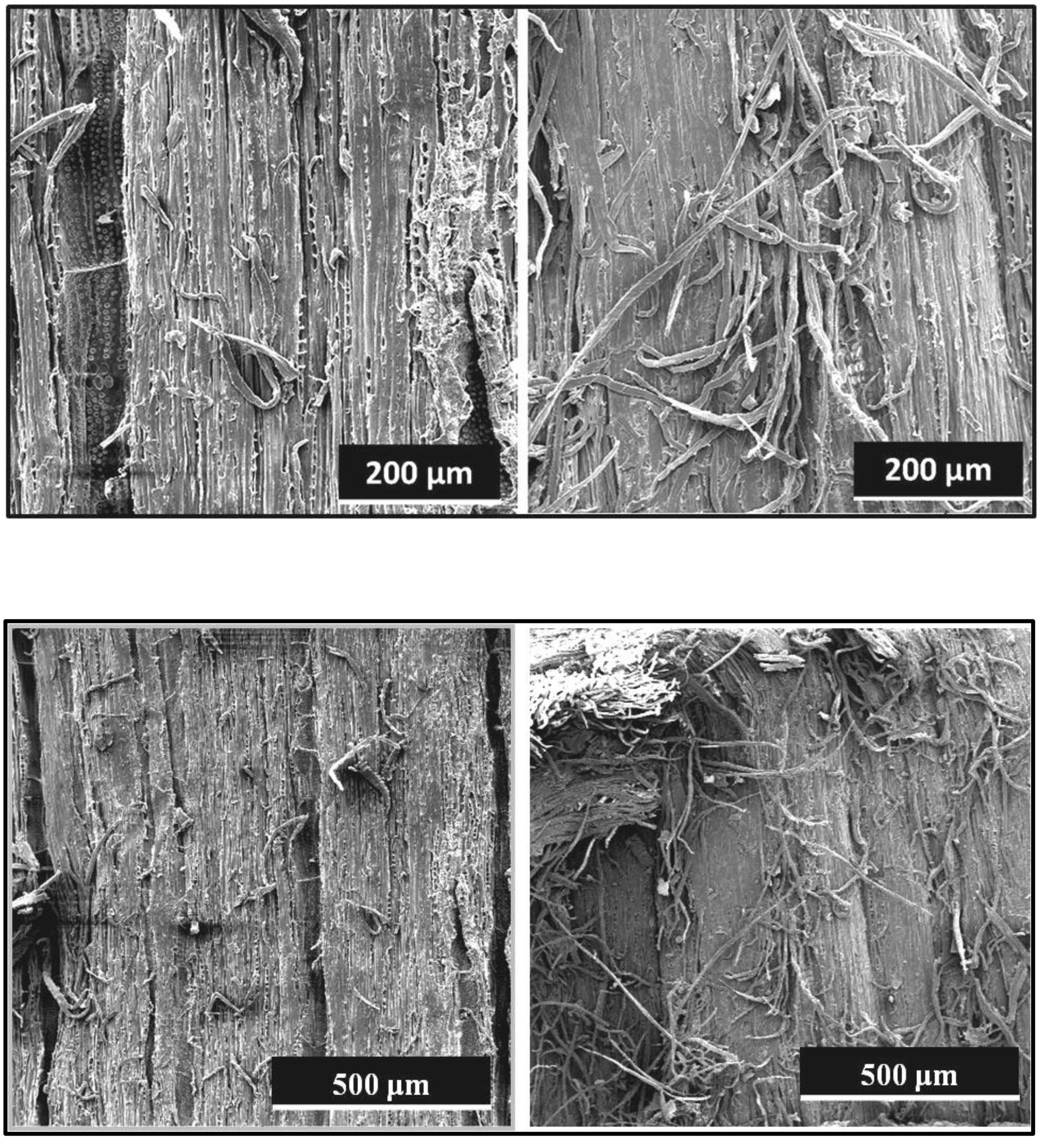


Fig 2.11: SEM images (tangential plane) of sapwood pulp (left) and heartwood pulp (right) of Eucalyptus.

2.4. CONCLUSIONS

- Most of the earlier research works focused on the negative effect of heartwood on delignification of the total wood but not on heartwood pulp in particular. Here heartwood and sapwood (chip size 425-2000 µm) are cooked at 170°C, 2hrs separately and their pulp characteristics were studied.
- From the experimental analysis, it can be concluded that though the amount of lignin is almost same in heartwood and sapwood for the given species, it is difficult to remove lignin from heartwood than from sapwood. This could be due the blockage of vessels and accumulation of secondary compounds in heartwood. Hence pulp mills can prefer the choice of cooking the heartwood and sapwood separately.
- From pulp analysis, the amount of residual lignin was higher for heartwood pulp (2.4-3.8%) than sapwood pulp (0.5-1.5%) indicating better delignification in sapwood cell interfaces and cell walls. Similarly the increase in water retention value is higher for sapwood pulp (0.84 to 3.06) than it is for heartwood pulp (0.85 to 2.33) due to the differences in their residual lignin content. The amount of ash is higher in sapwood pulp (0.44-0.4%) than in heartwood pulp (0.17-0.16%). Since heartwood contains less living matter than sapwood, the ash content i.e an indication of the amount of inorganic substances is expected to be higher for sapwood than for heartwood.
- The microscopic images revealed tracheids and fibers indicating better separation i.e higher delignification rate in sapwood pulps. Whereas cluster of fiber bundles and kinks were prominent in heartwood pulps. From FTIR analysis, the intensity of aromatic C-H out of plane deformation band around wavelength 890 cm^{-1} is considerably low for sapwood pulp than heartwood pulp. Therefore, it can be concluded that separation of heartwood and sapwood prior to delignification process yields better results.
- Based on the results it is also observed that chip size had a significant effect during pulping process i.e the amount of residual lignin (i.e. SW: 0.5-1.5%; HW: 2.4-3.8%) increased with increase in size (150-2000 µm) due to which the WRV was also found to be much higher for 150 µm size pulps. From FTIR analysis, the absorption peak at 2360 cm^{-1} corresponding to lignin is not observed in 425 µm pulp samples (unlike 2000 µm) indicating that size reduction has improved the delignification process. Hence, the above studies confirm the relative difficulty of delignification with increase in chip size and therefore selection of proper chip size is utmost important to achieve an optimum pulping performance.

CHAPTER - 3

Effect of Temperature on Sapwood and Heartwood Pulp Fibers

3.1. INTRODUCTION

In India, *leucaena leucocephala* commonly known as Subabul is considered as an ideal source for paper making. It is a very fast growing tree with fiber lengths 0.5 to 1.5mm, fiber diameter of 24.2 µm and cell wall thickness of 5 µm. It has been reported that Subabul can produce around 24-100 m^3/ha of wood per year (*Thomas et al. 1983*). As a pulpwood, subabul is among the best tropical hardwoods. The pulp is high in holocellulose and low in silica, ash, lignin, alcohol benzene solubles and hot water solubles. Subabul is highly consumed by the Indian paper industry. JK Paper Limited (leading manufacturer in India) covered 17,000 ha area under subabul plantation in 2016-17 (*report by Agarwal 2017*). Similarly intensive efforts mounted by paper mills including ITC Limited (leading manufacturer in India) have influenced plantation on about 900,000 ha all over India covering majorly Subabul, Eucalyptus and Casuarina which is meeting the demand of 9.83 million tonnes of wood by Indian paper industry. The species is also known by many different names in other parts of the world i.e Huaxin (Native America), ipil-ipil (Phillipines), White lead tree (Australia, USA), Guaje (Spain, Mexico), Yin-hue-whan (China), Reuse-wattle (South Africa) and Lamtoro (Indonesia). Capitalizing of common nouns has been rectified. Subabul wood is commonly used in producing dissolving grade pulp which is further used in the production of viscose (rayon) fibers where high quality cellulose pulp is needed.

The conventional softwoods and hardwoods used as raw material by paper and fiber based industries are depleting day by day. Grasim Industries (India) is now importing rayon grade pulp from Canada to produce viscose fiber in its plants in India. In this regard, the State and Central Governments have laid much emphasis on cultivation of multi-purpose fast growing tree species to bridge the short fall of raw materials (*Kirpal et al. 2006*). Pioneering research work has been carried out by the paper industry over the last three decades in promoting Eucalyptus and Subabul as pulpwood species. Subabul known for diversified uses has been taken for amenity planting in marginal, sub-marginal and rangelands. In the previous chapter Eucalyptus was used to study the effect of chip size on pulp characteristics and now Subabul (commonly used hardwood species for papermaking in India) was taken to study the effect of three different temperatures on pulp characteristics using almost same chip size.

Knowledge of delignification kinetics underlies improvements in kraft cooking and bleaching. The main aim of paper manufacture is to remove lignin from wood either by mechanical or chemical methods. Chemical process (Kraft process) involves effective removal of lignin from cell interfaces i.e compound middle lamella (CML) and also from cell walls (partly). The kraft process which uses NaOH and Na_2S has three distinct stages: the initial (ID), bulk (BD) and residual (RD) delignification phases. During the *ID stage*, wood chips are impregnated with cooking liquor and the temperature is elevated upto 140^oC. At this stage 15 - 25% of the total lignin is removed but the selectivity is low. In *BD stage* cooking temperature exceeds 140^oC, accelerating the depolymerization of lignin present in the middle lamella and partly from cell wall due to which approximately 90% of the total lignin is removed from chips. During the residual delignification stage, the depolymerization of cellulose increases notably and delignification decreases i.e. ~only 10% of the lignin (based on the residual lignin content present at the beginning of the residual delignification) is removed. Hence it can be stated that the pulping conditions greatly affect the residual lignin and cellulose content of the pulp. The temperature has a great effect on the lignin and high cooking temperature degrades more lignin, creating more free phenolic hydroxyl groups thus affecting the pulp properties such as cellulose and lignin contents. Therefore, this chapter focuses on influence of temperature (140^oC, 155^oC and 165^oC) on Subabul wood chips (Heartwood-HW and Sapwood-SW separately) during the kraft cooking. This study was conducted to provide a comprehensive collection of process parameters required for Kraft cooking to optimize the reactions so as to avoid the wastage of valuable materials, chemicals and energy. Characterization of pulp allows for easy comparisons at different temperatures. To simplify the cooking process and to estimate the parameters during pre and post cooking; a modelling tool was also developed based on experimental work considering two different temperatures (140^oC and 165^oC) and Subabul heartwood-HW and sapwood-SW.

3.2. MATERIALS AND METHODS

3.2.1. Chipping and pretreatment of sapwood and heartwood

The raw material Subabul wood used in this study was obtained from Kandukoor area, Ranga Reddy District, Hyderabad, India. The log selected was 7-8yrs of age and was cut 3ft above the ground level and it was 1m length and 20 cm in diameter. Around 60 % of the inner cross-sectional area was considered as HW and the remaining is considered as SW (Fig 3.1a). SW and HW were separated using a wood turning machine and were further cut down to chips of 20 x 20 x 2.5-3mm^3 dimensions (Fig 3.1b) with the help of a chisel. In normal use the moisture content of wood varies between 8% and 25% by weight, depending on the how green the wood and also depends on the relative humidity of the air. So to remove the bound moisture, the wood chips are dried at 103.5ºC in hot air oven (OSWORLD OOG-90). Both SW and HW chips were considered as two different raw materials in this study. The chips (HW and SW) were subjected to pre-treatment process at 120ºC for 1hour in an autoclave (Metalab MSI-41) to soften the lignin present at middle lamella (CML) and also to remove the organic extractives. Steaming at 120ºC also enables the chips to be more accessible to white liquor by creation of pore channels due to the removal of trapped air and it also enables better impregnation of white liquor during the cooking.

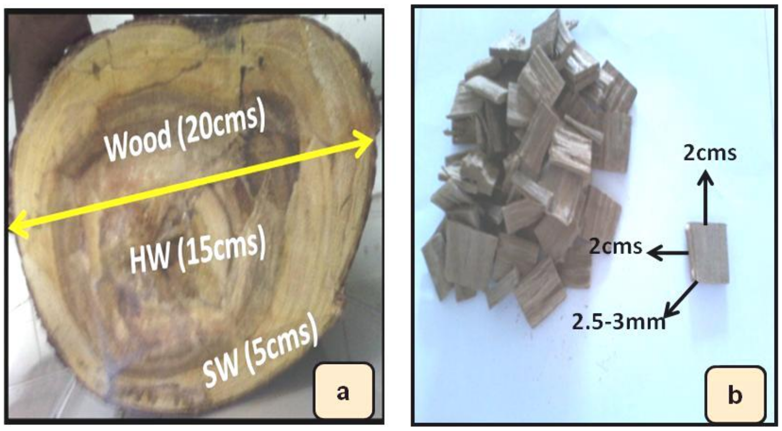


Fig 3.1: (a). Cross-section of Subabul wood log revealing heartwood (HW) and sapwood (SW); (b). Wood chips prior to kraft cooking process.
[Chips shown are pretreated with steam at 120ºC for 1 hour]

3.2.2. Kraft cooking of wood chips at 140 °C, 155 °C and 165°C

The delignification process was carried in Rotary Pulp digester (Fig 3.2) which is designed by Universal Engineering Corporation, Saharanpur, U.P, and India. The digester with 10 lit capacity is a pulping unit for producing pulps by cooking wood chips is normally used in pulp mills for preliminary studies. It features precise control of cooking variables such as temperature which ensures good repeatability of results.

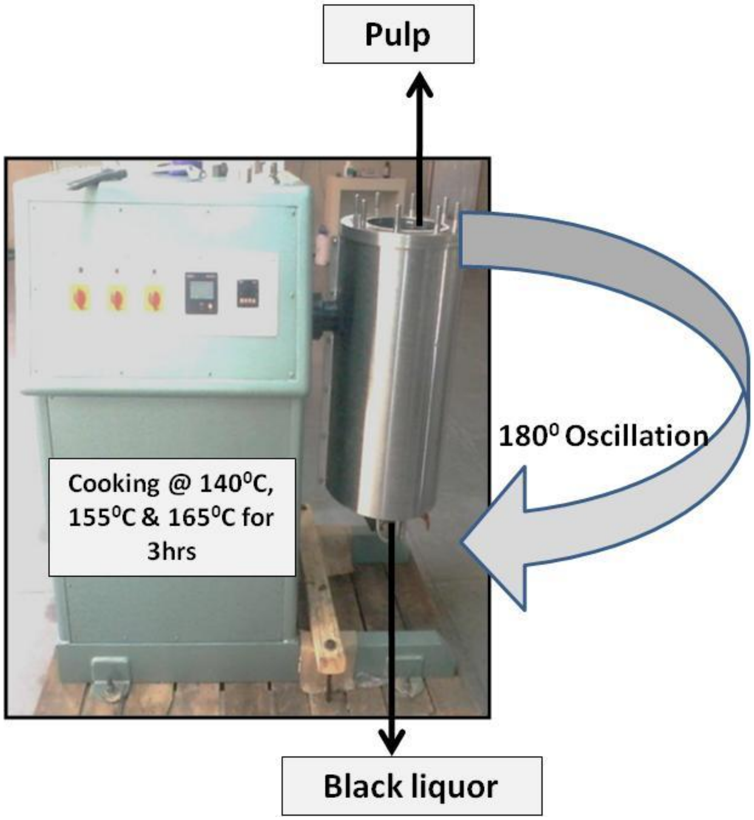


Fig 3.2: Rotary pulp digester was used for kraft cooking of wood chips at three different temperatures (140, 155 and 165°C)

Digital temperature indicator cum controller precisely controls the temperature range upto 200°C. The working pressure of the digester is 10 kg/cm^2. The rotation (180° rotation; 3 rpm) with change in turning direction provides efficient agitation to the cooking slurry. The digester body is made of acid proof steel and the exterior body is fabricated from stainless steel sheet. The equipment includes six elements placed on the digester body i.e. energy regulator, thermostat and necessary circuit breakers. On digester head, there is a pressure gauge, dial thermometer, de-gassing and safety valve.

The digester is brought to vertical position by turning the knob on the motor switch panel to “ON” position. The lid is separated from the digester by opening the bolts with the help of the supplied spanner. Since the lid is equipped with pressure gauge and safety valve it is carefully placed on side table. The reaction mixture of white liquor and wood chips are loaded in the digester from the top. The teflon gasket is cleaned to avoid leakage and then the lid or digester head is placed on the autoclave after which the bots are tightened. The degassing valve on top and sampling valve at the bottom are closed and the heater is switched “ON”. The wide rotation of the digester facilitates for better impregnation of cooking chemicals into the cell walls (5-8 µm thick) of the wood chips.

1kg of oven dried wood sample is subjected to cooking with wood: liquor ratio of 1:4, 28% Sulphidity (Na_2S and NaOH expressed as Na_2O) and 20% active alkali (as Na_2O). HW and SW chips are cooked separately for 3hours at temperatures 140^oC, 155^oC and 165^oC (pressure in between 5 to 8 bar). After 3hrs of pulping process, the digester is brought back to vertical position by turning “OFF” the digester and slowly releasing the gas and steam to lower the digester pressure from maximum to the blow pressure by slowly opening the de-gassing valve. The black liquor is collected from bottom and the pulp is separated from the black liquor by removing it from the top. Pulp is thoroughly washed with deionized water for 5-6 times to remove the residual black liquor adhered to the surface of the pulp fibers. During washing, filtration process is carried out using a cotton cloth to avoid the loss of fines. From the retentate (pulp), knots and uncooked chips (approximately 20-30% for 165^oC and 40-50% for 155^oC) are separated manually by handpicking. For 140°C, cooking did not progress to the thickness direction, so majority of the chips are considered as uncooked chips. The wet pulp samples obtained after filtration are dried at 103.5^oC in hot air oven for 12hrs prior to characterization. *[Note: For 155^oC, the wood chips are soaked for 1hr with white liquor in the digester before the 3hr cooking process]*.

3.2.3. *Analysis of wood and pulp*

The oven dried wood and pulp samples (HW and SW) obtained before and after kraft pulping process were analyzed using various characterization techniques such as: Klason lignin content, Cellulose isolation test, Water retention value-WRV, Ash test, Fourier Transform Infrared (FTIR) Analysis, Optical microscopy and Thermogravimetric Analysis-TGA. The results obtained are compared to understand the impact of the process parameters (temperature and time) on HW and SW separately. Here time indicates collection of black liquor after 1 hr, 2 hr and 3 hrs and not the pulp because digester can't be opened until cooking is completed i.e 3 hrs. Characterization of black liquor collected at different time intervals is discussed in Chapter 5.

(i). The experimental procedures for Estimation of Klasons Lignin Content, Determination of Cellulose Content in Pulp, Estimation of Water Retention Value, Estimation of Ash/inorganic Content, FTIR Analysis, Microscopic Analysis was discussed in Chapter 2 and also described in the publication ***(Madhuri et al. IPPTA - Indian Pulp and Paper Technology Association - The Official International Journal., 28, 130, 2016)***. For the imaging of wood and pulp samples, Stereo microscopy (OLYMPUS SZ17) equipped with 2.5 and 5X magnifications and optical microscopy equipped with 5X, 10X, 20X and 40X are used in both reflectance and transmittance modes.

(ii). Thermogravimetric analysis (TGA)

Thermogravimetric (SHIMADZU DTG60) analysis was carried out to determine the thermal decomposition of fibers after cooking. Studies were carried out from 20^{o}C to 600^{o}C at a heating rate of 20^{o}C /min under nitrogen atmosphere. Around 5 mg of HW pulp and SW pulp samples are considered to obtain the %weight reduction with increase in temperature.

3.3. RESULTS AND DISCUSSION

Figure 3.3 represents the ***images*** of oven dried kraft pulp samples (HW and SW) obtained after cooking. It is observed that separation of individual fibers is significant in both HW and SW pulps obtained after cooking at 165°C. Whereas for 155°C pulps, the soaking followed by cooking has resulted pulps of ~ 40% intact chips and 60% individual fibers. These fibers were actually separated during washing due to mechanical shearing and rubbing action by hand. Separation of fibers in vertical direction has occurred because fibers are aligned in vertical direction (longitudinal). These pulp fibers were mostly joined and entangled with each other. The % of uncooked chips is very high in 155°C pulps in comparison with 165°C pulps which indicates that, 155°C was insufficient to remove the lignin from all CML layers.

At 140°C of cooking temperature, the chips are mostly intact as shown in Fig. 3d and 3f indicating insufficient cooking wherein all CML layers are still rich in lignin without any pores which is also observed by *Lourenco et al. 2011*. Fiber peeling on both surfaces and surface fibrillation indicates that middle lamella lignin present on the surface has been degraded, but degradation is not percolated in the thickness direction due to the temperature induced diffusional constraints. Also, longitudinal breakage of chips due to the application of shear force was observed in case of SW pulp. At all the three temperatures, SW exhibited better fiber separation in comparison with HW because SW pulp has less lignin and less extractives compared to HW pulp. From Fig 3.3, it can be stated that the individual fibers are better separated in case of pulps obtained @ 165°C compared to pulps obtained at 140°C and 155°C.

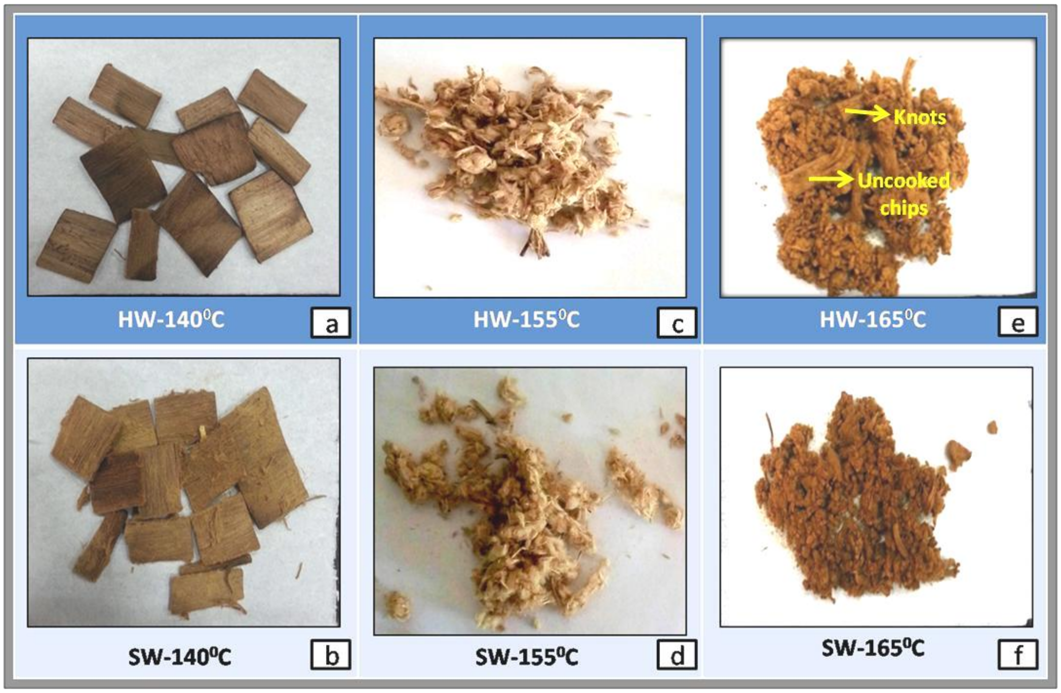


Fig 3.3: Images of pulps obtained after kraft cooking. Note the intact pulp fibers at 140^{o}C (fibers are not separated due to low cooking temperature) (HW-Heartwood and SW-Sapwood)

From pulps obtained at 165^{o}C, in addition to the well separated fibers, short and uncooked knots or specks are also found as shown in Fig. 3.3e. The % of uncooked chips is very high for 155^{o}C in comparison with 165^{o}C (not shown in the picture). As explained for 140^{o}C pulps, all chips are mostly intact and can be considered as uncooked chips.

Normally 140^{o}C temperature is referred as initial delignification stage/ heating up period which is controlled by diffusion. At this phase, removal of lignin only from middle lamella/CML (thickness: 0.2-1.0 µm) may initiate. The temperature is insufficient for the white liquor to reach between and within the cell layers and thereby affects the pulp quality (intact chips). At 165^{o}C, rate of delignification (bulk delignification phase) accelerates steadily with increasing temperature i.e. diffusion of cooking chemicals into the middle lamella/CML of wood chips proceeds at faster rate. The degradation of lignin in the CML region also increases the porosity of the cell wall which in-turn increases the diffusional rate of cooking liquor into the cell walls. At this phase, lignin removal mostly takes place within the cell wall layers i.e. primary-P and secondary layers S1, S3 and mostly from S2. It is difficult to remove the lignin from all the parts of S2 layer because lignin is spread as matrix in the cellulose microfibril-lignin nano-composite. The 155^{o}C represents a phase in between initial and bulk delignification and hence it can be stated that the temperature was not sufficient to reach to the secondary cell wall layers thus resulting in mixed results i.e uncooked chips and fully separated pulp fibers. Therefore it can be concluded that low impregnation of cooking chemicals into wood chips has resulted due to low cooking temperatures and ***hence the rate of delignification is temperature dependent.***

The anatomical and chemical differences between SW and HW often have a significant influence on cooking process and pulp yield. The mass loss of samples during cooking is mainly due to removal of extractives and dissolution of low molecular weight carbohydrates (hemicelluloses) and lignin *(Lourenco et al. 2010).* Since heartwood has high lignin content and ray parenchyma cells which are mostly filled with phenolic extractives, the impregnation of white liquor is difficult in heartwood compared to sapwood.

Yield is the ratio of pulp obtained (unscreened) to the amount of wood (steam pre-treated) used for cooking process. At all the three temperatures SW exhibited higher pulping yields compared to HW. The yield differences were expected, owing to lower cellulose content, higher extractive and lignin content in HW. *Morais et al. 2012* and *Miranda et al. 2007* reported a similar difference in pulp yields of E. globulus heartwood and sapwood. From this study, SW presented 20% higher yield than HW when pulp from

165^{o}C kraft cooking was considered. Similarly SW resulted in 22% higher yield than HW when pulp from 140^{o}C Kraft cooking was considered. But no significant difference in yield content was found when pulp from 155^{o}C kraft cooking was considered. This could be due to the soaking prior to cooking which was not carried for 140^{o}C and 165^{o}C kraft cooking temperatures. For Eucalyptus pulps (*Lourenco et al. 2010)* it is reported that SW has 8 %, 12 % and 14 % higher yield than HW when pulp from 170, 150 and 130^{o}C cooking temperatures was considered respectively. Chip size and pulp drying rates are responsible for the variability in yield difference between HW and SW pulps. But the trend of higher yields for SW compared to HW remains the same.

3.3.1. Comparision between wood and pulp characteristics

The composition differences, temperature variations, cooking time play a vital role in delignification process. To confirm the same, qualitative and quantitative analysis is carried out separaterly for the wood (prior to cooking) and pulp (after cooking) samples. Here pulps and wood chips are characterized for lignin, cellulose, water retention value and ash/inorganic contents as shown in Table 3.1. In this study cooking time of 3 hrs is kept constant and comparison is done between SW and HW and also between temperatures (165^{o}C, 155^{o}C and 140^{o}C). As a result of cooking, the pulp with high cellulose content and high porosity (increased number of small pores in the lignin matrix) with minimal damage to cell wall layers is obtained. A better understanding of kinetics of lignin degradation of HW and SW is important for potential usage of subabul wood in kraft pulping.

Table 3.1: Wood (heartwood and sapwood) chips and pulp characterization data
[Note: For comparison, pulp data from 165ºC cooking is considered]

Sample	**Lignin (%)**	**Kappa Number**	**Cellulose (%)**	**Water Retention Value-WRV**	**Ash / Inorganic (%)**
Heartwood Chips	35.3±0.1	235±0.6	51.4 ±0.2	1.1 ±0.2	1.32 ±0.11
Heartwood Pulp	2.8±0.3	19±2	71.2±1.7	14.3±0.7	29.8±0.3
Sapwood Chips	27.6±0.2	186±1.3	61.8 ±0.1	1.4 ±0.45	1.85 ±0.03
Sapwood Pulp	1.3±0.1	9±0.6	80.1±2.0	17.3±0.2	36.6±0.6

(i). Klason's lignin estimation:

From the results, it was observed that the amount of total lignin present in HW chips is approximately 8-9% higher than SW chips. For the same kraft cooking conditions, the amount of lignin decrease is 92% for HW and 95% for SW in comparison with their respective wood samples. Therefore the kappa number of HW and SW (*with residual lignin content of 2.8% and 1.3%*) is found to be 19 and 9. Generally residual lignin for mechanical pulps is >4% and sulphite pulps is 1-6.7% (for a pulp yield between 50-65%). During pulping process lignin is degraded by the active cooking species which are hydroxide and hydrogen sulphide ions. The depolymerization of lignin is mainly due to the cleavage of β-aryl ether linkages. The degradation products are dissolved and the fibers are separated from each other thus exhibiting less residual content (<4%) in the pulp fibers. The residual lignin in pulps is generally characterized by following features: less β-O-4 linkages; more phenolic hydroxyl groups; lower molar mass; more chromophores and more condensed lignin structures.

(ii). Cellulose content determination:

The cellulose% of both the pulps are significantly higher compared to wood samples as shown in Table 3.1. Total cellulose content of HW pulp is 71.2 % whereas total cellulose content of SW pulp is 80%. It is clear that total cellulose content increases from wood to pulp because of decrease in lignin content. Sulphidity is an important factor that enhances the rate of delignification without affecting the carbohydrates. For 28% sulphidity (maintained during pulping) the initial pH is maintained in the range of 13-14 due to the addition of sodium hydroxide *(Islam 2004).* This leads to degradation of organic extractives (resins, terpenes and phenols) and alkaline hydrolysis of glycosidic bonds (dissolution of lower and higher molecular weight lignin fractions in the phenolic units present at middle lamella and secondary cell wall layers) resulting in less residual lignin content and a higher cellulose % (Fig 3.4) in the obtained pulp fibers.

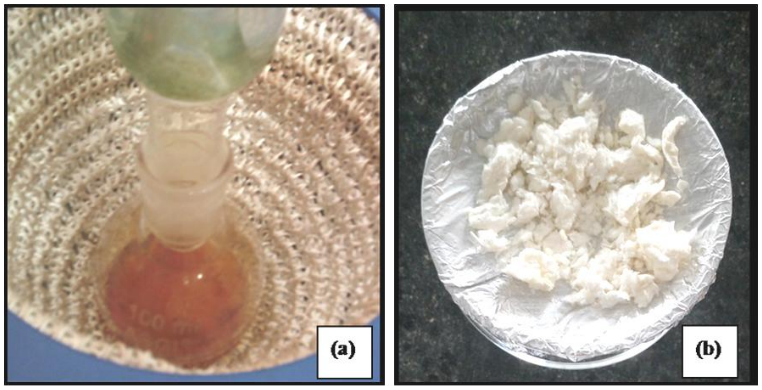


Fig 3.4: (a). Wood pulp sample during reflux; (b). Wood pulp sample after drying.
[Both images were taken as part of the cellulose content determination]

(iii). Water retention value:

Lignin polymer consisting of numerous aromatic groups as a network structure is highly hydrophobic in nature due to which the wood samples (HW and SW) have exhibited less WRV as shown in Table 3.1. Pulps revealed almost 12 fold increase in WRV compared to wood. But during the alkaline pulping process, the nucleophiles-sulphides and bisulphides get attached to the aromatic structure and increases its hydrophilicity. This phenomena depolymerizes the lignin molecule through cleavage of inter-unit linkages, creating numerous void spaces in the cell wall interfaces due to which WRV increases in pulp samples. The ***WRV increases*** because of internal fibrillation i.e. a widening internal pores and delamination's which is called as **"swelling"** along with development of external fibrils (which also serve to hold additional water). In Pulps (having less residual lignin and high cellulose content) water molecules diffuse into the amorphous regions of the cellulose structure and break inter-molecular hydrogen bonds. This allows an increase in the inter-molecular distance of the cellulose chains, which causes fiber swelling. Fiber swelling increases with decrease in lignin content.

(iv). Ash test:

The ash content of wood chips before delignification is 1.32% and 1.85% for HW chips and SW chips respectively as shown in Table 3.1. This could be due to the bulk and continuous structure of wood in which combustion (may be pyrolysis in the cell wall interiors) of cellulose-lignin composite structure happens simultaneously because it continues to decompose above 525^{o}C (*Yang et al. 2007*), whereas decomposition of cellulose ends by 400^{o}C. Generally wood has <2% ash content (*Fengel and Wegener 1989*), so the results shown in Table 3.1 are quite matching with literature and color of the ash is white as shown in Fig 3.5 because only inorganics such as K, Ca and Si are present. Though pulp contains more inorganics (added during cooking), its lower content of lignin (more pores in cell wall matrix) lead to partial combustion resulting in a black colour residue as shown in Fig. 3.5. After combustion, the white colour appearance of wood ash is due to complete oxidation of lignin-cellulose composite after 280^{o}C (*Brebu and Vasile 2010).* Whereas in pulp, the released gases during combustion will act as a protective cover to the remaining sample due to the pores thereby limiting the oxidation reaction which in turn results in partial combustion of the pulp. As shown in Fig. 3.5, the residue is white in colour for ash contents <2% but the residue turns to black colour for ash content above 20 %. This reminds the oxidation of PAN fibers at around 250°C during carbon fiber production, which is a necessary step because oxidation increases the thermally stability by increasing C-C bonds or cyclic groups (turning the white fiber into black fibers).

Fig 3.5: (a). Ash obtained from pulp (b). Ash obtained from wood chips.
[Note the color difference]

(v). Analysis using Fourier Transform Infrared (FTIR) spectroscopy:

The FTIR spectra of wood and pulp are displayed in Fig 3.6 (a and b). The absorption bands in the finger print region of 900-1800 cm^{-1} is related to various functional groups of lignin.

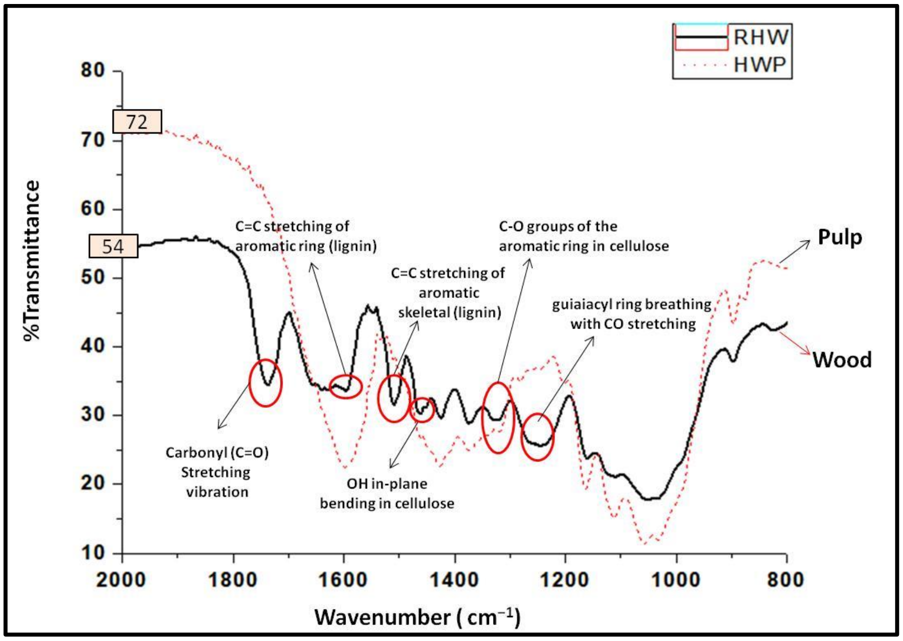


Fig 3.6 (a): The absorption bands from FTIR analysis of wood and pulp cooked at 165^{o}C *(RHW-Raw Heartwood; HWP-Heartwood pulp)*

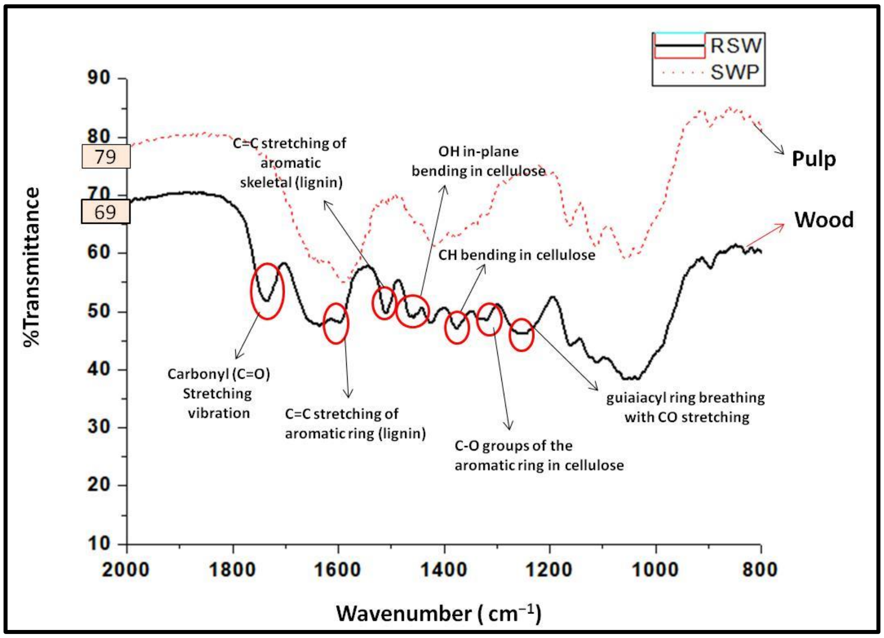


Fig 3.6 (b): The absorption bands from FTIR analysis of wood and pulp cooked at 165^{o}C *(RSW-Raw Sapwood; SWP-Sapwood pulp)*

The following intense peaks are observed only in wood and are relatively absent in pulp spectra. i.e. the presence of 1735 cm^{-1} peak due to the carbonyl (C=O, ester stretching) of the hemicelluloses and lignin; peak at 1593 cm^{-1} due to C=C stretching of aromatic ring (lignin); peak at 1515 cm^{-1} is attributing to C=C stretching of aromatic skeletal (lignin); peak between 1470-1455 cm^{-1} representing OH in-plane bending in cellulose; peaks observed in the region 1317 -1320 cm^{-1} corresponding to C-O groups of the cellulose; a broad peak between 1215-1200 cm^{-1} corresponding to guaiacyl ring breathing with CO stretching; peak at 1375 cm^{-1} representing CH bending in cellulose (observed only in sapwood sample). Therefore based on the percentage transmittance and the lignin peaks, it is confirmed that a considerable amount of lignin has been extracted from the wood cells during kraft pulping with the selected process parameters (165^{o}C, 3hr cooking).

3.3.2. Influence of temperature on heartwood and sapwood pulp characteristics

The chemical and physical analysis of pulps (HW and SW) such as Klasons lignin test, Cellulose isolation test, Water retention value, Ash test, FTIR analysis, Microscopic analysis and TGA are performed to study the influence of temperature. The results thus obtained for the unbleached kraft pulps exhibited significant differences with respect to varying temperatures (140, 155 and 165^{o}C) as presented in Table 3.2.

Table 3.2: Heartwood and Sapwood pulp characteriztion data for different temperatures

Sample	**Cooking Temperature** (^{o}C)	**Residual lignin %**	**Kappa Number**	**Cellulose content (%)**	**Water Retention Value-WRV**	**Ash/Inorganic content (%)**
Heartwood Pulp	140	31.2±0.2	208±1.3	44.5± 1.5	1.4±0.4	21.8±1
	155	9.7±0.3	65±2.1	67±5.2	11.2±0.4	3.4 ± 0.2
	165	2.8±0.3	19±2.1	71.2±1.7	14.3±0.7	29.8±0.3
Sapwood Pulp	140	20.1±0.4	135±2.7	49.1±3.0	1.66±0.4	25.9±0.7
	155	5.6±0.2	38±1.3	75±1	11.6±0.6	5.0 ± 0.3
	165	1.3±0.1	9±0.6	80.1±2.0	17.3±0.2	36.6±0.6

(i). Klasons lignin estimation:

A better understanding of kinetics of lignin degradation of HW and SW is important for potential improvements in Subabul wood pulping process. From the results, a significant difference in lignin% with respect to temperature is observed. The residual lignin content is found to be decreasing with increase in temperature i.e. pulps at 165^{o}C exhibited low lignin% in comparison with 140^{o}C and 155^{o}C. These results can be attributed to the fact that, at 140^{o}C only primary peeling of reducing end groups takes place; whereas at 165^{o}C, the increasing temperature accelerates the reactivity and depolymerization of lignin. In literature *(Willis et al. 1986)* it is reported that the main delignification takes place during the bulk delignification phase, which starts at about 150^{o}C during which lignin is degraded as a result of the alkaline cleavage of the β-O-4 aryl ether linkages. The residual lignin content of 31.2% and 21% for HW pulp and SW pulps at 140°C respectively indicates the negligible delignification in HW chips and slightly better delignification but only from the surface in SW chips. The degradation and dissolution of hemicelluloses at initial delignification phase (140^{o}C) also contributes to the removal of lignin from the cell wall and compound middle lamella during bulk delignification phases (150-165^{o}C). Therefore, as the porosity of cell wall increases, the diffusion of lignin degradation products from the cell wall to the liquid phase becomes easier with increase in temperature. Also from the data, it is observed that HW pulps have exhibited higher residual lignin than SW pulps for all three temperatures; confirming higher delignification rate in case of SW than HW. This observation could be attributed to the fact that, HW has ray parenchyma cells which are mostly filled with phenolic extractives *(Bamber 1976)*, which will have a negative impact during pulping by increasing chemical consumption and affecting process performance e.g., pitch deposits *(Lourenco et al. 2010, Miranda et al. 2007).* So it is necessary to cook the wood chips upto 165^{o}C, so that kappa number in the range of 8-16 is reached which is acceptable for bleaching.

(ii). Cellulose content determination:

This test is performed to understand the effect of temperature on polysaccharides (mainly cellulose) in which carbohydrates are degraded due to peeling and hydrolysis. From the attained data it is observed that the cellulose content of pulps is higher for 165^{o}C pulp and lower for 140°C pulp. Around 63% and 60% increase cellulose was found for SW and HW pulps respectively with increase in temperature from 140°C to 160°C. This is because pulping at 140°C (initial delignification stage) corresponds to the removal of extractives, acetyl groups and uronic acids from hemicelluloses as well as to a partial dissolution of lignin by cleavage of α and β-aryl ether linkages in the phenolic units at middle lamella whereas at 165°C (bulk delignification stage) most of the lignin at S2 cell wall layer is dissolved and alkaline hydrolysis of glycosidic bonds also takes place. Cellulose % in pulps has increased not because of increase in cellulose quantity rather it is due to decrease in lignin% in pulps. During cooking lignin is degraded or depolymerized as explained in above sections. Therefore it can be stated that higher the lignin removal, higher will be the cellulose% (in pulp) and the obtained results are reflecting this fact because cellulose and lignin are intermingled and intertwined in cell wall layers. The results also indicate that the %Cellulose of SW is significantly higher than HW at all the three temperatures. In comparison, the basic density of SW is less because of the absence of materials (extractives and tyloses) which may have been infiltrated into HW with respect to age, due to which SW has high cellulose content and lower amounts of lignin and lipophilic extractives *(Bertaud and Holmbom 2004).* From the results it can be concluded that SW pulp is preferred to make high strength papersheets due to high cellulose content.

(iii). Water retention value:

This test gives the water absorption capacity and the amount of lignin present in the pulp because it measures fiber swelling. From the results, the WRV of SW is higher than HW for all the three temperatures and also the water absorption capacity values are increasing with increase in temperature. WRV at 165°C is almost 10% higher than WRV at 140°C and not much difference was found between SW and HW. From an anatomical point of view, the extractive components are often concentrated by deposition of greater amounts in HW than the SW *(Britt 1970).* Impregnation of cooking chemicals is difficult in HW due to small pore sizes, different types of extractives deposited in the pit membranes and also due to the formation of tyloses (*Stamm 2007).* The composition differences and low cooking temperature (140°C) contributes to a general reduction of impregnation of the pulping liquor to the wood chips (*Hillis 1987*) resulting in higher residual lignin content and lower WRV for HW pulp at 140°C. The pulps at 165°C exhibits high porosity. When lignin is removed during pulping, pores are formed in the fiber cell wall which are uniformly distributed throughout the transverse direction of the cell wall. The lamellae consisting of both pores and matrix material - “pore and matrix lamella” also become wider (*Fahlen and*

Salmen 2005) due to negligible residual lignin in their fibers for which it could retain more amount of liquid than pulps at 140°C or 155°C.

Note the trend of residual lignin content, cellulose content and WRV with increase in temperature from 140°C to 165°C as shown in Fig. 3.7 and 3.8 for HW and SW respectively. It is clear that lignin content decreases and cellulose content and WRV increases with increase in temperature conforming the fact that, chosen three temperatures were able to remove lignin from CML and partly from cell walls with minimal degradation to cellulose exist in cell walls.

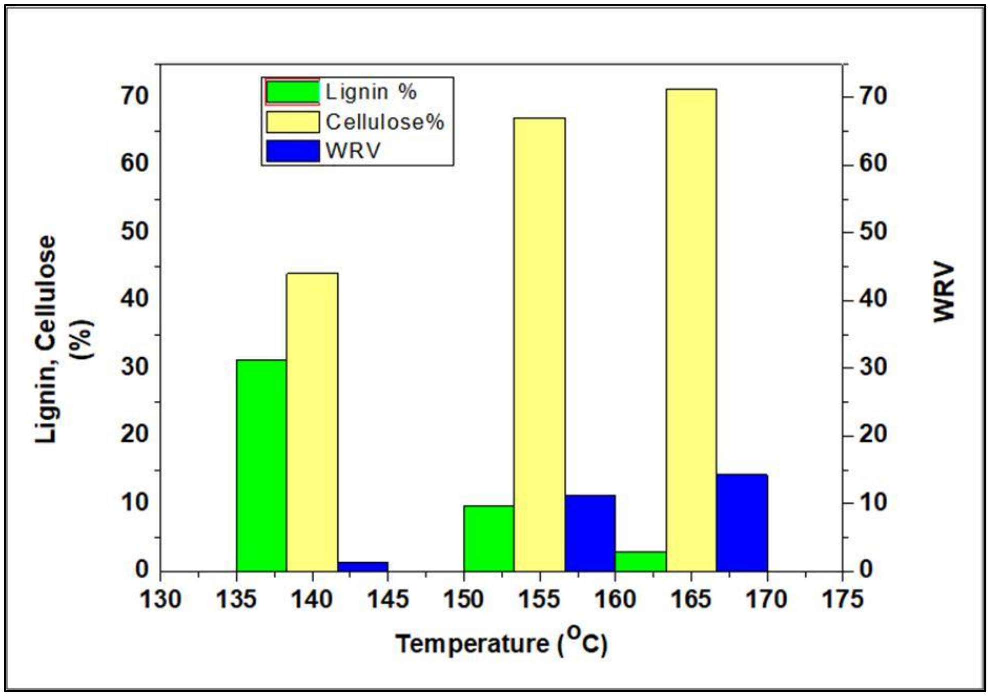


Fig 3.7: Heartwood pulp characterization data for different temperatures

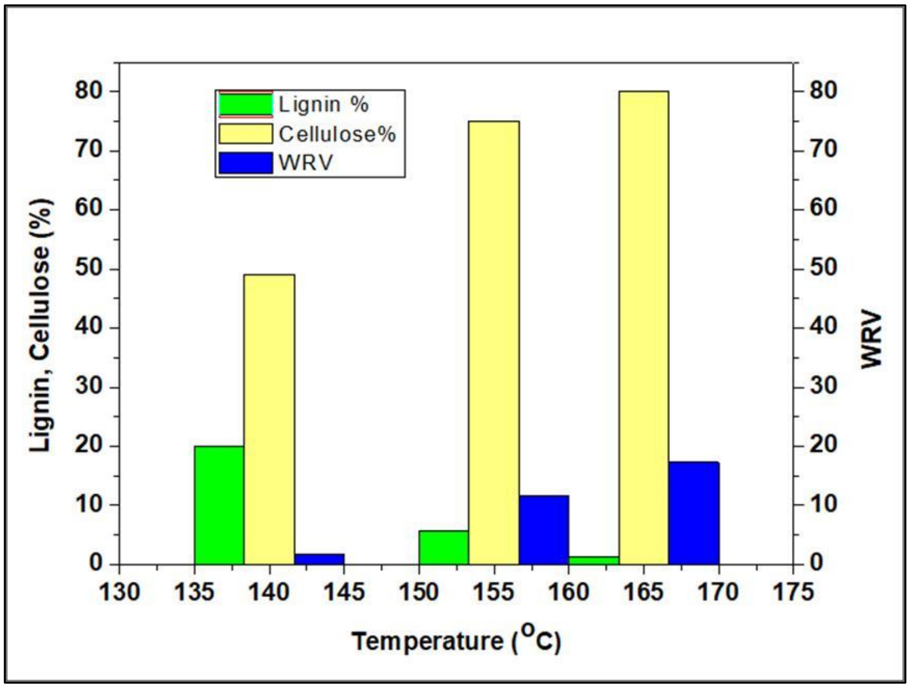


Fig 3.8: Sapwood pulp characterization data for different temperatures

(iv). Ash test

The pulp ash which is an indication of amount of inorganics depends on the severity of the pulping process. In this study ash content of pulp is changing with change in temperature as shown in Table 3.2. During the incineration process, pulp losses its mass at temperatures above 300°C, indicating degradation or modification of hemicelluloses, amorphous cellulose, lignin and also evaporation of extractives (*Yang et al. 2007)*. The % ash content of HW and SW pulp processed at 140°C temperature is <26% whereas value reached >30% for HW and SW pulp processed at 165°C. But pulps from 155°C exhibited ash% which is almost similar to % of ash measured for wood chips.

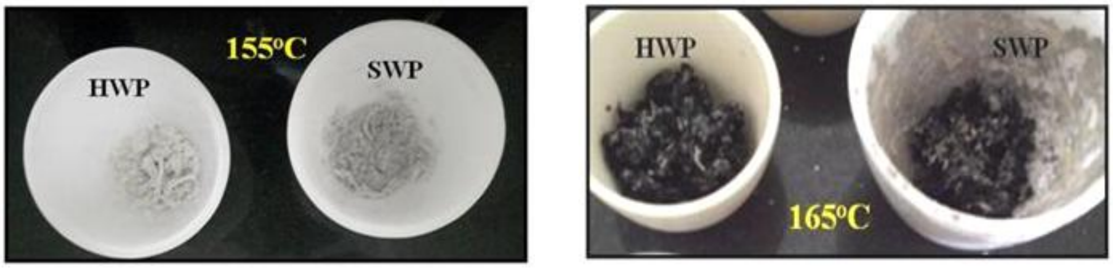


Fig 3.9: Ash obtained from wood pulp
[HWP : Heartwood pulp; SWP: Sapwood pulp]

This could be mainly due to the non-uniformity in its structure (manual separation of fibers; pulp with multistrands of fibers compacted together; higher percentage of uncooked chips when compared with 165°C) and uneven cooking conditions (extensive soaking of pulps in white liquor before cooking) which has caused deposition of inorganic constituents on the fiber surfaces causing differences in lignin reactivity during the incineration process thereby resulting in white colour appearance as shown in Fig 3.9 (no surface oxidation was observed resulting white colour ash similar to wood ash). It is noted that the residue is white in colour for ash contents <5% but the residue turns to black color for ash content above 20%. If the lignin content is very high like wood chips or lignin content is very low like bleached pulps (collapsed fibers), the interfacial pore area becomes very low which allows complete degradation of cellulose/hemicellulose/lignin leaving only inorganics. If the lignin content is medium, like unbleached pulps, the interfacial pore area becomes very high which allows slow evaporation of extractives, slower degradation of lignin fragments and giving enough heat and time so that cellulose can oxidise and form cyclic rings which can be noticed by observing black colour. From the attained results it is also observed that the percentage of ash content is higher in SW than in HW pulp at all the three temperatures. The lower lignin content and high amounts of inorganics enables SW (cells function as carriers of water, minerals in the plant) pulp to incinerate better than HW pulp resulting in high ash content (*Mariani et al. 2005)*.

(v). Analysis using Fourier Transform Infrared (FTIR) spectroscopy

The FTIR spectra of the kraft pulp fibers illustrated in the Fig 3.10 (a, b and c) shows the main infrared spectral differences, which allows the identification of the changes (functional groups) of delignified pulp fibers of HW and SW at all the three temperatures. The difference in peak heights we see in HW and SW pulp spectra is due to different amounts of lignin present, because the penetration of liquor in HW chips is different from the penetration in SW chips (baseline correction for all pulp samples have been carried out). Sharp peaks in SW pulp and slight clustered (concentrated) peaks in the spectra of HW pulp are observed. The principal peaks assigned to lignin structures at 1512 cm^{-1} and 1423 cm^{-1} (aromatic skeletal vibrations), 1462 cm^{-1} and 1370 cm^{-1} (C-H deformations) are present in all the spectra's of pulp indicating the presence of residual lignin. The absorption bands in the 1600–1400 cm^{-1} region in the spectra is attributed to the presence of aromatic or benzene rings in lignin. The aromatic C-H in plane deformation around 1160, 1114, 1055 cm^{-1} is present in all spectra's. The bands in the region 1300–1000 cm^{-1} involves the (C–O) stretching vibrations of primary and secondary aliphatic alcohols in cellulose, hemicellulose and lignin; and primary and secondary aromatic alcohols in lignin. The vibration peak detected at 899 cm^{-1} is due to C-H out of-plane ring stretching in cellulose due to the glycoside bonds, which are symmetric in polysaccharides (*Le Troedec et al. 2008*). The band at peak 1271 cm^{-1} for guaiacyl units of lignin is observed in HW.The bands around 2130-2135 cm^{-1} representative of C=C stretching are prominent in HW of all three temperatures (140°C, 155°C and 165°C) and SW of 140°C. Whereas the spectra at 2360 cm^{-1} representing lignin peaks are prominent only in HW pulp of 165°C; but are present in both HW and SW pulp samples for 140°C and 155°C. This clearly indicates and confirms that SW pulp at 165°C has low lignin and high cellulose. From the spectra, the %transmittance of SW pulps is higher than HW pulps. Therefore, based on the percentage transmittance and intensity of lignin peaks, it is qualitatively confirmed that the amount of lignin extracted is lesser for pulps processed at 140°C, and higher for pulps processed at 165°C, indicating improved delignification rate with respect to temperature.

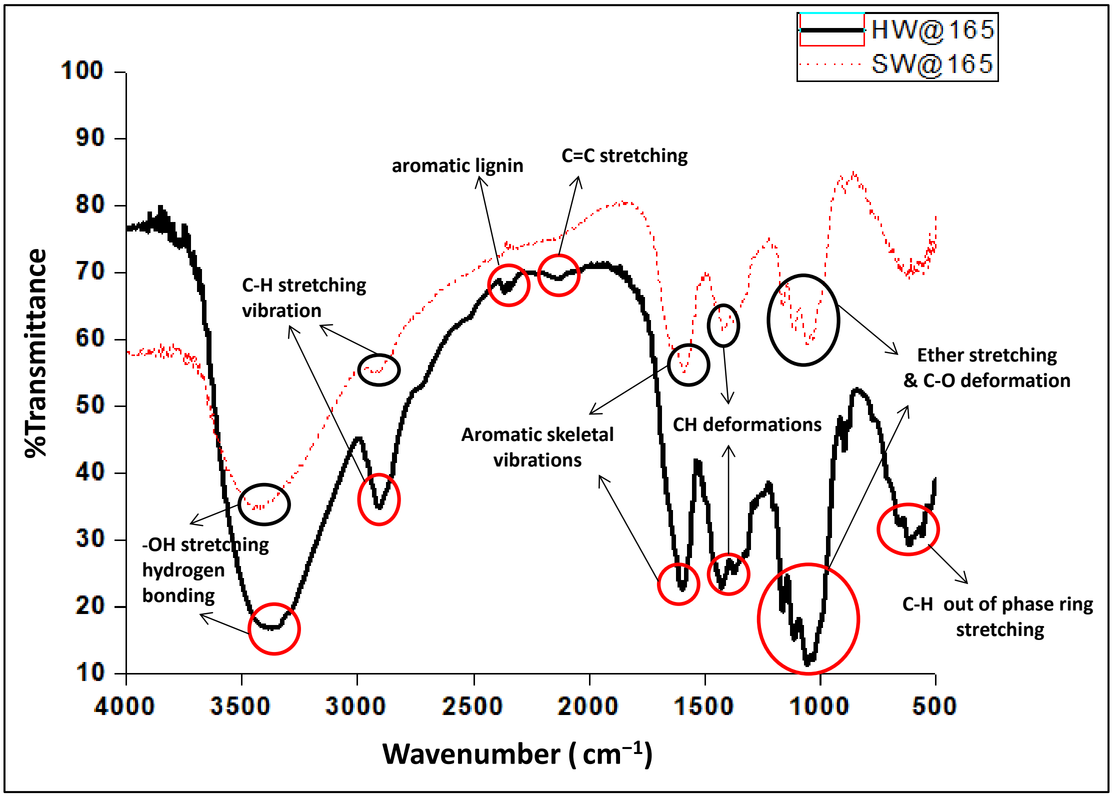


Fig 3.10 (a): FTIR analysis of pulp obtained from kraft cooking at 165°C

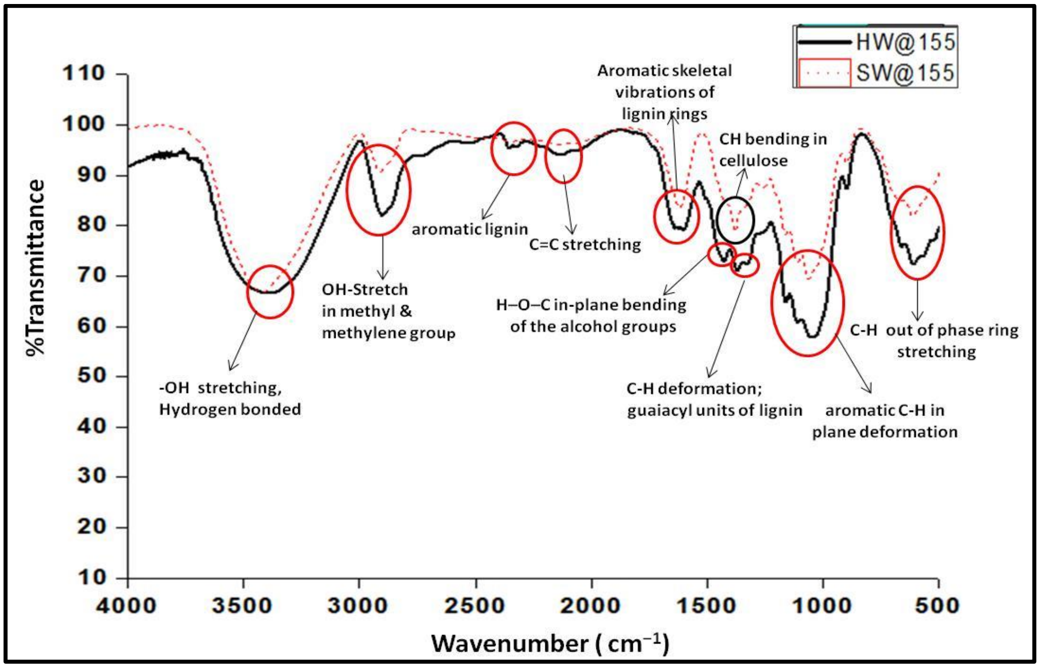


Fig 3.10 (b): FTIR analysis of pulp obtained from kraft cooking at 155°C

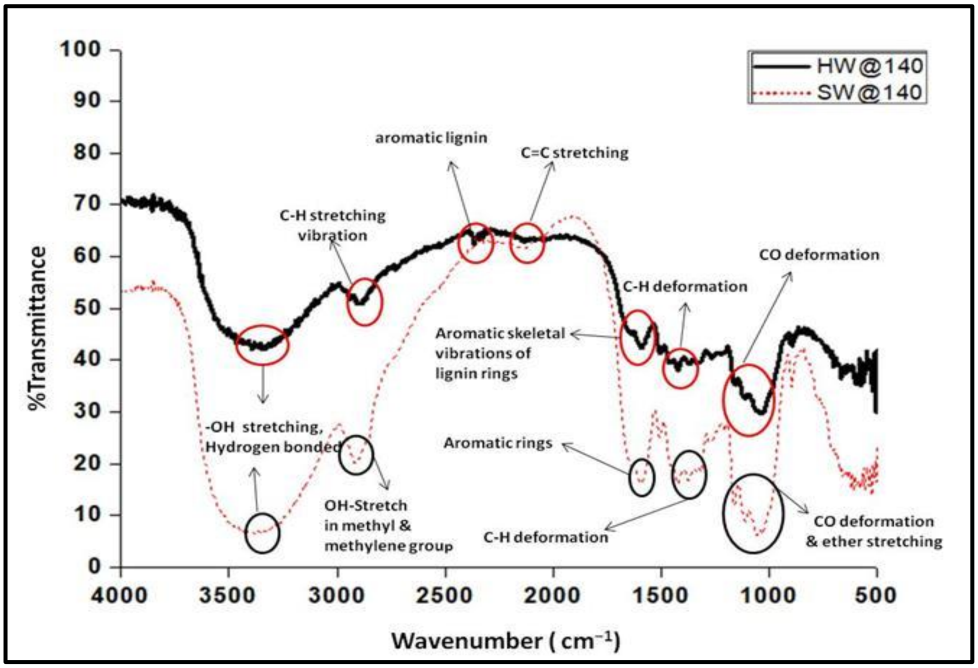


Fig 3.10 (c): FTIR analysis of pulp obtained from kraft cooking at 140°C.
[HW : Heartwood pulp; SW: Sapwood pulp]

(vi). Microscopic analysis

Extent of delignification and separation of wood chip into individual pulp fibers can be qualitatively compared based on microscopy data and it is important to analyze the fibers before utilization of pulp. Since vessels, kinks in the fiber, knots, uncooked chips, fines will reduce the quality of the paper sheet it is important to identify and separate them from the pulp slurry. For kraft pulps processed at 140^{o}C (Fig 3.11a and b), peeling of fiber bundles is observed only on the surface of the sample. Whereas, the pulps from 155^{o}C featured slightly loose fibers in network structure when compared to 140^{o}C (Fig 3.11 c and d). For kraft pulps processed at 165^{o}C, individual fibers due to degradation of middle lamella can be seen in both HW and SW pulp (Fig 3.11 e and f). The loose network structure is due to the entanglement of individual fibers resulting from drying of low consistency wet slurry. Among SW and HW pulps, better separation of vessels, libriform fibers and tracheids are evident in SW pulps (Fig 3.12 a). The surface looks denser and concentration of locally deposited phenolic extractives in vessels is found to be higher in HW pulps (Fig 3.12 b). Kinks followed by slight fiber peeling for surface fibers is also observed in case of HW pulps. Even from the uncooked pulp (chips from 155^{o}C), it is observed that the cracks present on SW pulp are much larger than HW in both longitudinal (Fig 3.12 c and d) and transverse direction (Fig 3.12 e and f). It is evident from uncooked chips or pulps, SW pulping process or kraft cooking is easier compared to HW pulping process.

Length and diameter of pulp fibers are given below :

Vessels: length = 39 μm ; diameter =23 μm.
Libriform fibers: length =237 μm ; diameter =11 μm.
Tracheids: length = 163 μm ; diameter =19 μm.
Axial Parenchyma cells: length=101 μm ; diameter =19.4 μm.

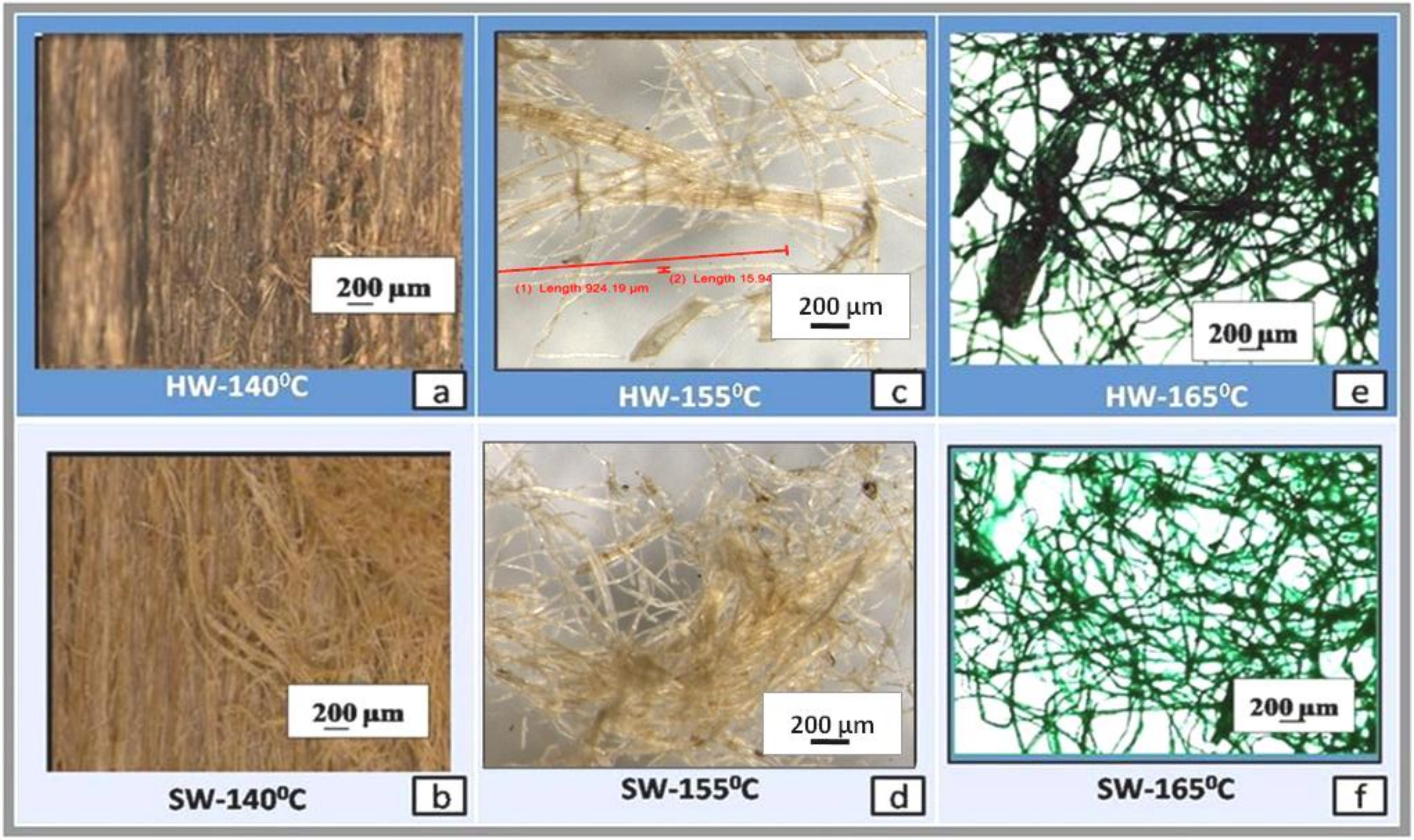


Fig 3.11: Optical images of pulp fibers kraft cooked at 140°C, 155°C and 165°C

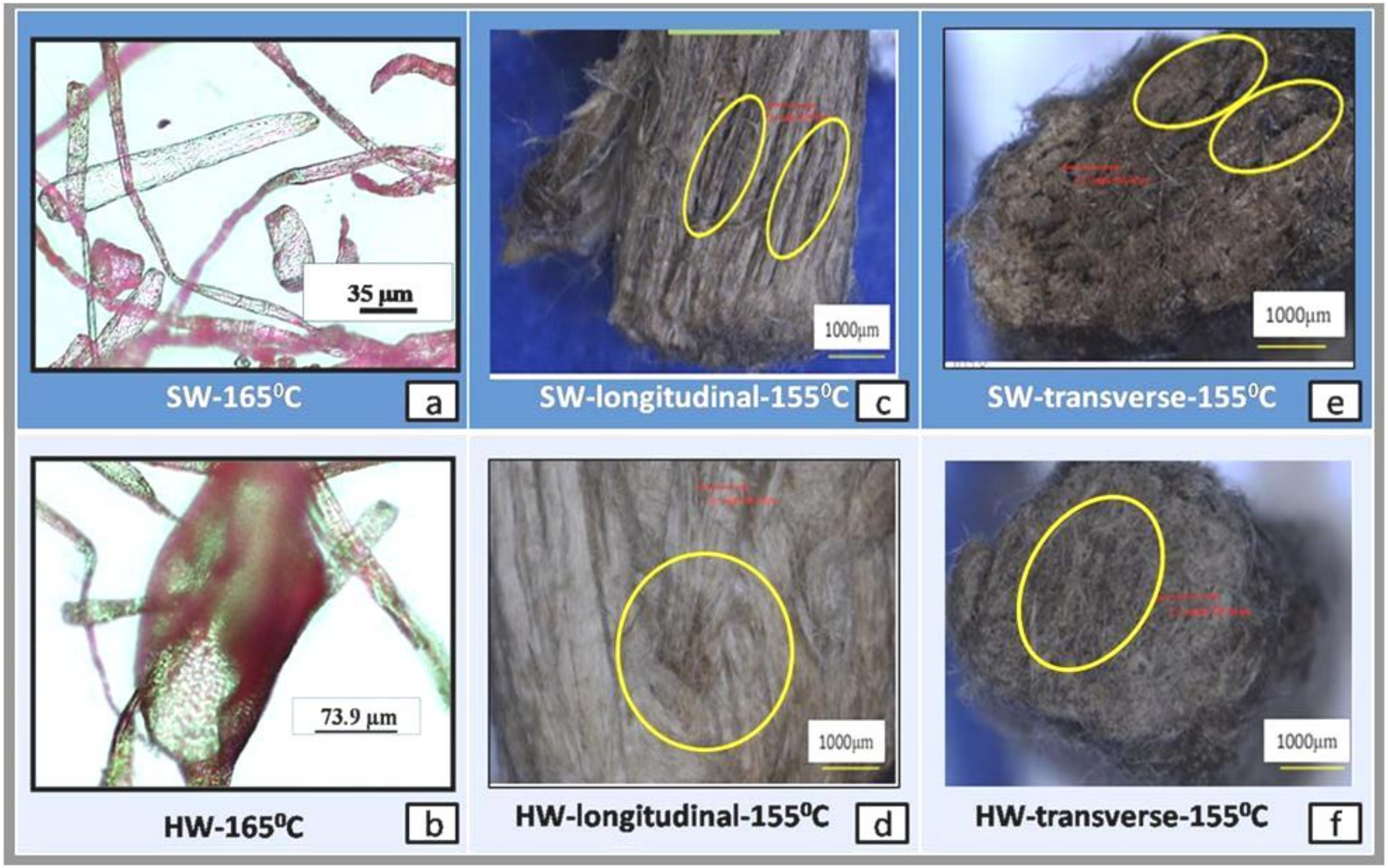


Fig 3.12: Optical images of pulp fibers- kraft cooking at 165°C and 155°C [Note: (a). SW pulp fibers with libriforms, trecheids and vessels filled with starch; (b). HW pulp vessel filled with extractives]

(vii). Thermo Gravimetric Analysis (TGA):

TGA is carried out to investigate the thermal degradation behaviour of HW and SW pulps processed at 165^{o}C. Thus, the results obtained are compared to understand the effect of lignin content on thermal degradation because HW pulp has 2.8% of residual lignin and SW pulp has 1.3% of residual lignin. In ***TGA analysis***, it is widely reported that the primary thermal decomposition of cellulosic materials occur between 200^{o}C to 400^{o}C and the initial decomposition takes place in the amorphous regions *(Fisher et al. 2002; Mostashari and Moafi 2007).* From the data shown in Fig 3.13 it is observed that, there is a slight decrease in the SW pulp weight below 100°C which corresponds to water vaporization or removal of volatile organic extractives. From Table 3.2, it is known that SW pulp has higher WRV compared to HW Pulp, so the observed 20% weight loss of SW pulp shown in Fig 3.13 could be due to the removal of water.

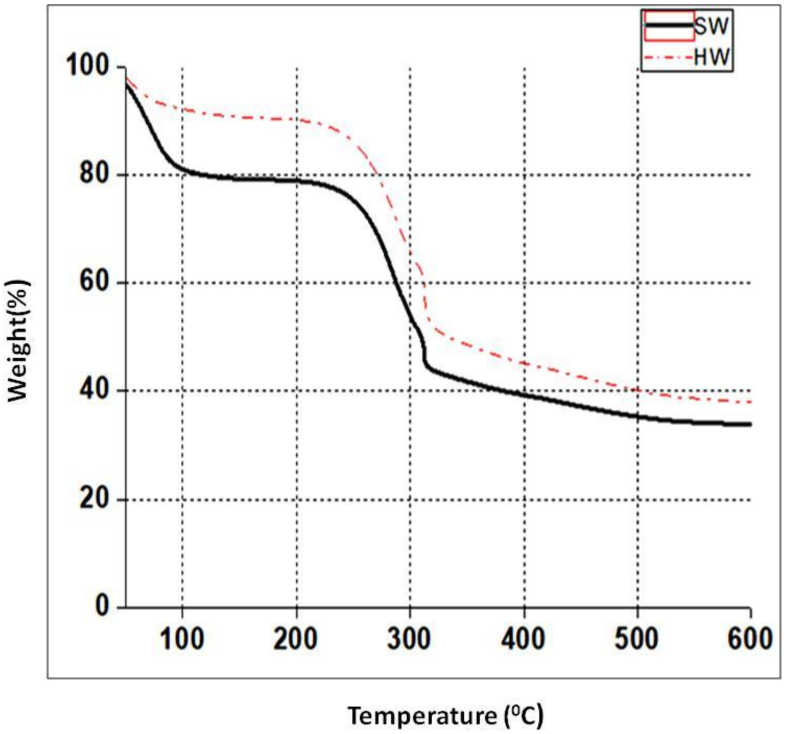


Fig 3.13: Thermogravimetric analysis of HW and SW pulp samples obtained from kraft cooking at 165^{o}C, 3hrs

The degradation temperature for SW and HW pulp was in between 245°C to 310°C and the overall weight loss was 12% for HW and 29% for SW. This could be due to the heterogeneity of the micropores exist in cell wall (composite) of individual fibers. As described previously, SW pulp has more water retention capacity, low lignin content and high cellulose content, so the weight loss is high for SW pulp in comparison with HW pulp until 600°C. Between the degradation temperatures, the maximum weight loss can be attributed to degradation hemicelluloses and partial degradation of lignin. Both SW and HW are changing their colour, resembling a charcoal at around 320°C forming cyclic structure having C-C bonds. Both HW and SW pulps between 320°C to 600°C temperature range are exhibiting very little amount of weight loss due to presence of inorganic fragments. The residual weight of both pulps is almost 40% and it is slightly higher for HW pulps due to the higher % of residual lignin.

3.3.3. Modelling of kraft cooking process using MATLAB

MATLAB was used for developing a mathematical model and MINITAB for regression analysis. It is a statistical process for estimating relationships among the variables. The model was developed using design of experiments in which response surface method was used. From this modelling, parameters like yield and lignin content in pulp, water retention value can be predicted by changing input parameters like cooking temperature, WRV of wood chips (WRVW), water absorption capacity (moisture content) of wood chips and lignin content in wood. Using these models, correlations such as yield vs cooking temperature and lignin content in pulp vs temperature can be obtained. In this model, the equations were framed using iterative (hit and trial) approach to model yield and lignin content in pulp (LP) using various input parameters. The operating cooking conditions are temperature, time, wood: liquor ratio, active alkali and sulphidity. The independent variables are temperature (140^{o}C and 165^{o}C), LW (27.6-35.3%), WRVW (0.34-1.4) and WACW (3.7-5.6%) and their ranges are closer to the values mentioned in Table 3.1. As reported, wood contains hydrophillic cellulose microfibrils, reinforced with hemicellulose-lignin matrix. Here lignin is hydrophobic, amorphous in nature and is present as continuous layers in cell walls and middle lamella. Temperature is taken because lignin and low molecular weight hemicelluloses degrade faster than cellulose with increase in temperature. Since lignin is present as thin layers, its content in wood plays a significant role in cooking. As explained WRVW and WACW corresponds to cellulose content in wood and the reason for taking these two independent variables is because micro/nano pores exist in wood. The dependent variables in the program are yield, LP and WRVP. The cooking chemicals (20% NaOH, 28% Na_2S), time (3hrs) and wood: liquor =1:4 are taken as constant values. The input parameters in the model are temperature (140^{o}C-165^{o}C), LW and relative output parameters are yield, LP, WRVP. The equations developed are as follows:

1. **Yield= -2050 + (134*LW) + (0.1792*T) - *2.116*$LW^2) - (0.0005106 * LW * T)$**
2. **LP=-810.4 + (34.08*LW) + (2.005*WRVW) + (25.36*MACW) + (11.19*yield) - (0.000701* $yield^2$)-(0.5182*LW*yield)**
3. **WRVP= 32.97 - (9.573*WRVW) - (0.04876*LP) - (0.7825*yield) + (2.036*$WRVW^2$) - (0.000177*LP^2) + (0.005573*$yield^2$)**

[LW: Lignin in wood sample (%); T: Cooking temperature (^{o}C); LP: Lignin in pulp (%); WRVW: Water retention value in wood sample; WACW: Water absorption capacity in wood sample (%); WRVP: Water Retention Value in pulp sample]

Yield is calculated as ratio of oven dried pulp obtained (unscreened) to the amount of oven dried wood used for cooking process. Wood weight is calculated before pre-treatment. For determining water absorption capacity (WAC) in wood and pulps: A humidity chamber is used (*T550 om-08; Madhuri et al. 2016)* as shown in equation 2. In this study ~1.5-2 g of oven dried sample is taken as dry pulp weight and kept in humidity chamber at 22^{o}C, 66% RH till constant weight is obtained which is taken as pulp weight (~24 hrs).

WAC= (pulp wt-dry pulp wt) / dry pulp wt

1. Program to calculate cooking temperature :

In this model the input parameters required are yield percentage of pulp and %lignin content in wood. The estimation of operating temperature can be found by making back calculation from the equation-1 which relates yield to temperature and lignin content in the wood.

```
fprintf(′ This program is valid for calculating operating temperature fprintf(′ This program is valid
for calculating operating temperature for permissible value of yield
you enter and lignin percentage of wood species ′);
yield = input(′\nEnter permissible yield percentage ′); LW
= input(′Enter the lignin percentage of wood species′);
```

$$\mathbf{T} = \frac{(\mathbf{yield + 2050 - 134 * LW + 2.116 * LW * LW})}{(\mathbf{0.1792 - 0.0005106 * LW})}; \ldots\ldots\ldots\ldots\ldots\ldots\mathbf{Eq\ 1}$$

```
if T > 165
fprintf(′ Yield not possible cellulose starts degrading\n ′);
T = 165;
```

$$\mathbf{yield = -2050 + 134 * LW + 0.1792 * T - 2.116 * LW - 0.0005106 * LW * T;} \ldots\ldots\ldots\ldots \mathbf{Eq\ 2}$$

```
end
fprintf('The operating temperature yield are respectively');
disp(T);disp('and');disp(yield);
```

Examples for the above program:

(a). This program is valid for calculating cooking temperature for the required permissible value of yield and lignin percentage of wood species. The values mentioned below are arbitrary values.

- Enter permissible yield percentage -53
- Enter the lignin percentage of wood species -27

-Yield is not possible as cellulose starts degrading* (Please see the program in which cellulose degradation temperature ≥165°C)

-*The operating temperature and yield are 165*°C *and 52.7293 respectively.*

(a) This is same as (a), but permissible yield is taken slightly higher than the value mentioned in (a)

  - Enter permissible yield percentage 53.7
  - Enter the lignin percentage of wood species 27.3

The operating temperature and yield are 143°C *and 53.7 respectively.*

2. Program to calculate pulp characteristics

Our main aim is to calculate pulp characteristics like yield, % lignin in pulp and water retention value of the pulp. Here the input parameters are temperature, % lignin in wood, water retention value of wood and water absorption capacity of wood.

```
LW = input('Enter the lignin percentage of wood');
  T = input('Enter the operating temperature');
WRVW = input('Enter the water retention value of wood');
```

$$\mathbf{yield = -2050 + 134 * LW + 0.1792 * T - 2.116 * LW * LW - 0.0005106 * T;\ldots\ldots\ Eq\ 2}$$

```
WACW = input('Enter the water absorption capacity of the wood");
```

$$\mathbf{LP = -810.4 + 34.08 * LW + 2.005 * WRVW + 25.36 * WACW + 11.19 * yield - 0.000701 * yield * yield - 0.518 * LW * yield;} \ldots\ldots\ldots\ldots\ldots \mathbf{Eq\ 3}$$

$$\mathbf{WRVP = 32.97 - 9.573 * WRVW - 0.04876 * LP - 0.7825 * yield + 2.036 * WRVW * WRVW - 0.00017 * LP * LP + 0.005573 * yield;} \ldots\ldots\ldots\ldots\ldots \mathbf{Eq\ 4}$$

```
fprintf(′The yield % of pulp is ′);
disp(yield)
fprintf(′The lignin percentage of pulp is′);
disp(LP)
```

Example for Program 2

The output for the program to calculate pulp characteristics is as follows:

The input parameters values are entered, i.e.

- Enter the lignin percentage of wood - 28.884
- Enter the operating temperature – 140^{o}C
- Enter the water retention value of wood - 0.396
- Enter the water absorption capacity of the wood -5.59

Therefore the output is calculated using equations 2, 3 and 4 from program 2.

The yield percentage is 78.13

The lignin percentage of pulp is 17.1

Based on the developed model plots have been constructed correlating percentage yield vs temperature and percentage lignin content in pulp vs cooking temperature (Fig 3.14).The plot implies that yield of SW is higher than HW and this trend continued until 165^{o}C, because HW has more cross-linked lignin, higher content of extractives and influence of extractives in initial phase of heating. During the initial stages of cooking, bulk lignin present in CML is removed at lower temperatures and further increase in temperature removes the final traces of lignin (residual lignin) present in secondary cell walls, resulting in decrease lignin content in pulp with increase in temperature as shown in Fig. 3.14 (experimental data). Hence it can be concluded that the temperature can be used as optimization parameter. Also, the cooking kinetics and pulp physical characteristics play an important role in estimating the final lignin content of pulp, so in the proposed modelling we have used WRV, WAC and LW to predict the correlation as shown in Fig.3.14 (model data). The modelling of delignification is found to be similar for HW and SW and attained plots indicate a good correlation between experimental and model data. Hence, the developed models can be used in packaging sector to generate different grades of unbleached pulp and it is economical to produce such grades of chemical pulps than mechanical pulps. The average percentage deviation between experiment and model for SW and HW is appr.6.6 and 5.6% respectively.

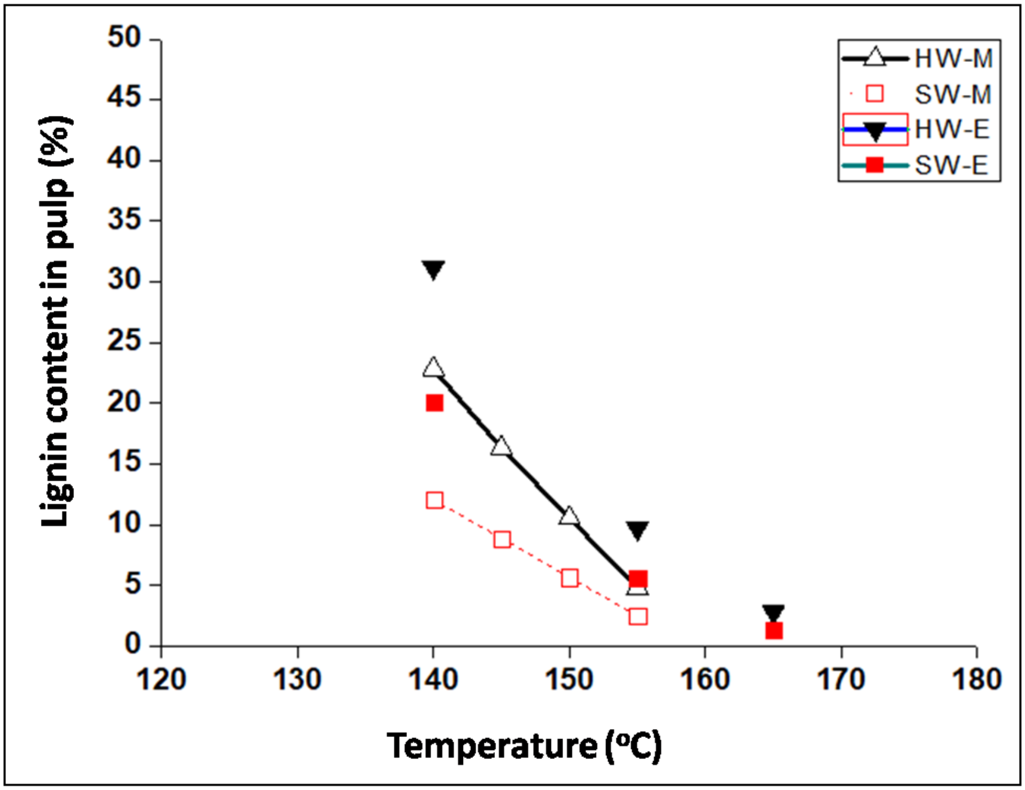


Fig 3.14: Plot of Lignin content in pulp (%) vs Cooking temperature (°C). HW-Heartwood, SW-Sapwood, M- Modelling data and E- Experimental data. (a).

3.4. CONCLUSIONS

- There was a striking difference in pulp characterization results obtained at temperatures 165°C, 155°C and 140°C. The rate of delignification was found to be temperature dependent i.e., an increase in pulping temperature decreased lignin content and increased cellulose content and water retention values. Hence optimization of pulping temperature is important to improve the quality of pulp and paper.
- The study concludes the relative difficulty of delignification of heartwood compared to sapwood at a given pulping temperature, using established experimental procedures. Hence to separate the sapwood and heartwood prior to pulping is economical and eco-friendly. The knowledge of these differences will provide a better control of the process during pulping and papermaking and also for estimation of final product properties.
- The experimental data for both HW and SW was found to fit the developed model fairly well. Therefore, such models can be used in packaging sector to generate different grades of unbleached pulp and it is economical to produce such grades of chemical pulps than mechanical pulps.

3.5. COST ANALYSIS FOR KRAFT COOKING OF HEARTWOOD AND SAPWOOD

Upto 1970's heartwood and sapwood were separately used for furniture and paper making respectively. The source of the wood was basically forest produce and not at an industrial scale. So due to unreliable and longer times for supply of wood, whole wood log was utilized in paper making to meet the demand and this practise is in vogue till date.

But in current scenario, the supply of wood was mechanized and plantation grown wood species (smaller in diameter) are mostly used as raw materials for paper making and hence the raw material for paper demand is easily being met.

Despite easy availability of raw material, industry is still traditionally using whole wood log for paper making as the separation of HW and SW is time consuming and it is assumed that the typical 6 year plant doesn't have any significant HW portion and lignin content.

But this research work concluded that 6 year plant consists of atleast 60% HW cross-section corresponding to 28-35% lignin content, that adversely impact the kraft cooking process in form of high chemical usage and energy consumption (time and temperature).

Also this is an applied research work, in which the sample size itself is in order of kgs (1-2 kgs log) for characterization and analysis. Hence this infers that this research work can easily be implemented/ramped up to industrial scale with minimum or no modifications of the equipment. Due to seperate processing of heartwood and sapwood, the paper process parameters can be very tightly controlled to get desired consistent results (good quality paper with less rejections). The time taken for of separation of HW/SW outweighs the benefits that accrued with separate HW and SW kraft cooking process. With low usage of chemical and energy consumption, this research data can directly lead to a successful green technology in pulp and paper making.

Process 1 (Existing)	***Process 2 (Proposed)***
Industrial process of using directly raw wood logs.	Process performed after separating Heartwood and Sapwood from Raw wood logs. It is easy to separate based on color and density.

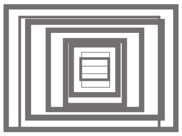
Chipping process to separate the heartwood and sapwood from raw wood logs

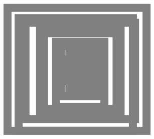
Raw wood consists of 60% heartwood and 40% sapwood. From klason's lignin analysis, it is found that the lignin percentage in sapwood reduced from 29 % to ~1 % where as in heartwood it got reduced from 35 % to ~3 % when wood chips are subjected to kraft cooking at 165°C for 3 hours. When entire wood logs are subjected to cooking, it is possible to reduce the cooking time of heartwood by 30 mins as from UV analysis it can be confirmed that black liquor samples collected after 2.5 hour and 3 hour have shown same absorbance predicting no further removal of lignin from cell walls happened between 2.5-3 hours.

	Rawwood	Heartwood	Sapwood
Quantity	1 kg	~600 gms	~400 gms
Pulp yield	0.7609	0.6844	0.8195
Time required for kraft cooking	3 hours to attain about 2.5% lignin in pulp	2.5 hours to attain about 2.7% lignin in pulp	3 hours to attain about 1.2% lignin in pulp
Bleaching process	Chemical quantity is almost x grams	Chemical quantity is almost x grams	Chemical quantity is almost y grams (y < x), due to less lignin

Considering the same amount of chemicals used for kraft cooking in Process 1 and Process 2, the yield obtained in both the processes are almost equal but there will be a reduction of bleaching chemicals almost to half the quantity that are used in Process 1 and also the energy is conserved to an extent as the heartwood cooking is performed in almost 2.5 hours (reduction of 30 minutes).

OPERATING PARAMETERS :


Sapwood


Heartwood

Both heartwood and sapwood were cooked at 165^{o}C for 3 hours maintaining 1:4 wood to liquor ratio. For the same conditions, the percentage of lignin removed from heartwood is lower than sapwood. Hence it could be concluded that different set of parameters are required for heartwood as lignin is tightly bonded to hemicellulose and cellulose fibrils as shown in above schematic diagram. Hence it is advisable to separate heartwood from sapwood before considering the wood log for kraft cooking. Optimizing the parameters for sapwood cooking and heartwood cooking separately reduces the chemical consumption not only during pulping but also during bleaching process. This enables the process to be more economical (cooking at lower temperature) and ecofriendly (reduction of bleaching stages).

CHAPTER - 4

Effect of Temperature on Kraft Cooking of Whole Bagasse and Depithed Bagasse

4.1. INTRODUCTION

Sugarcane bagasse (SCB) is the second most commonly used non-wood fiber for paper production because of its availability and low silica content (a component of ash) compared to other fibers. SCB is found to be the best alternative of wood for papermaking because of its low cost, low refining energy consumption, low fiber lengths, high fiber bonding potential, good sheet formation and paper smoothness (*Verma et al. 2014, Rajesh et al. 1998*). SCB is characterized by high cellulose (40-50%), high hemicelluloses (xylan: 28-30%), but lower lignin contents (19-21%) compared to Eucalyptus. Because of its lower lignin content, SCB is more easily delignified, requiring milder and shorter cooking conditions than wood sources (*Agnihotri et al. 2010*). SCB consists of 60% fiber, 30% pith and 10% dissolved matter in the form of fiber bundles, vessels, parenchyma cells, epithelial cells. The latter ones are mostly categorized as ‘pith’ whose presence is detrimental to the paper making. Presence of pith results in increased holding of chemicals in pulping and bleaching process due to the high porous structure of pith. It also causes filtration issues in brown stock washers and drainage issues in paper making due to the shorter pith cells. Pith composed of thin walled parenchyma cells has lower aspect ratio with a maximum length of 0.52mm and a diameter of 140 μm (*Paul et al. 1998*). The pith cells are of irregular size and shape and are characterized by their absorption properties (*Aguilar-Rivera. 2016*). Hence it is important to remove pith from bagasse before kraft cooking using mechanical shredders equipped with hammer mill and screens. Since it is difficult to remove pith completely, most of the depithed bagasse used in paper production has 15-20% pith remaining.

Kraft pulping is an alkaline process that utilizes NaOH and Na_2S as active chemicals in the liquor in which the delignification proceeds through the cleavage of β-aryl ether linkages that degrade and dissolves the lignin, thereby single cells or fibers are separated (*Smook 1992, Britt 1970*) from the wood or bagasse. The studies on pulping of non-woods materials like bagasse was reported by various researchers (*Rainey 2012, Agnihotri et al. 2010, Sanjuan et al. 2001, Gazy 2016*). The studies discussed the whole and depithed bagasse pulp characteristics followed by paper and black liquor characteristics separately. Though it is acknowledged that, bagasse cannot be depithed completely, scientific studies focussing on comparision of pulp characteristics from whole bagasse and depithed bagasse are negligible. Hence a detailed study on influence of parameters (cooking temperature and time) involving both whole bagasse and depithed bagasse with respect to kraft pulping were carried out and comparisons were made between two bagasse samples and two temperatures.

4.2. MATERIALS AND METHODS

4.2.1. Grinding and pretreatment of Whole bagasse and Depithed bagasse

The raw material used in the study are whole bagasse (WB) and depithed bagasse (DPB). The depithed bagasse was obtained from CPPRI (Central Pulp and Paper Research Institute), Saharanpur, India. The whole bagasse was obtained from Hyderabad, India. Both bagasse raw materials were grinded and are oven dried at 103.5^oC in hot air oven (Osworld OOG-90) for 1 hr to remove the unbound moisture from cells. The dried samples were subjected to pre-treatment process (steaming) in autoclave (Metalab MSI-41) at 120^oC for 1hr. Steaming enables in removal of organic extractives and softening of lignin which accentuates better penetration of cooking chemicals during the delignification process.

4.2.2. Kraft cooking of bagasse at 140 ^oC and 165^oC

The pulping process is carried out in Rotary pulp digester (UEC-2015, India) which rotates 180^O during cooking. White liquor (NaOH and Na_2S) and bagasse samples were cooked with the following cooking conditions: cooking temperature-140^oC or 165^oC (pressure 5 or 8bar), cooking time-1hr, Wood: liquor ratio=1:7; 28% sulphidity (Na_2S and NaOH expressed as Na_2O) and 20% active alkali (as Na_2O). Continuous rotation of the digester (180^O) during cooking allows better impregnation of cooking chemicals into bagasse cell walls. During the pulping process, the black liquor (~15ml) is collected from bottom of the digester at two intervals (0.5 hr, 1 hr) to understand the extent of delignification with respect to time. After the cooking process (1hr), the delignified pulp samples were separated from the black liquor and thoroughly washed with deionised water for 4-5times to remove the extractives and residual black liquor adhered to the surface of the pulp fibers. The pulp samples are then dried at 103.5^oC in hot air oven for 12hrs (attainment of constant weight). Thus the pulps obtained are characterized to analyze the amount of lignin remaining (residual lignin) in the pulp using various characterization techniques.

4.2.3. *Analysis of bagasse and bagasse pulp*

The oven dried raw bagasse and pulps obtained are characterized using the following qualitative and quantitative methods: Klasons lignin test, %Cellulose, Water retention value (WRV), Water absorption capacity (%), Ash content (525^{o}C), FTIR, Optical microscopy and TGA. The pulp properties from the characterization methods will serve as a foundation to develop a criterion for the selection of non-wood species and optimization of process parameters to improve the pulp and paper quality.

(i). Klasons lignin estimation:

The lignin content of both bagasse and delignified pulps was estimated using klasons lignin protocol -TAPPI T222 and TAPPI UM250 (*reference: Chapter 2*).

(ii). Cellulose isolation test:

The study indicates the amount of cellulose present in the sample after kraft cooking process. The cellulose% is estimated using the standard protocol (*reference: Chapter 3).*

(iii). Water retention value:

The water absorbtion capacity is estimated by performing WRV test (*reference: Chapter 2)* using refrigerated table top centrifuge *(Rota 4R-V/FM).*

(iv). Water absorption capacity:

The moisture absorption capacity of both bagasse and pulps was estimated using T550 om-08 protocol. To calculate water absorption capacity, oven dried samples of 5gms each are kept in a humidity chamber at a relative humidity of 66% at 22^{o}C until a constant weight is obtained (apprx. 3-4hrs). The water absorption capacity is calculated by the equation:

Water absorption capacity = (pulp weight-dry weight)/dry weight

***(v). Ash test* (TAPPI T211)**:

The Ash content for both bagasse and pulp fractions is determined using TAPPI T211 method (*reference: Chapter 2).*

(vi). FTIR Analysis:

The samples (wood and pulp) were analyzed using Fourier Transform Infrared (FTIR) spectroscopy *(JASCO 4200, transmittance mode*) to detect the various functional groups of cellulose, hemicelluloses and lignin. FTIR spectra of the samples were recorded over the range of wave number: 800-2000 cm^{-1}. (Sample preparation for analysis: *reference-Chapter 3).*

(vii). Microscopic analysis:

This analysis gives a proper structural characterization of pulp fibers. The imaging using Stereo microscope *(OLYMPUS SZ17)* was carried using 0.8X magnifications. (sample preparation for analysis: *reference- Chapter 3)*

(viii). TGA:

Thermogravimetric (SHIMADZU DTG60) analysis is carried out to determine the thermal decomposition of fibers after kraft cooking process. The temperature was swept from 20^{o}C to 600^{o}C at a heating rate of 20^{o}C/min under nitrogen atmosphere for a sample of 4 mg DPB and WB pulp samples. TGA test is carried out to investigate the suitability of pulp for further processing.

4.3. RESULTS AND DISCUSSION

4.3.1. Bagasse and bagasse pulp characterization

Fig 4.1 (a) represents the images of oven dried raw bagasse (prior to cooking) samples. It is observed that a higher degree of separation of cellulose fibers was observed in all the pulp samples (Fig. 4.1 b and c) in comparison with raw bagasse indicating the impact of the selected process parameters. At both the temperatures, whole bagasse (WB) pulps have exhibited denser network of fibers entangled with each other due to presence of pith. The increase in temperature accelerated the pulping reactions and started spreading from the initial reactive sites, hence the fibers were better separated in case of 165^{o}C cooking.

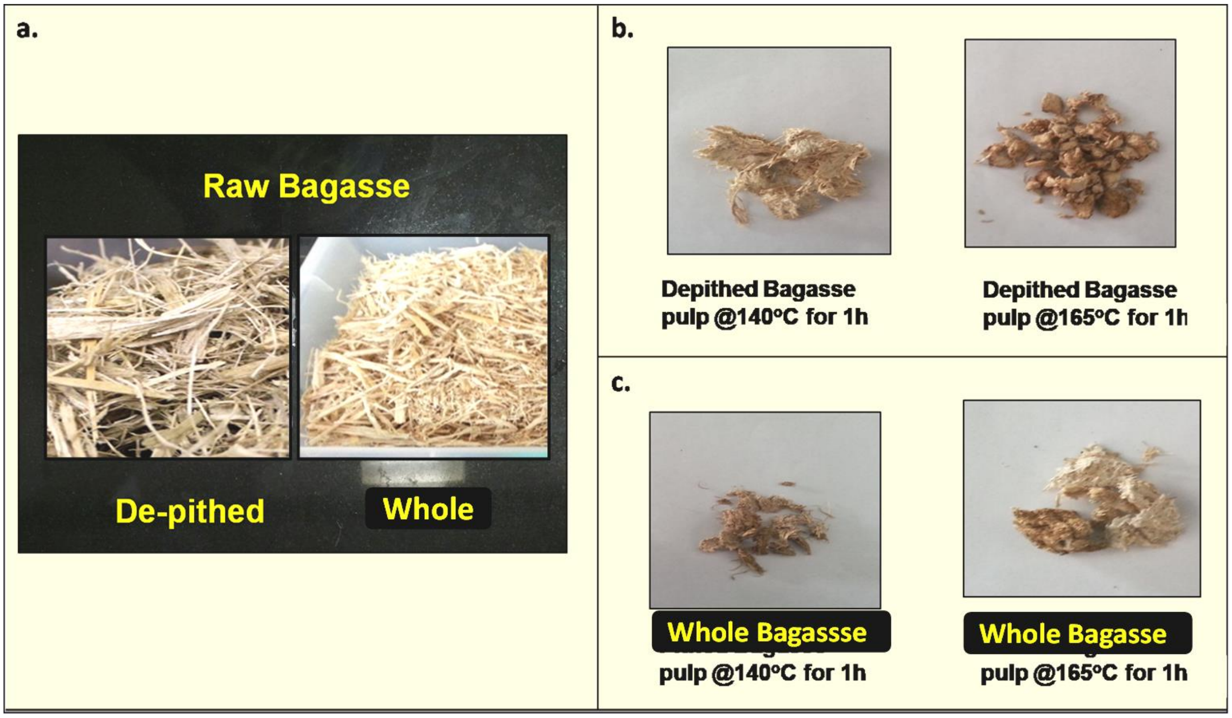


Fig 4.1: Images of bagasse samples before kraft cooking (a) and after kraft cooking (b,c)

The ***pulp yield*** (Table 4.1) slightly decreased with increase in temperature and it is quite matching with the reported values by *Agnihotri et al. 2010* (yield decreased from 49% to 41% with increase of temperature from 140^{o}C to 160^{o}C). This reduction is due to carbohydrate degradation or dissolution of cellulose-lignin composite structure and also could be due to the lignin removal from cell walls. The peeling and dissolution of low molecular weight carbohydrates in alkali are the main reasons for yield loss during kraft cooking (*Vaaler et al. 2005*). At both temperatures (140^{o}C, 165^{o}C) WB pulps presented slightly higher yields compared to DPB pulps. The yield differences were expected, owing to presence of pith which holds certain amount inorganics and cooking chemicals resulting in improper impregnation of white liquor into the bagasse cell wall layers thus obstructing the lignin removal.

Table 4.1: Pulp yield (%) of whole bagasse and depithed bagasse

Sample (Pulp)	**Kraft cooking temperature (1hr)**	**Yield (%)**
Whole bagasse	@ 140°C	34±1.41
	@ 165°C	31±1.1
Depithed Bagasse	@ 140°C	32±1.32
	@ 165°C	30±1.06

The chemical characteristics of raw bagasse (whole and depithed) and their respective kraft pulp samples (at 165°C) are compiled in Table 4.2.

Table 4.2: Bagasse and Bagasse pulp characterization data
[Note: For comparision, pulp data from 165°C is considered]

Sample	Lignin (%)	Kappa Number	Water Retention Value	Water absorption capacity (%)	Ash (%)
Whole bagasse	26.66±0.1	179±0.6	4.52±0.39	0.56±0.15	0.85±0.35
Whole bagasse pulp	1.53±0.02	10±0.13	4.72±0.12	1.78±0.16	4.52±0.38
Depithed bagasse	26.9±0.3	181±2.1	1.91±0.26	1.19±0.18	1.17±0.17
Depithed bagasse pulp	1.08±0.04	7±0.27	6.44±0.17	4.31±0.33	1.75±0.07

(i). Klasons lignin estimation:

From klason lignin estimation (Table 4.2), it is evident that % of lignin (raw bagasse) is reduced from 26% to <2%, as a result of cooking (140°C and 165°C). When bagasse is mixed with the cooking chemicals (white liquor) during kraft pulping, the reaction between chemicals and lignocellulosic components (in bagasse) initiates certain number of reactive sites which could be on the surface or interior of bagasse structure. This reaction degrades lignin into smaller units by cleaving inter unit linkages. Degradation reactions leads to liberation of lignin fragments and ultimately to their dissolution. The most prevalent degradation reactions occurring during kraft pulping include the cleavage of α-aryl ether and β-aryl ether bonds. These degradation reactions are therefore desirable to kraft pulping process. Hence, due to the above reasons, the pulp fibers have exhibited less residual lignin content.

(ii). Water retention value:

It is a qualitative analysis used to assess the approximate removal of lignin during cooking process because fiber swelling increases with decrease in lignin content. Lignin is hydrophobic in nature due to presence of aromatic groups, therefore greater the removal of lignin from the cell walls and cell interfaces, higher the water retention value (WRV) of the sample. The WRV (Fig 4.2) of both the pulps are significantly higher compared to raw bagasse samples.

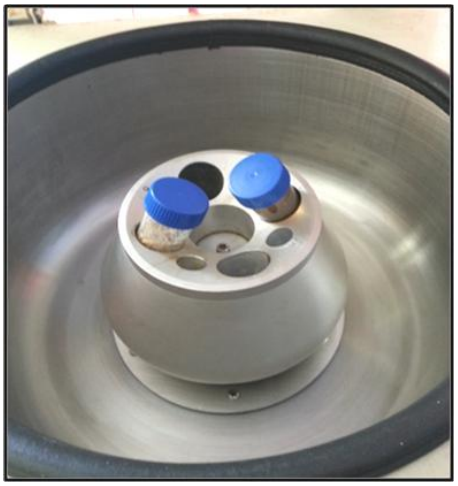


Fig 4.2 : Bagasse pulp samples during centrifugation

Kraft delignification occurs by modifying the structure of lignin in two different ways, to enhance its dissolution. The first is degradation (*as discussed above*), and the second is to introduce hydrophilic groups into the polymer and cleaved fragments, making the lignin more soluble in the cooking liquor. This phenomena occurs when linkages holding the phenyl propane units together are cleaved, thereby generating free phenolic hydroxyl groups. The presence of these hydroxyl groups increases the hydrophilicity of the lignin and lignin fragments. Thus, the solubility of the lignin in the cooking liquor is increased and converts the raw material into fiber mass which exhibits high porosity and thereby high water absorption capacity (WRV). From the results it can also be concluded that the raw WB has exhibited 136% higher WRV compared to DPB, because pith has large amount of short cells which are coarse, porous and has higher water permeability in its tissues (*Rainey 2012*). Pith is majorly made up of holocellulose with numerous pores, hence water is easily absorbed resulting in higher WRV.

(iii). Water absorption capacity:

The water absorption capacity of the wood and pulp is critical to meet the demands for the end-use of the product being made. The water absorption capacity of pulp is considerably higher than that of raw bagasse. The deposition of moisture into a sample is substantially influenced by its porosity, capillarity, and dimensional stability. The raw bagasse pores are filled with residual organic constituents (lignin, extractives etc) due to which the moisture could not diffuse through the fibers. Whereas, lower lignin percentages in pulps creates loose network followed by external and internal fibrillation of fibers thus exhibiting relatively high water absorption capacity. Among all the four samples, the water absorption capacity of raw WB is lower than raw DPB due to continuous layer of bark, which acts as a protective layer i.e. it prevents the absorption of moisture in to the bagasse cells. DPB also has bark, but it is in fragmented form. At cellular level, pith has much higher specific surface area which should result in higher water absorption capacity.

(iv). Ash test:

Ash is the remaining inorganic fraction after the bagasse sample is carbonized in a muffle furnace. In general, raw bagasse composition involves 1-4% ash. Bagasse pulp is made up of fibers (fiber bundles, vessels) and pith (parenchyma and epidermal cells) and their ash contents (obtained) are 1.1 and 5.4 wt% respectively (*Sanjaun et al. 2001*). As shown in Fig. 4.3, the WB ash is dark brown colour and WB pulp ash is white/light brown color and it contains ~60% crystalline silica as reported by *Ganesan et al. 2007*. The raw bagasse has slightly lost more weight than pulp during the incineration process. This could be mainly due to the structural and composition differences of bagasse and pulp that creates variations in dissipation of heat (during the burning process) through the samples. The bagasse consists of strong bonding of fibers that has prevented surface oxidation. The major elemental constituents of *S.officinarum* are carbon-44%, O-47%, H-5.7%, S-0.09%.

The rapid combustion of these elements in raw bagasse gives CO_2, H_2O, NOx and N_2. But SCB also accumulates amorphous silica within cells typically at an average rate of 1.509% by mass. When this organic matter is burnt, it results in an ash that is much higher in silica. It is stated that the bagasse ash contains a large amount of crystalline silica appr.62% *(Ganesan et al. 2007)* followed by CaO, MgO, K_2O etc. Whereas, the fibrated pulp fibers have inorganic constituents accumulated in the cell layers during pulping due to which a slight high ash% is observed.

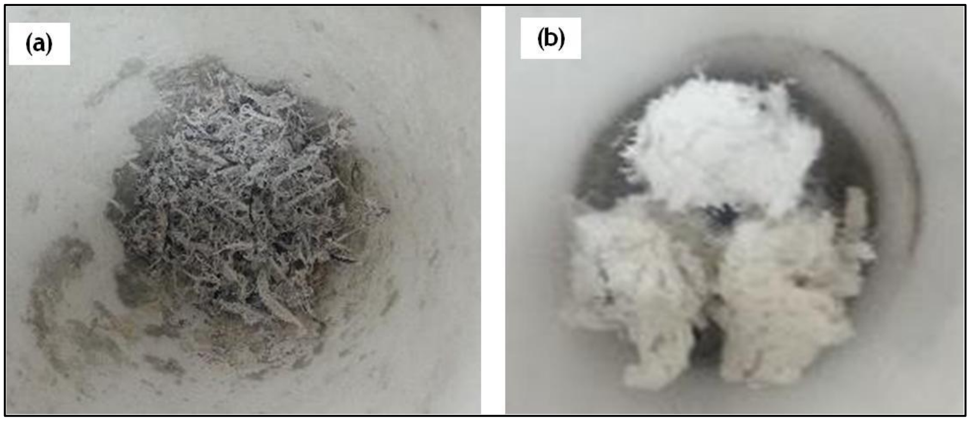


Fig 4.3: Bagasse (a) and bagasse pulp (b) samples after ash test.

(v). FTIR Analysis:

The FTIR spectra of wood and pulpare displayed in Fig 4.4 *(*for comparision, depithed raw bagasse and depithed pulp from 165^{o}C are considered)*.The absorption bands in the finger print region of 900-1800 cm^{-1} is related to various functional groups of lignin. Unlike pulp sample, a number of clustered peaks are observed in raw bagasse. The main differences between wood and pulp spectra are: presence of 1735 cm^{-1} peak due to the carbonyl (C=O, ester) of the hemicellulose and lignin; 1515 cm^{-1}peak representing C=C stretching of aromatic skeletal (lignin); prominent peak between 1278-1248 cm^{-1} indicating C=O stretching etc., are observed only in raw bagasse sample. Whereas, a concentrated peak at 1635 cm^{-1} representing OH deformation of absorbed water from cellulose is observed only in pulp sample. Therefore based on the lignin and prominent cellulose peaks, it can be qualitatively confirmed that dissolution of lignin fragments from cells wall layers has occurred during kraft pulping with the selected process conditions.

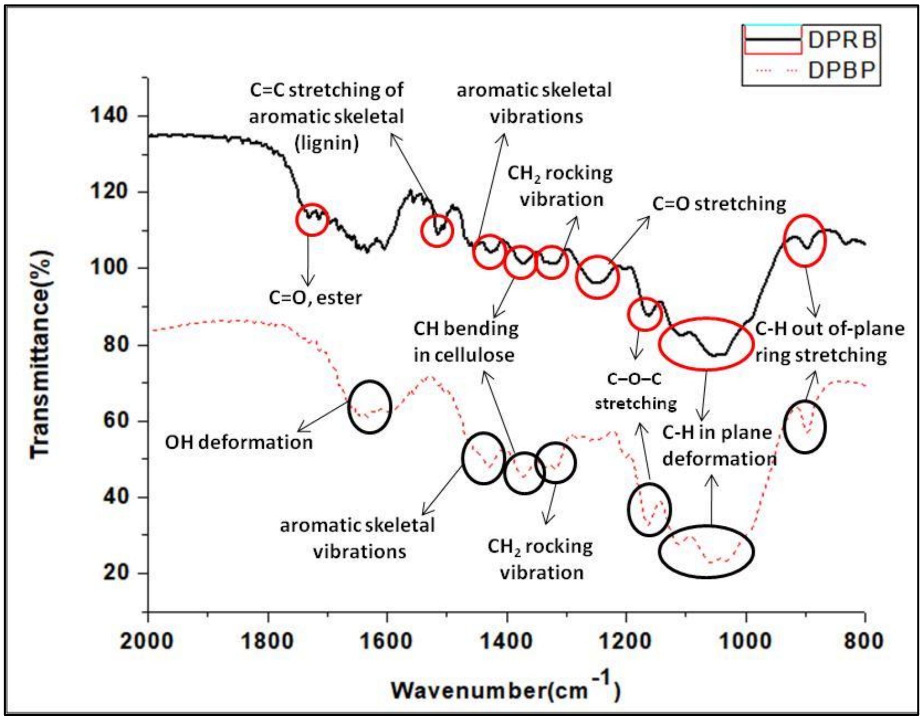


Fig 4.4: The absorption bands from FTIR bagasse and pulp analysis (DPRB- Depithed raw bagasse, DPBP- Depithed bagasse pulp)

4.3.2. Influence of temperature and Pith on pulp (whole bagasse and depithed) characteristics

The chemical analysis of pulps (WB and DPB) for various characterization methods such as Klasons lignin test, Cellulose isolation test, Water retention value, Ash test, FTIR analysis, Microscopic analysis and TGA are performed. The results thus obtained for the kraft pulps exhibited significant differences w.r.t pith and temperatures (140, 165^{o}C) as presented in Table 4.3.

Table 4.3: Characterization of whole bagasse and depithed bagasse (after cooking)

Sample	Kraft Cooking Temperature	Residual lignin (%)	Kappa Number	Cellulose (%)	WRV	Water absorption capacity (%)	Ash (%)
Whole Bagasse	@ 140°C	1.66± 0.04	11±0.27	57.94±2.74	4.39±0.13	1.29±0.14	2.87±0.38
	@ 165°C	1.53±0.02	10±0.13	69.41±0.9	4.72±0.12	1.78±0.16	4.52±0.38
Depithed Bagasse	@ 140°C	1.48±0.03	10±0.21	67.72±1.1	5.52±0.18	2.41±0.26	1.38±0.35
	@ 165°C	1.08±0.04	7±0.27	75.42±1.7	6.44±0.17	4.31±0.33	1.75±0.07

(i). Klasons lignin estimation:

From the results shown in Table 4.3, it is observed that the amount of residual lignin was higher for WB pulps compared to DPB pulps at both temperatures, but the difference is more prominent for 165°C pulps. The presence of pith (consisting barrel-like, thin walled ray parenchyma cells) results in low penetration of cooking chemicals to the bagasse cell walls. As explained before, increase in temperature caused more lignin degradation, hence % of residual lignin is slightly low for 165°C pulps compared to 140°C pulps and it is quite matching with the reported values by *Agnihotri et al. 2010* (lignin content decreased from 5.1 % to 3.4 % with increase of temperature from 140°C to 160°C). The delignification reactions are very temperature dependent like in wood, wherein small increase in temperature has a greater effect on the delignification rate. The delignification reactions are very rapid at high temperatures (160-175°C) due to alkaline cleavage of β-O-4 aryl ether linkages (*Fengel and Wegener 1989*) which increase the rate of lignin dissolution as reflected in the obtained results of DPB pulps (27% decrease was observed for 25°C of increase in temperature).

(ii). Cellulose isolation test:

The study indicates the amount of cellulose present in the pulp (after kraft cooking). As shown in Table 4.3, the % cellulose content of DPB pulps is slightly higher than WB pulps at both the temperatures. It is obvious that higher the residual lignin, lower the %cellulose content in pulp, hence the results shown in Table 4.3 are reflecting this fact. In comparison with whole bagasse samples, the basic density of depithed pulps is less because of the absence of pith and lower amounts of residual lignin. It can be seen that pulp samples cooked at higher temperature(165^{o}C) resulted in higher cellulose content (Fig 4.5) due to alkaline hydrolysis of glycosidic bonds with random scission which is leading to secondary peeling reactions (*Gazy 2016, Sanjaun et al. 2001*). But the pulping at 140^{o}C corresponds to partial dissolution of lignin by cleavage of α and β-aryl ether linkages in the phenolic units at middle lamella. Hence the decrease of %residual lignin and increase of %cellulose content in pulp is evident as the reaction temperature (140^{o}C to 165^{o}C) increases.

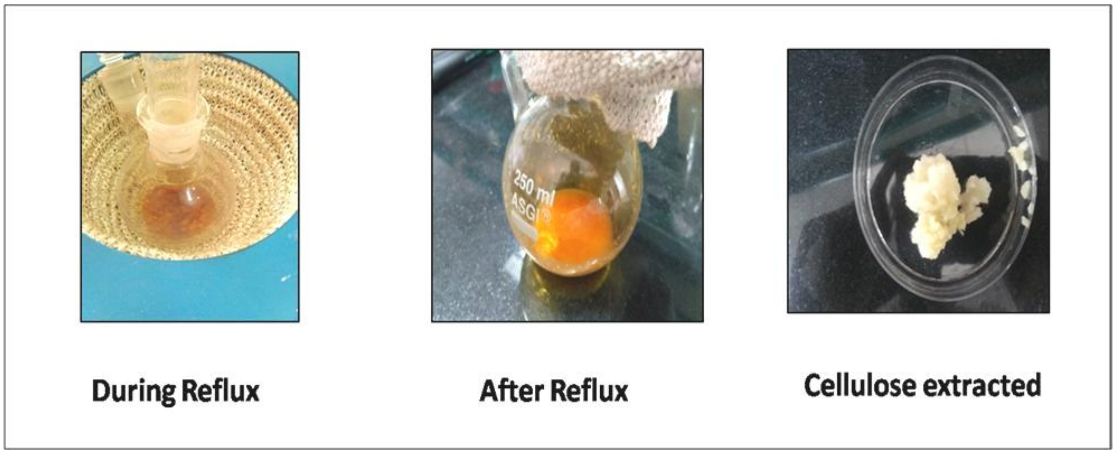

During Reflux **After Reflux** **Cellulose extracted**

Fig 4.5: Bagasse pulp samples during and after cellulose test

(iii). Water retention value:

WRV is a qualitative analysis measured to assess the approximate removal of lignin during kraft cooking process. The aim is to measure the capacity of fibrillated samples to hold water under centrifugal force and pressure filtration. This will also illustrate the degree of fibrillation and network structure of the samples. As shown in Table 4.3, the pulp samples from WB have exhibited slightly lower WRV at both the temperatures in comparison with DPB because pith consisting of micro network of porous short cells got slightly damaged as a result of cooking and extent of damage differs between WB pulp and DPB pulp involving diffusional constraints and availability of net surface area. This can also be attributed to the fact that presence of pith consumes and stores the white liquor in its pores during cooking process which decreases the degree of delignification. For both WB and DPB pulp samples, cooking temperature of 165^{o}C resulted slightly higher WRV compared to 140^{o}C pulp, because at 140°C, the white liquor could not diffuse into the cell interfaces and cell walls resulting in higher residual lignin content and less WRV for 140°C pulp. From comparison between Table 4.2 and Table 4.3, DPB pulp has shown almost 3 fold increase in WRV as a result of cooking, but almost no change in WRV between whole bagasse and whole bagasse pulp indicating no significant change in the net cellulose content prior to and after cooking. This can be understood that quantity of pith cells are reduced (around 30% fines with a length of <200µm as per *Agnihotri et al. 2000*), but more fiber are exposed (middle lamella lignin is removed) as a result of cooking.

(iv). Water absorption capacity:

The water absorption capacity of DPB pulp samples is 86% (140°C) and 142% (165°C) higher than WB pulp because of three reasons. First reason could be WB pulp has slightly higher amount of residual lignin, second reason could be the presence of bark on surface of WB pulp and third reason could be formation of glue like layer as a result of cooking in case of WB pulp. From an anatomical point of view, the diffusion of cooking chemicals is difficult in WB due to pith and small size pores. As a result, cellulose content and water absorption capacity of WB pulp is lower than DPB pulp. The binding property of paper depends on its capability to hold moisture because of improved hydrogen bonding between fibers, so it is difficult to make strong wet sheet using WB pulp. DBP pulp processed at 165°C has highest water absorption capacity (4.3%) and it should also be able to absorb more ink, which is one of the primary requirement of the writing paper. From the WRV, cellulose content and water absorption capacity it is clear that DPB pulp processed at 165°C is a better alternative compared to other three pulps because of high cellulose content and high specific surface area of the pulp fibers.

(v). Ash test:

From the results shown in Table 4.3, it can be clearly seen that presence of pith resulted increase in ash content compared to DB pulp samples. WB pulp obtained at 165°C has the ash content of 4.5% which is 150% higher than DPB pulp and this difference could be due to the presence of lignin sulfonates and also because of difference in silica contents (*Rainey and Covey 2016).* The ash content of both pulps at 140°C was notably lower compared to 165°C, which was probably a consequence of slow impregnation of cooking chemicals and continuous structure of fiber cells which also includes middle lamella in few cases. It is evident from our previous studies *(Madhuri et al. 2016, Puntambekar et al. 2016*) that ash contents are low for continuous structures such cellulose-lignin composites because of less number of pores which is evident from low residual lignin contents. In contrast to pulps, the ash content of WB (0.85%) is 50% lower than DPB (1.17%) and it could be due to the complete and continuous degradation of whole bagasse (WB) due to the small size pores and higher proportion of carbon content. In fact whole bagasse is used in energy production because of slow and complete degradation.

(vi). Analysis using Fourier Transform Infrared (FTIR) spectroscopy:

The differences in the spectra and attained peak heights in case of 140^{o}C (Fig 4.6) and 165^{o}C (Fig 4.7) is due to the structural composition differences of the pulp (i.e. amount of residual lignin%, extractives, pith and inorganics deposits etc). The absorption bands in the finger print region of 900-1800 cm^{-1} is related to various functional groups of lignin; bands around 1600–1400 cm^{-1} region in the spectra is attributed to the presence of aromatic or benzene rings in lignin; and the region between the wavelengths of 1450 to 1300 cm^{-1} involves several modes of vibration of lignin and carbohydrates *(Puntambekar et al. 2016).* The band at 898 cm^{-1} characteristic of C-H out of-plane ring stretching in cellulose due to the glycoside bonds is observed in both WB and DPB samples for both the temperatures. The main differences in the spectra from 165^{o}C are: The band around 1160, 1055 and 1114 cm^{-1} representing aromatic C-H in plane deformations *(Garriga et al. 2003)* are present in both the spectra, but are prominent in DPB pulp. The peaks around 1248cm^{-1} representing C=O stretching; 1375 cm^{-1}assignedtoCH bending in cellulose are observed only in DPB pulp samples. The principle peak around 1430 cm^{-1} associated with the amount of the crystalline structure of the cellulose *(Poletto et al 2014)* is present only in DPB pulp sample. The presence of 1735 cm^{-1} peak in WB sample could be due to the carbonyl (C=O, ester) of hemicelluloses and lignin. The bands around 1610-1640 cm^{-1} corresponds to OH deformation could be due to the water present in cellulose. Whereas, in case of 140^{o}C: The principal peaks assigned to lignin structures at 1512cm^{-1} and 1423cm^{-1}(C=C stretching of aromatic skeletal lignin); C–O symmetric stretching in pyranose ring at 1200-1215cm^{-1} is present only in WB.

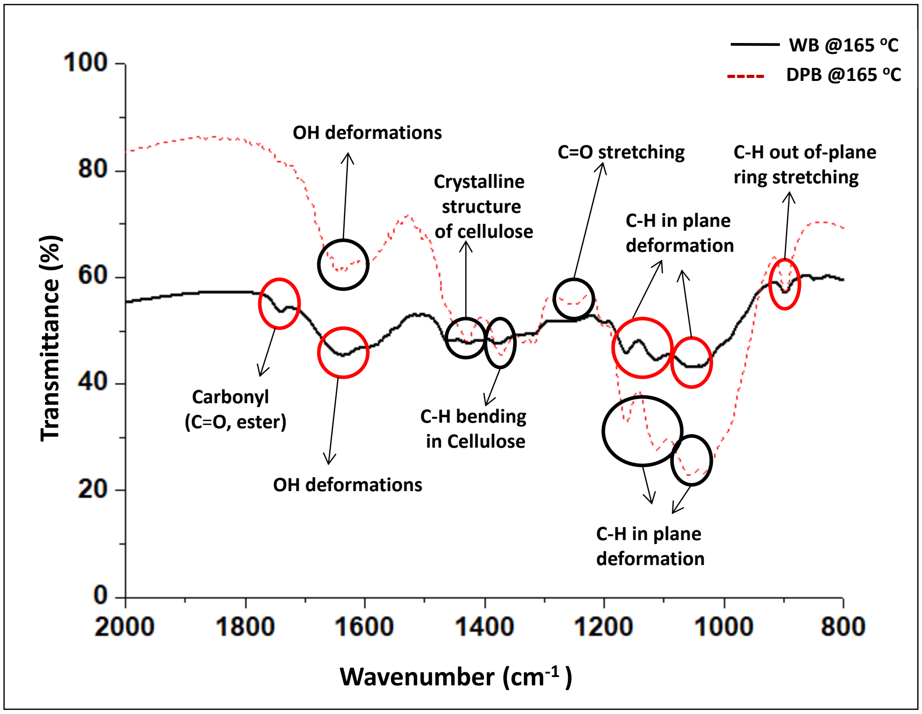


Fig 4.6: The absorption bands from FTIR pulp analysis- Kraft cooking at 165ºC *(WB- Whole bagasse, DPB- Depithed bagasse)*

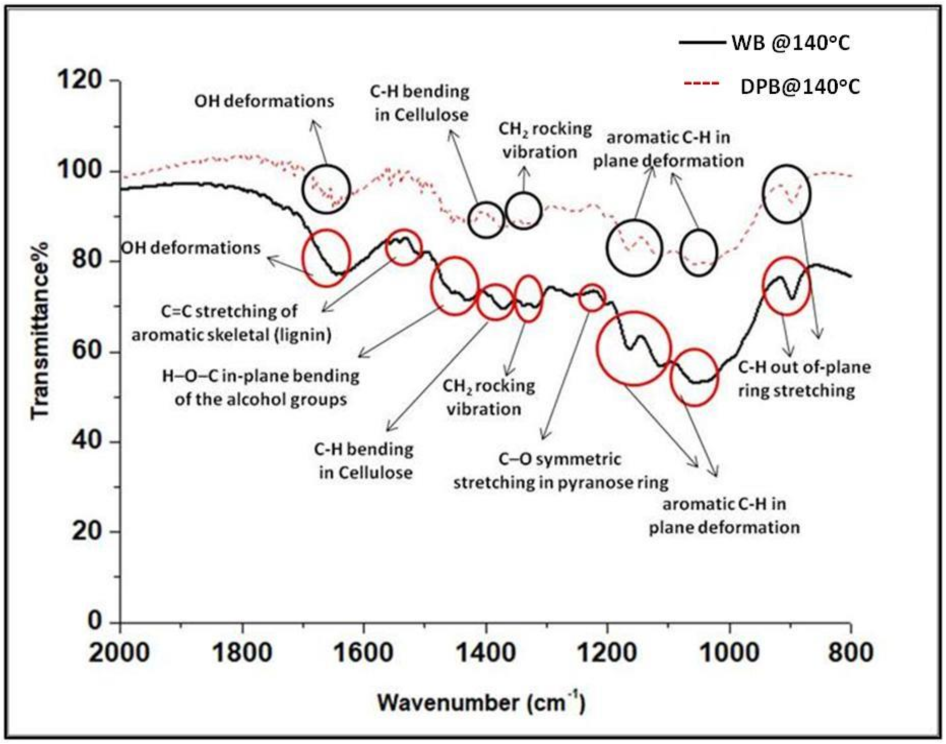


Fig 4.7: The absorption bands from FTIR pulp analysis- kraft cooking at 140ºC *(WB- Whole bagasse, DPB- Depithed bagasse)*

(vi). Microscopic analysis:

The pulp images shown in Fig. 4.8 and 4.9 features loose fibers among the depithed pulp samples compared to the whole samples. The whole pulp samples exhibited a dense structure with fibers clustered together as a bundle. Also, the presence of pith has resulted in a slurry formation around the edges of fibers and vessels (fig 4.10). Therefore, the presence of pith resulting in fiber clusters is generally not preferred for a good quality paper. The degree of separation was higher for pulp samples cooked at 165°C, qualitatively indicating greater degree of delignification as explained above.

As shown in Fig. 4.9a and 4.9b, the pulps processed at 140°C revealed parenchyma cells (length is between 350-600 µm; diameter is between 50-150 µm) and individual long fibers with diameter of 10-20 µm and length of 300-3000 µm. The length and diameter of fibers and pith cells are quite matching with reported values (*Agnihotri et al. 2010)*. More number of parenchyma cells and glue like thick layer (see the red circle in Fig 4.9d) can be seen in case of whole bagasse (Fig. 4.9b, 4.9d). It should be noted that vessels normally have less width and less length compared to parenchyma cells.

The pith is totally made of sponge like holocellulose which could be easily punctured (fig 4.11) due to the presence of loose short cells. The morphological study of WB and DPB enabled to demarcate the bark, fibers and pith as shown in Fig 4.12. Long continuous fibers running beside pith can be clearly seen in Fig. 4.12a. The whole Bagasse (WB) is made of parenchyma cells of pith (290 µm) and fibers is shown in Fig. 4.12b. The DPB also has pith but the quantity is low compared to the WB. The images also show a well intact bark for WB whereas DPB has bark as fragmented regions because of damage during the depithing process.

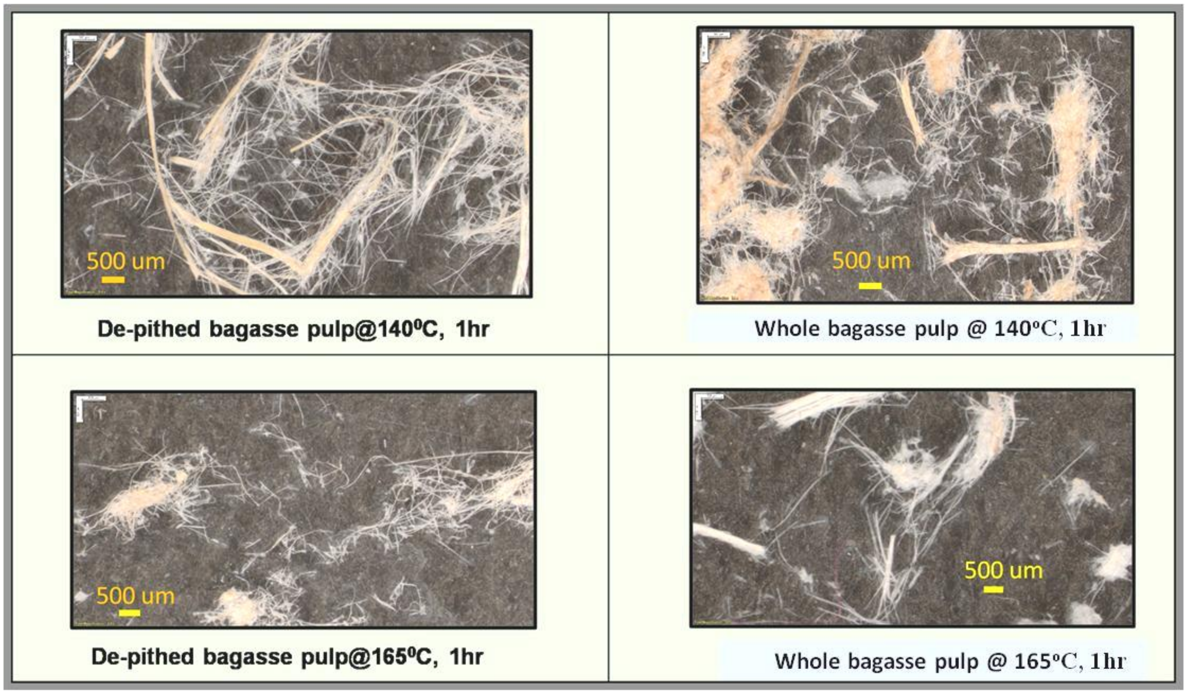


Fig 4.8: Stereomicroscopy images of bagasse pulp samples. 1-2 mm length fibers and 200-500 μm length vessels are visible.

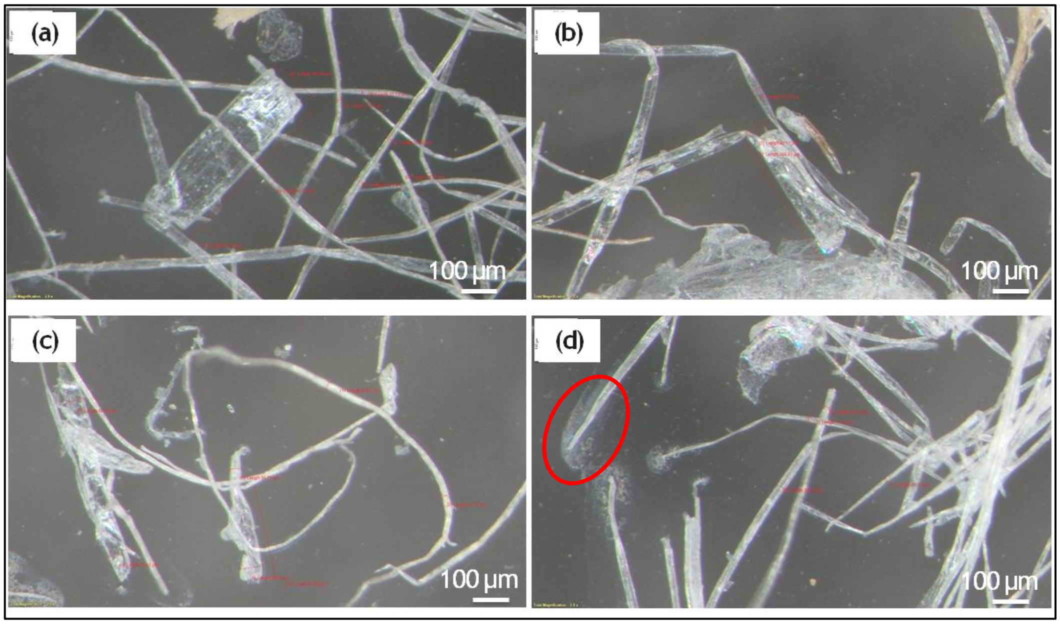


Fig 4.9: Stereomicroscopy images of bagasse pulp fibers. Fiber diameter of 11-22 μm and vessel diameter of 40, 50, 80 and parenchyma cell diameter of 140 μm are visible. a: Depithed bagasse pulp @140^{o}C; b: Whole bagasse pulp @140^{o}C; c: Depithed bagasse pulp @165^{o}C; d: Whole bagasse pulp @165^{o}C, 1hr

Fig 4.10: Stereomicroscopy image of whole bagasse pulp fibers pith. (The three red circles indicate glue like material which has resulted due to the degradation of pith cells at 165°C)

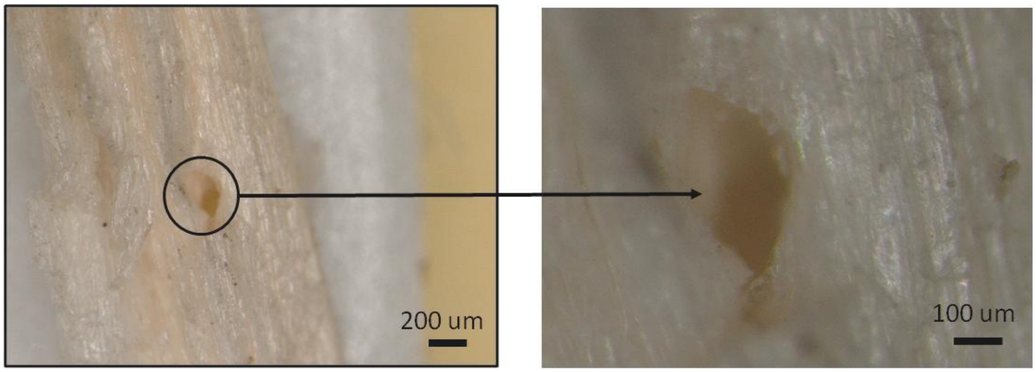


Fig 4.11: Stereomicroscopy images of whole bagasse (the pith part is easily punctured resulting in a hole)

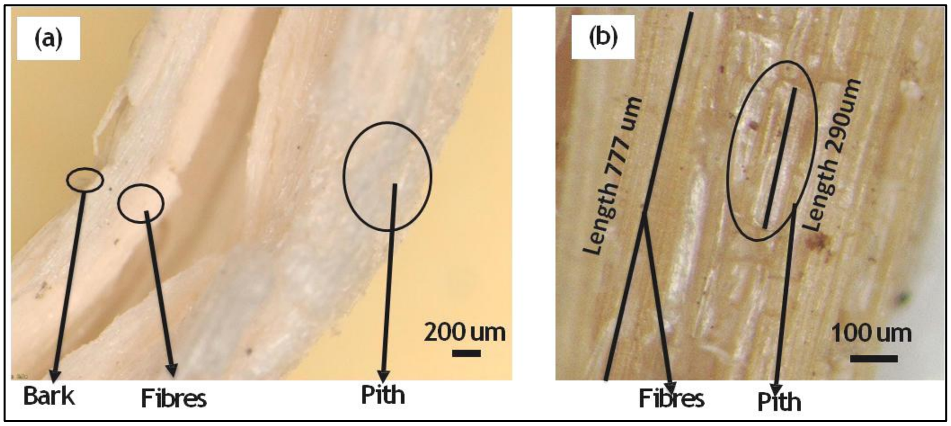


Fig 4.12: Stereomicroscopy images of bagasse revealing bark, pith and fibers (prior to cooking). a: Depithed bagasse; b: Whole bagasse

(vii). Thermo gravimetric analysis:

As shown in Fig. 4.13, the 5% decrease in weight of pulp by 100^{o}C corresponds to water vaporization or loss of volatile components. The main degradation step is found between 225^{o}C to 375^{o}C for WB and DPB pulps. In the case of DPB pulps, 25% decrease in weight of the pulp was observed by 280^{o}C (165^{o}C cooking temperature) and by 330^{o}C (140^{o}C cooking temperature). In the case of WB pulps, same 25% decrease in weight of the pulp was observed by 300^{o}C (165^{o}C cooking temperature) and 330^{o}C (140^{o}C cooking temperature). So the thermal stability of the WB pulp is found to be high compared to DPB pulps if 165^{o}C cooking temperature is considered and it could be due to the more number of parenchyma cells which might have formed a glue like layer in WB pulps as shown in Fig. 4.8d. The kraft cooking has degraded the amorphous lignin matrix from middle lamella but not all the pith cells so the WB pulp has cellulose fibers of high crystallinity.

For WB pulp fibers at 140^{o}C there was sharp reduction in its weight from 75% to 25% for increase of temperature from 280-380^{o}C. This second sigmoid (in case of WB pulp) could be due to parenchyma cells of pith region and also due to composite structure with less number of pores. For DPB pulp fibers at 140^{o}C there was sharp reduction in its weight from 75% -25% for increase of temperature from 300-370^{o}C. This second sigmoid (in case of DPB pulp) could be due to less number parenchyma cells of pith region and also due to cellulose-residual lignin composite structure with less number of micron sized pores. From the Fig. 4.13, it can be said that the pith is thermally stable from 100-250^{o}C, after which a drastic weight loss (upto 60%) was observed between narrow band temperature range 250-350^{o}C; WB pulps @165^{o}C has changed its path at around 350^{o}C and becomes thermally stable compared to the pulps @ 140^{o}C and it could be due to the higher amount of crystalline cellulose. It can be confirmed from the Fig. 4.14, where final ash of WB pulp of 140^{o}C is brown in color, but the same pulp ash for 165^{o}C sample became white in colour. Between the degradation temperatures, the maximum weight loss can be attributed to degradation of hemicelluloses and partial degradation of lignin.

The WB pulp showed greater heat resistance in comparison with DPB pulp at both the temperatures due to micron sized pores and gel like layers in WB pulps. Among two temperatures, the pulp samples kraft cooked at 140^{o}C showed greater thermal resistance compared to 165^{o}C samples until 50% wt reduction and it could be due to the higher percentage of residual lignin and composite structure (cellulose-lignin network) of cell walls. The temperature range of hemicellulose decomposition is from 190 to 300°C; for cellulose it ranges from 250°C to 350°C and lignin decomposition ranges from 190 to 500°C. The maximum mass loss rates for all the three main components are 250°C, 330°C and 430°Cas reported by *Morais et al. 2017*. Therefore the obtained data infer that at the pyrolysis stage the crystalline region of cellulose starts to destruct and the polymer decomposes simultaneously resulting in an increase of amorphous structure and decrease in degree of polymerization (*Yang et al. 2006*). The most part of volatile content in biomass are generated from the decomposition of hemicelluloses and cellulose. The high mass loss of pulp can be attributed to the presence of thermally unstable hemicelluloses and partial degradation of lignin fragments (*Lemos et al. 2017*).

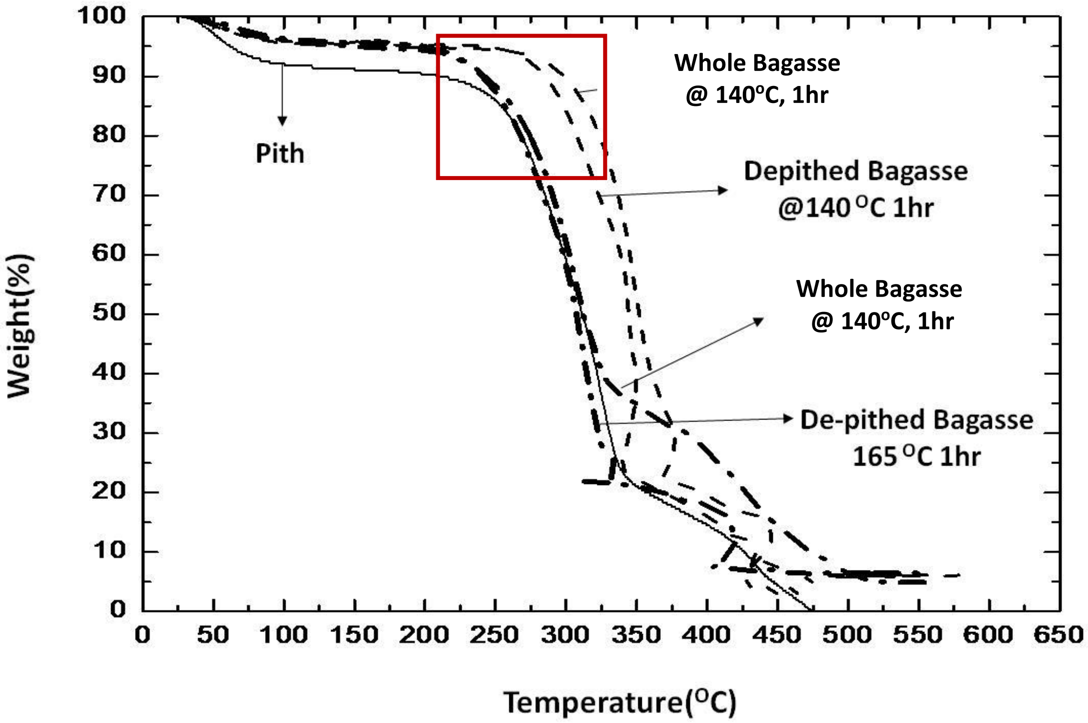


Fig 4.13: Thermogravimetric analysis (TGA) of whole bagasse pulp, depithed bagasse pulp and uncooked pith

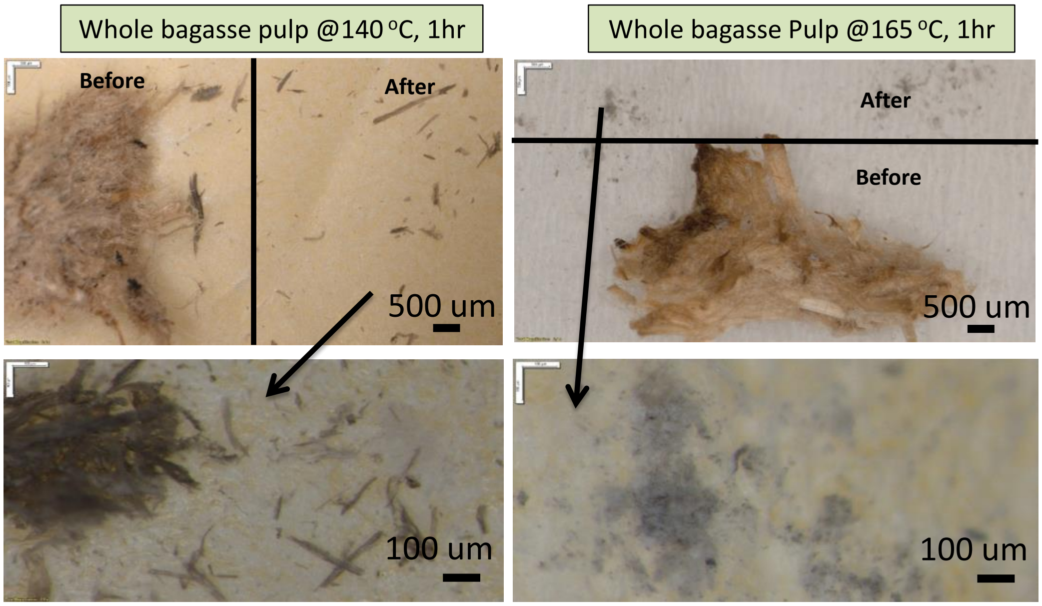


Fig 4.14: Microscopic images of whole bagasse pulp before and after TGA test

4.3.3. Comparision of wood pulp and bagasse pulp characteristics

In Mysore Paper Mills (Karnataka) wood as a raw material is used for paper making in the first 9 months of the year (mostly plantation grown trees) and bagasse is used for the next 3months (due to the shortage of essential raw material). The rapid deforestation, along with inadequate aforestation efforts and the Government's short-sighted policy of refusal to permit captive plantations have enabled the industry in utilization of bagasse as alternative for wood in papermaking.

Table 4.4: Characterization of wood pulp and bagasse pulp (after cooking)

Sample	Cooking temperature (^{o}C)	Residual lignin (%)	Kappa Number	Cellulose (%)
Subabul Rawwood Pulp	165^{o}C, 3hrs	1.6±0.3	11±2	74.2±1.2
Depithed Bagasse Pulp		1.3±0.1	9±0.6	78.2±1.1

Although the lignin content in raw bagasse (27%) is very close (comparable) to Subabul (28.2%); the pulp results (Table 4.4) obtained indicate that their delignification rates are quite different. For the same pulping conditions, bagasse has exhibited higher cellulose content and less residual lignin% than wood pulp. The literature states that though bagasse

(*Saccharum officinerum)* has 71.36% useful, long, and thick-walled fibers; the rigidity coefficient is less (0.39) than that of *Eucalyptus (0.72) and Subabul (0.89).*The pentosan content (retention or loss of hemicelluloses) will be generally on the higher side in sugarcane bagasse (23.90%) compared to *E. globulus*-17.64% and *Subabul*-17.21% (*Agnihotri et al. 2010).* In terms of guaiacyl (G), and syringyl (S) units of the lignin polymer, a study with model compounds indicated that β-aryl ether of S-lignin is cleaved more easily than G-lignin *(Tsutsumi et al.1995).* The 'lignin' from hardwoods and non-woods differ in composition, chiefly in methoxyl substitution and the degree of carbon-carbon linkage between phenyl groups. In this context, the lignin in bagasse is highly S-rich (60 in molar composition; *Del Rio et al. 2015).* Of significance, the fact is that, the structure of lignin in sugarcane bagasse is more open and looser and the morphological characteristics (shorter fibers, thin walls) and its chemical compositions are very different from woods. For these reasons SCB needs, in general, milder pulping conditions (lower temperatures, cooking time and chemical charges) than wood. Many researchers: *Lal et al. 2010, Lopez et al. 2010 and Jahan et al. 2009 etc* have reported such conditions in their research work.

4.4. CONCLUSIONS

The bagasse kraft pulping is very important to understand because it contains pith (parenchyma cells of 50-150 µm diameter) in variable quantities. The bagasse pulp is strongly affected by temperature and time of cooking. The pulp characterization results attained at temperatures 140^{o}C and 165^{o}C indicated that an increase in pulping temperature had a significant effect on the residual lignin, cellulose content and water retention value. The study also concludes the relative difficulty of delignification of whole bagasse at a given pulping time and temperature, using established experimental procedures. The presence of pith has affected the cooking process in a non-effective manner resulting in different levels of thermal stability and inferior pulp quality due to the composite nature of unbleached pulp. Hence, it is essential to optimize the process parameters and depith the bagasse before the pulping process so that bagasse can be used as an alternative to Subabul or Eucalyptus pulp in making quality writing paper.

CHAPTER-5

Effect of Temperature and Time on Black Liquor Characteristics

5.1. INTRODUCTION

Black liquor, the spent pulping liquor, is a dark viscous liquid extracted as a by-product during the pulping or cooking process *(Trung et al. 2015).* The chemical composition of the black liquor depends on the nature of raw material used i.e. wood, bagasse, bamboo etc., cooking chemicals used and process conditions (temperature, time) set in Kraft cooking. The black liquors after Kraft cooking consists mainly of lignin and carbohydrate degradation products in addition to a small fraction of extractives and their reaction products. The lignin fraction in black liquor is mainly composed of high molecular weight material. The range of molecular weight distributions of dissolved lignin is wide, consisting of fragments with a molecular weights above 100,000 Da (*Frederick 1997*). The weight average molecular weight (Mw) of wood black liquors is typically in the range of 2500 - 5000 Da. Black liquor normally contains more phenolic and carboxyl groups. Aliphatic carboxylic acids present in black liquor as sodium carboxylates are mainly formed as a result of the degradation reactions of the polysaccharides (cellulose and hemicelluloses) (*Sjostrom 1993; Alen 2000).*

Acids can be divided into volatile and non-volatile acids. Acetic and formic acids in black liquor are volatile acids and non-volatile acids include numerous hydroxy mono and dicarboxylic acids. Black liquor composition also involves wood extractives consisting of resinous compounds, volatile extractives (mainly terpenes) and fatty acids recovered as tall soap (*Sjostrom 1993*) as shown in Table 5.1. Black liquor also consists of inorganics mainly residual cooking chemicals, NaOH and Na_2S and conversion products of the cooking chemicals such as sodium carbonate (main component), sodium sulfate, sodium thiosulfate, polysulfides, sodium sulfite and sodium chloride; inorganic cations and anions (referred to as non-process elements) derived from the raw material such as calcium, potassium, magnesium, silicon and irons salts (small amounts) (*Liu et al. 2013; Zhang et al. 2013*). The black liquors from non-wood alkaline pulping differ from those of wood Kraft pulping, especially black liquors from agricultural residues. The molecular weights (4,000 – 5,300 Da) determined for the dissolved lignin are quite high compared to wood black liquor lignin and total amounts of main aliphatic carboxylic acids are much lower (in a range of 13-20% of the black liquor dissolved solids) compared to those of wood black liquor values (*Feng 2001).* The black liquors from agricultural residues contain significant proportions of non-process elements such as silica, potassium and chlorides *(Gupta et al. 2001)*. The high silica content in black liquors decreases causticizing efficiency and also causes difficulties in white liquor clarification *(Misra 1982).*

The physical and chemical properties of black liquor are very important in the recovery of heat and white liquor. The changes in composition of the raw material after pre-treatment and pulping can significantly alter the characteristics of the black liquor, therefore it is necessary that evaluation of black liquor characteristics should be studied to find out the effect of cooking parameters (temperature, time) on black liquor properties. *Therefore the aim of this chapter is to understand the effect of cooking time during the pulping of heartwood and sapwood at 140, 155 and 165ºC; and also during cooking of whole and depithed bagasse at 140 and 165ºC.*

Table 5.1: Black liquor composition *(Clay 2011)*

Alkali lignin	30-45%
Wood acids and polysaccharides	30-45%
Inorganics, salts	30-45%
Resins, Fatty acids	3-5%
Methanol	~1%

5.2. MATERIALS AND METHODS

5.2.1. Collection of black liquor samples at different time intervals.

- As discussed in the previous chapters *(3 and 4)*, the final pulps obtained after the 3hrs cooking (pulping) are analyzed for various properties (lignin%, WRV, Cellulose%, optical microscopy, FTIR, TGA etc) to understand the impact of the process conditions. But the extent of delignification in pulp could not be studied as a factor of time due to technical/fabrication limitations of Rotary Pulp Digester equipment. To address this gap, and to account for the lignin removed from the CML and cell walls, black liquor samples (wood and non-wood) were collected at different time intervals from the bottom of the digester (Fig 5.1) and analyzed.

- The diameter of valve used to collect the black liquor is around 19mm.
- During the pulping process of heartwood and sapwood at different temperatures 140, 155 and 165°C (*reference-chapter-3*), black liquor of appr.15-20ml was retrieved from bottom valve of the digester (Fig 5.1) after 1, 2 and 3hours. *[As the delignification process during kraft cooking is known to be divided into three dominating phases i.e. initial, bulk and residual., a time interval of 1, 2 and 3hr were selected for evaluating the black liquor properties]*
- ***Note:*** For kraft pulping of heartwood and sapwood at 155°C, the wood chips were soaked for 1hr before the cooking process. When the degassing valve (*the pressure inside the digester is reduced by releasing the valve and is then allowed to cool down*) was opened after 3hrs of cooking, some amount of black liquor with fines were released along with steam from the valve. Also, it was observed that the black liquor collected from bottom of the digester had approximately 5-10% fines in it. The fines present in the sapwood black liquor are slightly higher in quantity compared to fines in heartwood black liquor.
- During the pulping of whole and depithed bagasse at different temperatures 140 and 165°C (*reference-chapter-4*), black liquor of approximately 15-20 ml was collected from the digester after 0.5 hrs and 1 hr for depithed samples. For the whole samples, black liquor was collected at the end of the cooking period i.e. after 1hr.

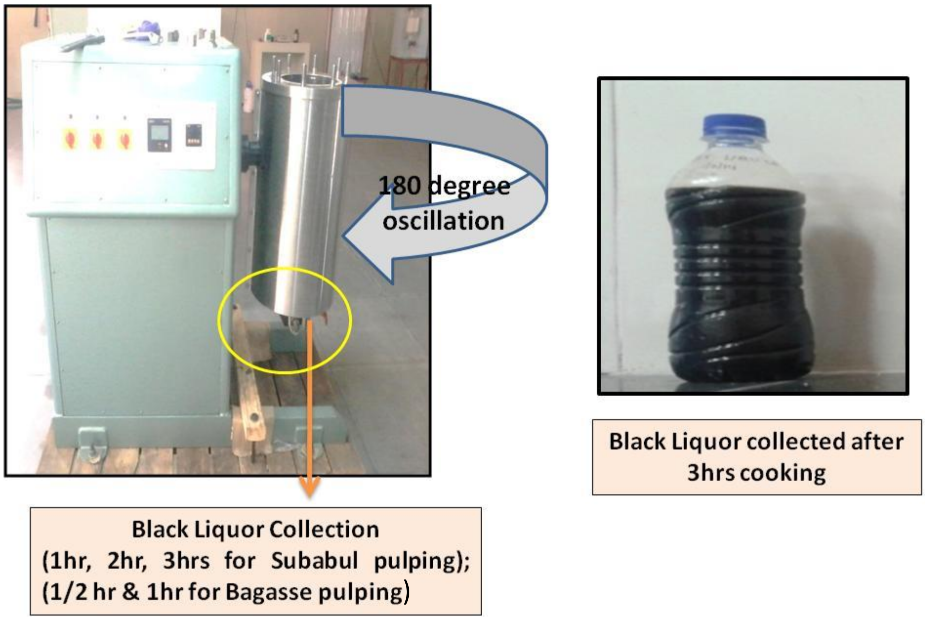


Fig 5.1: Photographs of (left) digester showing the black liquor collection valve and (right) black liquor collected in a bottle.

- The viscosity and turbidity of black liquor was studied (Fig 5.2). From the experimental results, it is observed that sapwood black liquor has a higher viscosity and turbidity (3.84 cP and 6.65 NTU) when compared to heartwood black liquor (2.08 cP; 0.41 NTU) due to the presence of more fines. This test was performed for 3hrs black liquor (155^{o}C) collected from Subabul wood cooking. Viscosity and turbidity of black liquor depends on the cooking conditions. *Andreuccett et al. 2011* reported that for 15% solid content, the viscosity value for Eucalyptus black liquor is 2.92 cP. *Liu et al. 2013* reported that the turbidity of pre-hydrolysis liquor of kraft based dissolving pulping process ranges in between 3.0 to 15.3 NTU. Similarly *Norgren (2003)* reported that softwood kraft cooking black liquor turbidity in alkaline solution (pH=10.5) ranges between 1.5 to 6.2 NTU.
- Viscosity/turbidity of black liquor depend on the solid content, the composition of the liquor samples, viscosity test temperature, cooking conditions, alkali content etc. Since the cooking conditions, alkali content and test temperatures are maintained same for both heartwood and sapwood samples, therefore the viscosity differences are due to solid content and composition variations. The viscosity increases if there are fines (solid content) present in the black liquor. This supports the hypothesis that

there is higher degree of delignification in case of sapwood than heartwood due to which more fines were added in sapwood black liquor.

Fig 5.2: Black Liquor sample during turbidity measurement using Nephelometer

- The fines in black liquor may contain amorphous cellulose and hemicellulose along with lignin. Most cellulosic materials consist of crystalline (eg: cellulose such as cotton linters whose crystallinity is 71.3%) and amorphous domains which allows easy penetration of liquids and are susceptible to hydrolysis reactions. In hemicelluloses, mainly Galacto-glucomannan monomer with degree of polymerization (DP) of 100 has acetyl groups that are easily cleaved by alkali solution.

5.2.2. Analysis of black liquor using UV-Vis Spectrophotometer

UV-Visible Spectroscopy (HITACHI U2900; Fig 5.3) reveals the possible electronic transitions by measuring the absorption spectra of a sample that has been excited with ultraviolet light. The UV-Vis characterization was done for black liquor solutions collected at different time intervals (Fig 5.4). The main purpose of doing UV analysis is to search for the lignin peak (phenolic groups) and qualitatively confirm its presence, as the absorbance is directly proportional to purity level of lignin. Such tests were done by *Jablonsky et al. 2015, Kumar et al. 2016 etc.* to find the peaks in precipitated lignin, Sugarcane bagasse, Softwood and Hardwood black liquor samples.

Fig 5.3: UV-Vis spectrophotometer used for black liquor analysis

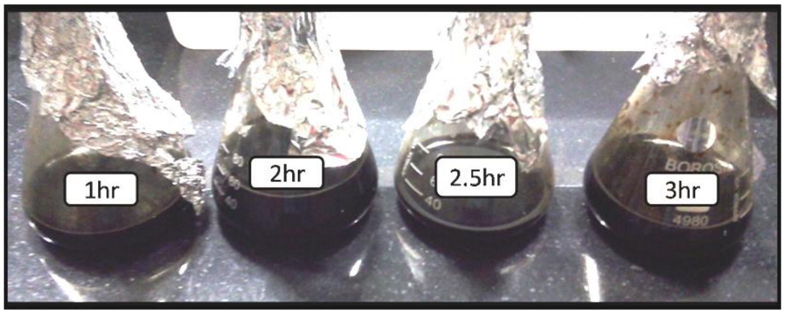


Fig 5.4: Black liquor samples (heartwood) collected from Rotary pulp digester at different time intervals.

The absorption spectra are recorded from wavelength 180 to 300 nm for wood samples and 180-440 nm for bagasse samples. About 0.1 ml of heartwood black liquor sample was diluted with 19 ml of water and about 0.01 ml sapwood black liquor sample was diluted with 200 ml of water before doing UV analysis. Similarly for bagasse, about 0.1ml of black liquor sample was diluted with 100ml of water for obtaining lignin peaks using UV-visible spectrophotometer.

5.2.3. Analysis of black liquor using fractional distillation

Black liquor solution mainly comprises of 15% solids by weight of which 10% are organic chemicals and 5% are inorganic chemicals. Normally the organics in black liquor are 40-45% soaps, 35-45% lignin and 10-15% other organics. The organic matter in the black liquor is made up of water/alkali soluble degradation components from the wood. Lignin is degraded to shorter fragments with sulphur content at 1-2% and sodium content at about 6% of the dry solids. Cellulose and hemicellulose is degraded to aliphatic carboxylic acid soaps and hemicellulose fragments. The collected black liquor samples were subjected to fractional distillation (Fig. 5.5) in order to separate organics from inorganics.

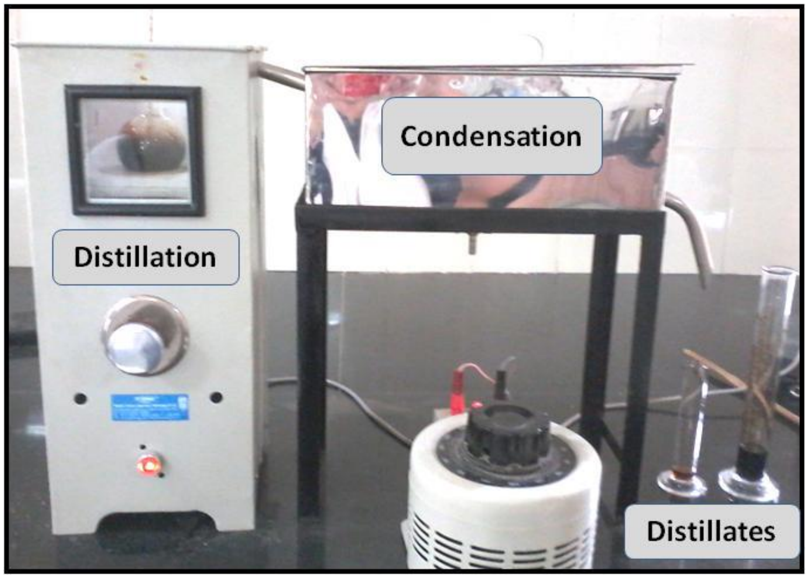


Fig 5.5: Fractional distillation of black liquor samples collected at different time intervals (1hr, 2hr and 3hr).

Around 25ml of black liquor sample was heated for about 85minutes at 105^{o}C and the volatile organic components were collected separately within 30 minutes after condensation. The distillates of each black liquor samples (HW, SW and bagasse) were collected at different time intervals i.e. first distillate after 30 mins and second distillate after 40 mins. During the fractional distillation process, white bubbles on the top layer of black liquor are normally observed indicating organic/volatile fractions. The collected volatile organic distillates were further analyzed using UV-Visible spectroscopic analysis to qualitatively confirm the presence of lignin fragments in the distillate fraction of the solution. The spectra's were obtained by diluting 0.1ml of black liquor solution in 10 ml (approximately) of water.

Relevant knowledge on the chemical and physical properties of black liquor is of great economic and technical importance for efficient control of kraft pulping process. Therefore the analysis is used to understand the extent of delignification with respect to time and temperature and also to detect lignin peak to qualitatively confirm its presence, as every material has its own characteristic absorption peak.

5.3. RESULTS AND DISCUSSIONS

5.3.1. Influence of cooking temperature and time on black liquor characteristics using UV-vis spectrophotometer

From UV analysis of ***Subabul sapwood and heartwood*** for different temperatures i.e. 140°C (Fig 5.6), 155°C (Fig 5.7) and165°C (Fig 5.8) and at different time intervals i.e. 1hr, 2hr and 3hr., significant lignin peaks were observed in all the samples over the time intervals. This indicates effective removal of lignin from the wood cell interfaces (compound middle lamella) and partly from cell walls during the pulping process as it is influenced by temperature and time.

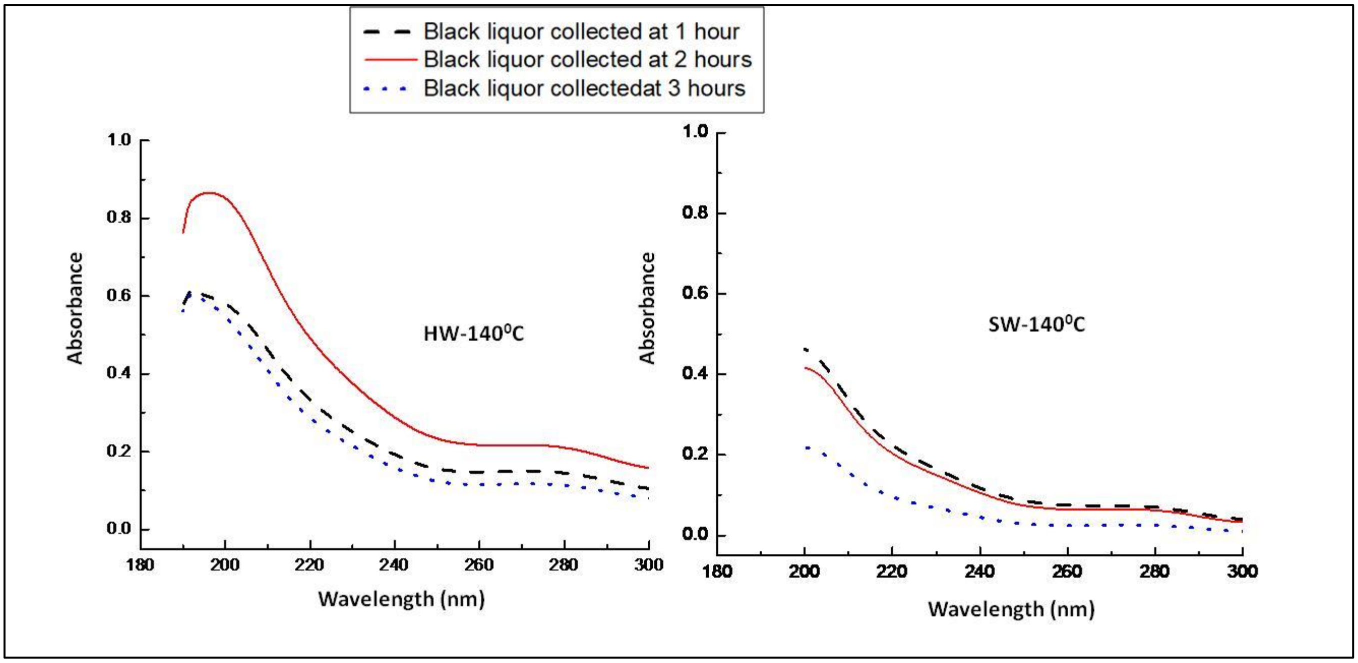


Fig 5.6: UV analysis for black liquor samples collected at different time intervals.
[Kraft cooking @140°C; HW-Heartwood, SW-Sapwood]

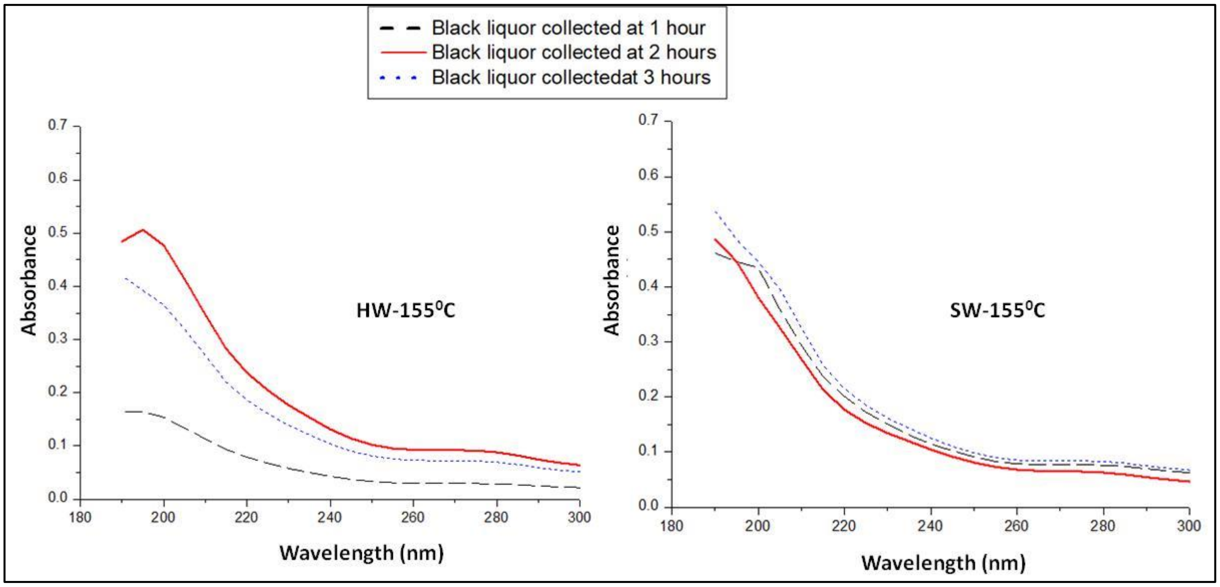


Fig 5.7: UV analysis for black liquor samples collected at different time intervals *(Kraft cooking @155°C ; HW-Heartwood, SW-Sapwood).*

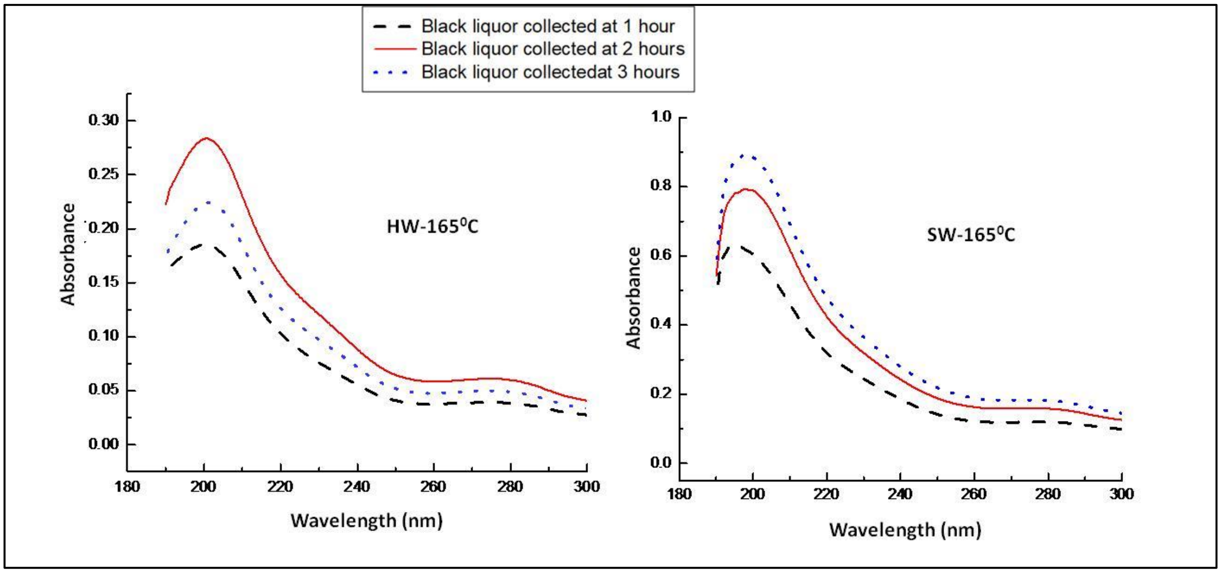


Fig 5.8: UV analysis for black liquor samples collected at different time intervals *(Kraft cooking @ 165°C ; HW-Heartwood, SW-Sapwood).*

Generally lignin shows spectrum at wavelength of 205-210 nm and the appearance of two characteristic peaks in the lignin spectrum is due to non-condensed phenolic groups (aromatic ring) in lignin. Compounds containing multiple bonds like aromatic compounds, alkenes, alkynes generally undergo $\pi - \pi^*$ transitions and absorb between 190-205 nm and absorbance of 1 at 200 nm represents phenols.

From Fig 5.8 (HW vs. SW at 165^{o}C), the absorbance is quite less for heartwood black liquor (0.23) compared to sapwood black liquor (0.89) for 3hr cooking time. This qualitative analysis indicates the differences in the sample composition and varying delignification rates under similar process conditions, as observed in the quantitative pulp analysis (*chapter 3*) of pulp fibers such as klason's lignin, water retention value etc. From above plots it can be stated that for sapwood, highest absorbance is found at 3hr time interval (0.2-140^{o}C; 0.55-150^{o}C, 0.99-165^{o}C) and for heartwood highest absorbance is found at 2hr time interval (0.9-140^{o}C; 0.5-150^{o}C, 0.28-165^{o}C) for all the three temperatures.

Heartwood black liquor (at all the three temperatures) exhibited peaks at <200nm wavelength with maximum absorbance for 2hr cooking time followed by 3hr cooking time. After 2 hrs, a decrease in absorbance is observed for all three temperatures. Also, even after 2 hr cooking time, the absorbance is decreasing from 0.9 to 0.28 with respect to increase in temperature i.e. 140^{o}C to 165^{o}C. In heartwood the cells are closely packed due to presence of lignin and extractives (polyphenolics). It is assumed that in HW, the bonding is relatively stronger between cellulose fibrils and lignin matrix (continuous phase) at middle lamella and secondary cell wall layers. During initial delignification state, the diffusion of chemicals within the middle lamella (brittle) might happen rapidly after forming the small pores in lignin matrix. Due to the removal of lignin in the form of fragments, separation of fibers occurs within 2hrs of pulping process. But as the cooking time progresses only the traces of residual lignin within the secondary cell wall layers is removed, resulting in low absorbance % after 3 hrs.

To confirm the above phenomena, the black liquor collected at 2.5 hr and 3 hrs during pulping (@165^{o}C) are subjected to UV analysis (Fig 5.9). The absorbance is same indicating no change of lignin composition between these intervals of cooking. This is because, after a certain pulping period the diffusion of white liquor into wood cell walls becomes difficult because of the accumulation of extractives and high lignin concentration in secondary cell wall (high density) i.e. approximately 44% of total lignin.

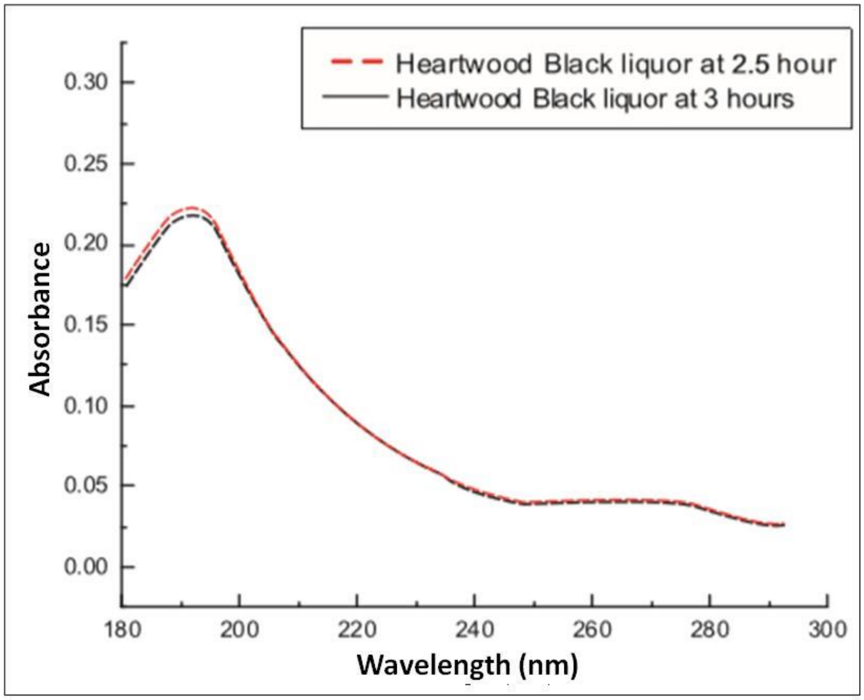


Fig 5.9: UV analysis for heartwood black liquor collected after 2.5 hours and 3 hours of cooking (@165°C).

The **Sapwood** black liquor (@155 and165°C) have also shown peaks at 200nm wavelength with high absorbance for 3hr cooking time interval, which indicates that most of the lignin is extracted from the sapwood after three hours of cooking process i.e. rate of delignification is increasing with increase in cooking time. It is also observed that the corresponding sapwood black liquor peak obtained at 200 nm in case of 3hrs sample (165°C) is observed at 195 nm in case of 1 hr sample. The peaks were found to be shifted about 5 nm as the time of cooking increased, probably due to the electronic transitions in phenols of sapwood during the delignification. For 140°C pulping temperature, high absorbance was observed for 1hr cooking time. This indicates the maximum degradation of lignin present at middle lamella (*initial delignification phase*) happened within 1hr. For further degradation, temperature is needed and not the time. The phenolic hydroxyl groups are ionized during different phases of pulping and due to which the absorption intensities changes with respect to time and temperature.

Kraft black liquor is a complex mixture with lignin as main organic component that accounts 35-45% total black liquor solids. The cleavage of ß-aryl ether bonds in non-phenolic lignin units is the rate controlling reaction. The heavily lignified middle lamella and cell corner areas are attacked strongly and the lignin is rapidly dissolved in the initial delignification phase. The height of the aromatic absorption band decreases with decreasing lignin content of the pulps. The absorption properties of lignin units are unchanged in neutral and alkaline medium, whereas the maximum absorption bands of phenolic shifting to longer wavelengths could be due to ionization of phenolic hydroxyl groups. Hence, the appearance of minute concentrated peaks (250-300 nm) in the attained spectra is due to electronic transition in phenols during delignification process.

From ***Bagasse (whole and depithed)*** black liquor UV analysis (Fig 5.10 and 5.11)., the highest absorbance peak (at 200nm) was observed for 1hr kraft cooked depithed black liquor in comparison with 1/2 hr sample for both the temperatures (140^{o}Cand 165^{o}C) and the absorbance (%) increased with cooking time. The peaks were shifted about 3-5nm as the cooking time increased. This can be attributed to the electronic transition of phenols and other low molecular weight extractives removed during delignification process. Significant sharp peaks were observed for all the samples between 200-208 nm which infer conjugated C=C and major σ - π^* transitions in the complex aromatic rings of the lignin molecule. It is observed that, the absorbance for black liquor obtained for 140^{o}C - 1hr is almost similar to the absorbance of black liquor obtained for 165^{o}C - 1/2 hr which clearly indicates that increase in temperature can reduce the cooking time from 1 hr to1/2 hr. The broad peaks at 270-300 nm representing n-π^* transitions are due to the various byproducts (mostly inorganics) that are formed during the pulping process. A typical absorption peak near 280 nm is due to free and etherified hydroxyl groups that contribute to the characteristic absorption of minimum lignin *(Jablonsky 2015)*. The typical absorbance peak at 280 nm shifted to a shorter wavelength (277 nm) that indicates un-conjugated guaiacyl and 3,4-dimethoxy-phenyl model compounds.

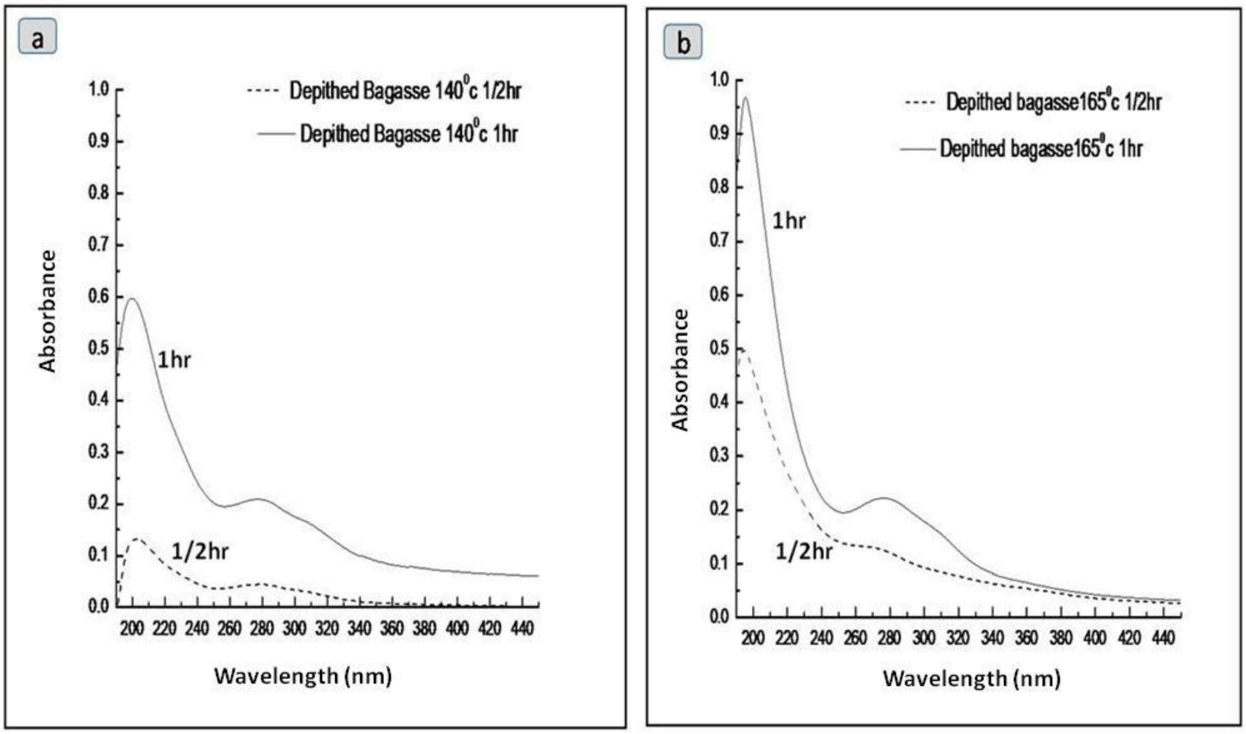


Fig 5.10 : UV analysis of depithed bagasse black liquor collected from digester at 1/2hr and 1hr of cooking

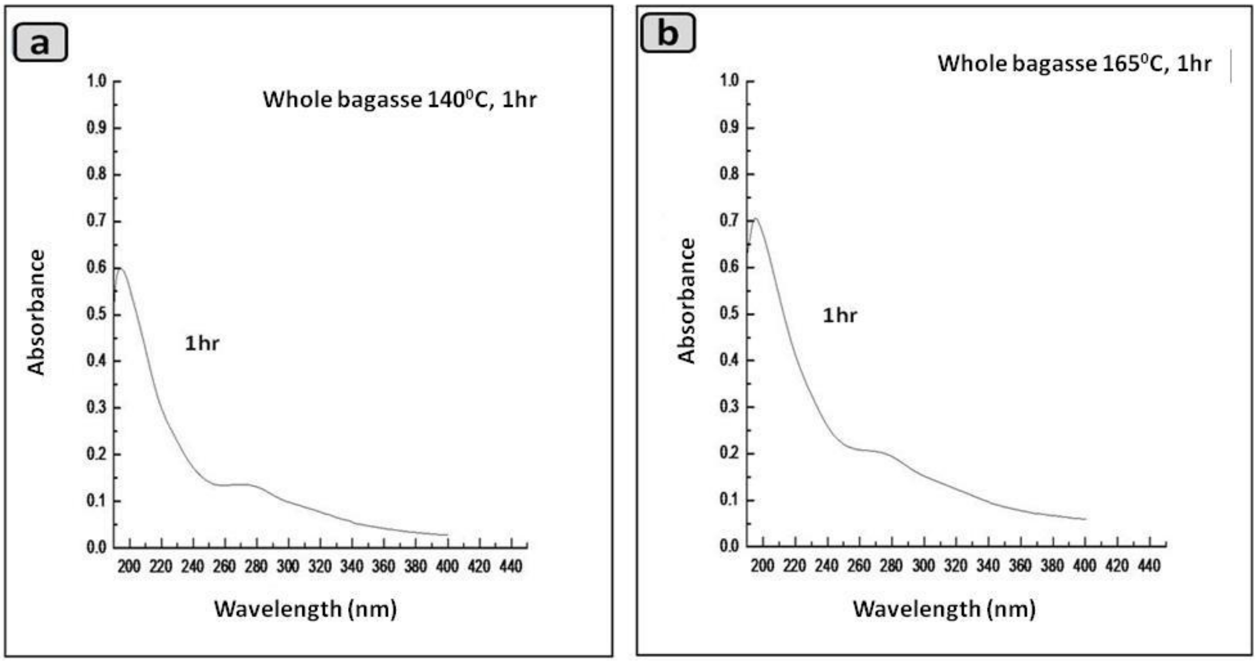


Fig 5.11 : UV analysis of whole bagasse black liquor collected from digester after 1hr of cooking

It is also observed that the absorbance of whole and depithed bagasse black liquor for 140°C - 1hr are equal (0.6), whereas the absorbance of depithed (0.9) black liquor for 165°C - 1hr is higher than whole (0.7) bagasse. This is mainly due to temperature and chemical composition differences. Regarding temperature, 165°C represents bulk delignification phase in which high amount of lignin is removed from compound middle lamella, primary and secondary cell wall layers. Regarding chemical composition, the presence of pith (ray parenchyma cells) results in low penetration of cooking chemicals into the cell walls resulting in minimal removal of lignin (*pulp residual lignin: 1.53%).* The basic density of depithed bagasse is less due to the reduction of pith content and bark content hence better impregnation of white liquor takes place resulting in higher amount of lignin removal (*pulp residual lignin: 1.1%).* These differences in the lignin removal from pulp has been reflected in obtained black liquor UV results. In fact presence of pith allows more white liquor penetration, but it absorbs and hold white liquor in its pores and not allowing it to react with lignin. That's why at 140°C, same amount of lignin is removed from whole and depithed bagasse, but increase in temperature caused more diffusion of white liquor into the cell walls in case of depithed bagasse.

From the above qualitative analysis regarding whole and depithed bagasse it can be stated that with the desired temperature, the cooking process can be optimized with respect to time.

5.3.2. Influence of cooking temperature and time on black liquor characteristics using fractional distillation

The distillate samples (approximately 5-10ml) collected during distillation process are checked for their pH, volatile fatty acids (VFA), boiling points followed by UV analysis. Properties of retentate samples are determined using viscosity and ash tests.

The sapwood and heartwood distillates corresponding to 165°C, 3hrs kraft cooking have exhibited pH values ranging from 5.9 to 8.3. *Jingjing 2011 reported that the pH value of kraft lignin of (pine, spruce, birch, aspen) softwood black liquor ranges between 2 - 7.* The above samples are also checked for their concentrations and it was observed that heartwood distillates (0.2 kg/m^3) have exhibited higher concentration of VFA than sapwood distillates (0.07 kg/m^3). *Kevlich et al. 2017 reported that the typical concentration ranges of extractives in Kraft black liquor range between 0.1-2.1 kg/m^3.*

VFA values contribute to the presence of various volatile fractions such as carboxylic acids, fatty acids, formic acid, terpenes etc in black liquor distillates. From previous experimental analysis *(reference-chapter 2*) it is observed that the lignin and extractive content are higher for heartwood than sapwood, thus the volatile fatty acid results are reflecting the above conclusion.

The ***boiling point*** of heartwood and sapwood black liquor distillates is estimated using *Distillation Analyzer* (ESTANIT 40.10). The distillation process was carried out at 103ºC. The solution for testing comprises of 16ml of distillate sample obtained from fractional distillation +34ml of water i.e. a total of 50ml solution was considered. The condensation and receiver temperatures were in between 30-35ºC and 20-25ºC respectively. The initial boiling point of sapwood and heartwood distillates is found to be 93.5ºC and 97.1ºC. The entire processing has taken ~30-40 mins and extensive foaming was observed during heating like in fractional distillation.

The foaming (Fig 5.12a) is mainly due to organic acids, gums, polymeric compounds, resin acids etc. The boiling point of sapwood corresponds to release of ether compounds (butyrate of methyl, acetate of propyl, formate of butyl, propionate of ethyl etc). The ether has R-group that could be linked to alkyl or aryl groups and aromatic polymer lignin has mostly ethyl (β-O-4 or α-O-4) linkages. The boiling point of heartwood corresponds to release of alcohols (mainly propyl alcohol).

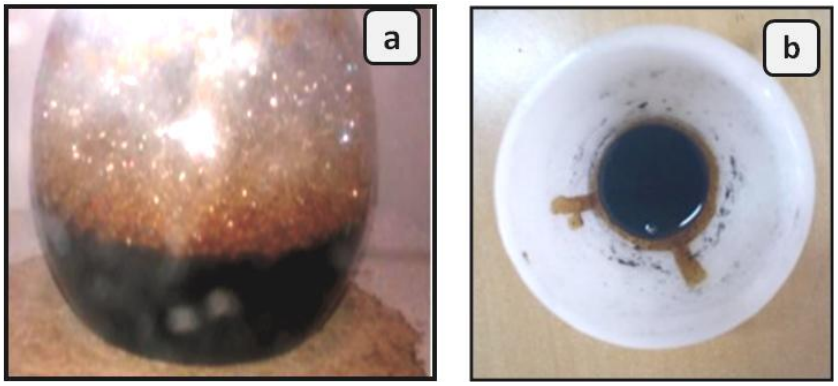


Fig 5.12: (a). Foaming of black liquor during distillation process *[Note: white bubbles on the top layer indicates organic fraction];* (b). The retentate of black liquor after distillation process.

The ***viscosity of retentate*** (Fig 5.12b- 165°C sample; left over residue after distillation process) corresponding to heartwood and sapwood is evaluated using Redwood viscometer. It is observed that viscosity of retentate increased with time due to the removal of more volatiles i.e. extractives and lignin. From the tests, it is also found that the viscosity of heartwood (2.92, 3hr distillate) is slightly higher than sapwood (2.81, 3hr distillate). Retentate contains organic compounds of high boiling point and inorganic compounds and attempt was made to find the composition using XRD technique.

Retentate samples were subjected to ***Ash test*** (@525°C, 3hrs in muffle furnace) which represents the inorganic content in a particular species. The results have confirmed the above hypothesis i.e. sapwood retentate exhibited higher ash content (36%) than heartwood retentate (12%). After the test, three important physical features are observed i.e. loss in weight, increase in volume and increase in density. It is reported by *Alen (1994)*, that black liquors swell (Fig 5.13) considerably in the temperature range of 180-270°C. This is because, extensive degradation of organic material and formation of volatile degradation products take place in this temperature region and the swelling results from hindering of the volatile products within the particles. Aliphatic carboxylic acids are the primary source of the volatile degradation products necessary for swelling, while lignin fragments have an important role in hindering the escape of the volatile products. Black colour appearance of the ash is due to carbon coke (reduction).

Fig 5.13: Retentate after incinerating in muffle furnace at 525°C

Fig 5.14 represents the collected organic fractions of heartwood (Fig 5.14 a) and sapwood (Fig 5.14 b) ***black liquors distillates*** during ***fractional distillation process***. Where (1) indicates the first fraction and (2) indicates the second fraction obtained after 10 mins. Distillate of 3 hrs sample (3-2 and 3-1) followed by distillate of 2.5 hour, 2 hour and 1 hour samples indicates black liquor collected after 3 hrs, 2.5 hrs, 2 hrs and 1 hr from the bottom of the digester and subjected to fractional distillation.

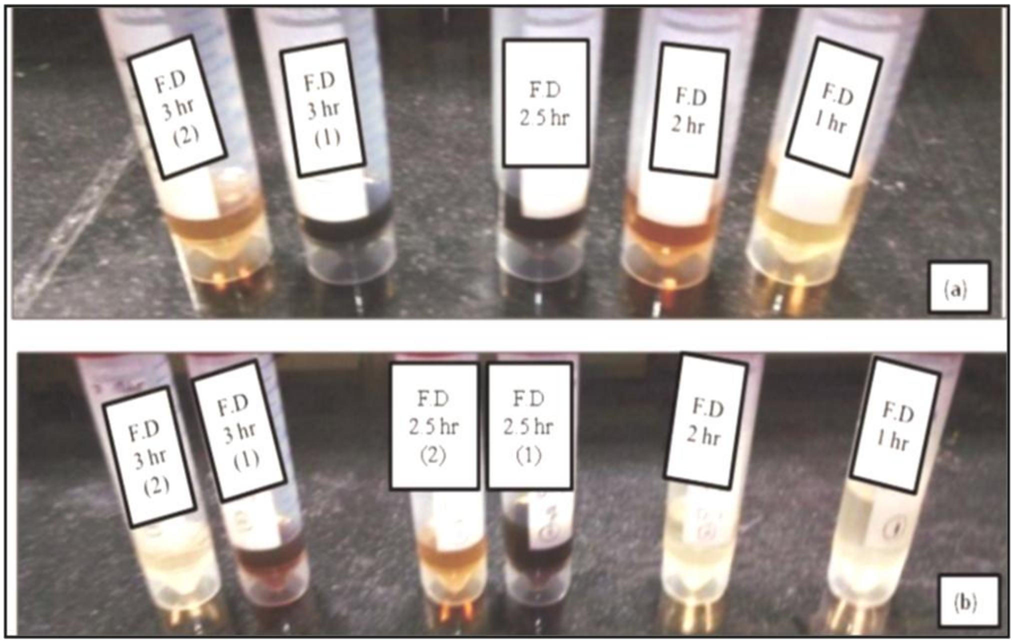


Fig 5.14: (a). Heartwood black liquor (b) Sapwood black liquor *[left to right: distillate of 3 hour sample (3-2and3-1) followed by distillate of 2.5 hour (2.5-2 and 2.5-1), 2 hour and 1 hour samples]*

From the images it is evident that the increasing intensity of colour from light yellow to dark brown of the distillates as the cooking time increases from 1 hour to 3 hours (considering only the first fraction). Similar trend was followed for both heartwood and sapwood black liquor samples as shown in Fig. 5.14 a and b. Heartwood distillates are darker than sapwood distillates at every interval of the sample collected confirming that more number of chromophores are extracted in heartwood kraft cooking than in sapwood cooking. To confirm this, UV analysis of distillates were performed.

During fractional distillation, the distillates of heartwood and sapwood are collected between 80^{o}C-105^{o}C. The prominent volatile fractions between these temperatures are mainly Phenolic components (benzene), Terpenes, Methyl mercaptants, H_2S, Dimethy sulphide etc. Hence peaks corresponding to the above fractions are expected during distillates UV analysis.

From the analysis we can observe that there is gradual increase in the absorbance for distillates of heartwood black liquor samples collected at intervals of 1 hr and 2hrs as shown in Fig.5.15. In the UV analysis of sapwood distillate, we can observe clearly no change in the absorbance for distillates collected at intervals of 1 hr and 2 hr. But the distillates of black liquor samples collected after cooking (3hrs) showed difference in absorbance percentage between first distillate (darker, 30 mins) and second distillate (lighter, 40 mins) as shown in Fig. 5.14 and5.15. Hence it can be concluded that intensity of colour of distillate (Fig. 5.14) is characteristic of absorbance (Fig. 5.15).

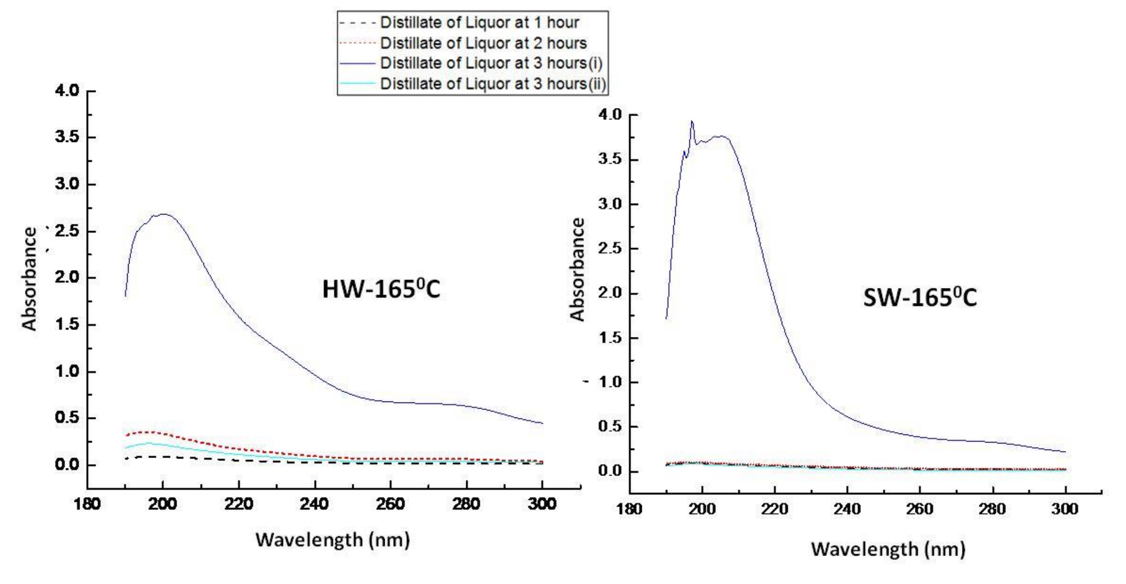


Fig 5.15: UV analysis for black liquor distillates. Black liquor was collected after 1 hour, 2 hours and 3hours of cooking at *165^{o}C. [Note: Here (i) indicates first distillate (darker, collected in first 30 minutes) and (ii) indicates second distillate (lighter, collected after 60 minutes)].*

In case of distillate UV analysis of black liquor cooked at 140^{o}C, no significant peaks and differences in the absorbance (Fig 5.16) is observed for sapwood and heartwood distillate samples except the heartwood distillate exhibited concentrated peak with high absorbance at 2 hour, whereas sapwood distillate exhibited similar behavior at 3hour. This is mainly due to high concentration of aromatic constituents of lignin in black liquor extracted from heartwood cells (compound middle lamella) during initial delignification stage (140^{o}C) of pulping. The distillates exhibited peaks between 200-205 nm indicating presence of poly-unsaturated and aromatic compounds (mainly benzene and its derivatives). The variations in peaks between sapwood (high cellulose, inorganic and mineral content) and heartwood (high lignin and extractive content) is due to their structural and composition differences. Therefore, no change of lignin composition after 2hrs is observed for HW, whereas for SW lignin degradation is gradually increasing with time.

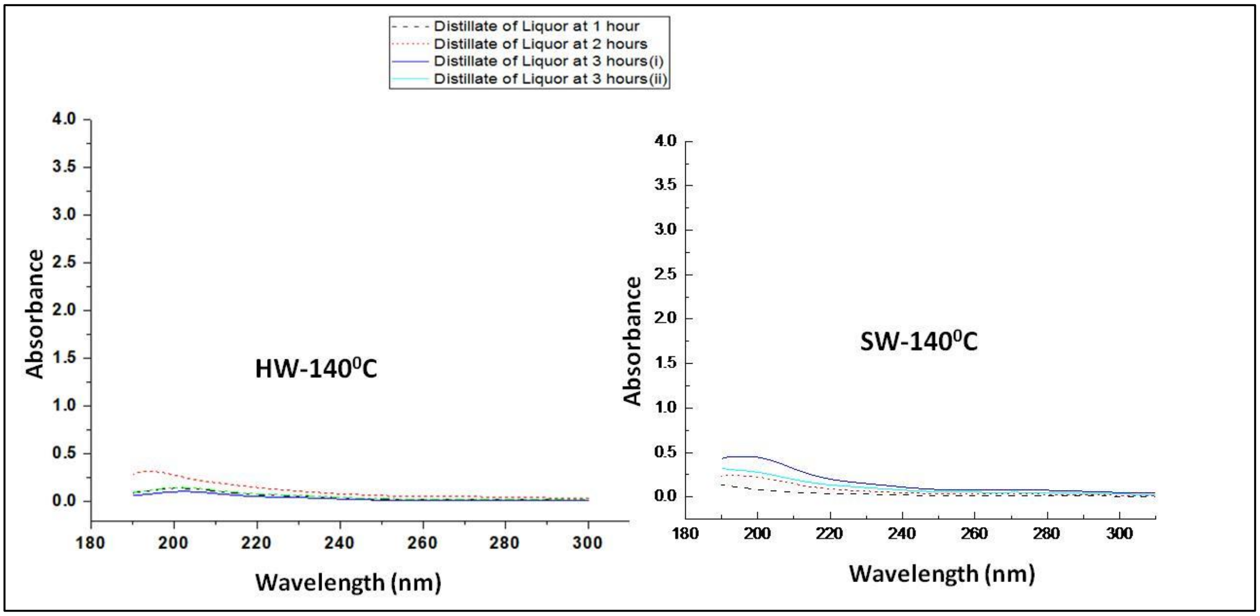


Fig 5.16: UV analysis for black liquor distillates. Black liquor was collected after 1 hour, 2 hours and 3hours of cooking at *140^{o}C, 3hrs. [Note: Here (i) indicates first distillate (darker, collected in first 30 minutes) and (ii) indicates second distillate (lighter, collected after 60 minutes)].*

In comparision with 165^{o}C, the absorbance is relatively very low for 140^{o}C. At 140^{o}C only initial delignification happens, that indicates only low molecular weight lignin fragments are dissolved from middle lamella (CML) regions and loss of acetyl groups and uronic acids of hemicelluloses (about 40%) takes place *(Alen 2000*). This non-uniformity of delignification process because of low temperature results in high residual lignin content in pulps and less volatile fraction in black liquor. Hence the UV results (peaks) thus obtained have confirmed the above hypothesis. From 155^{o}C distillate UV analysis (Fig 5.17), concentrated sharp peak with high absorbance is observed for sapwood and heartwood distillates between 200-205 nm indicating aromatic building units of lignin.

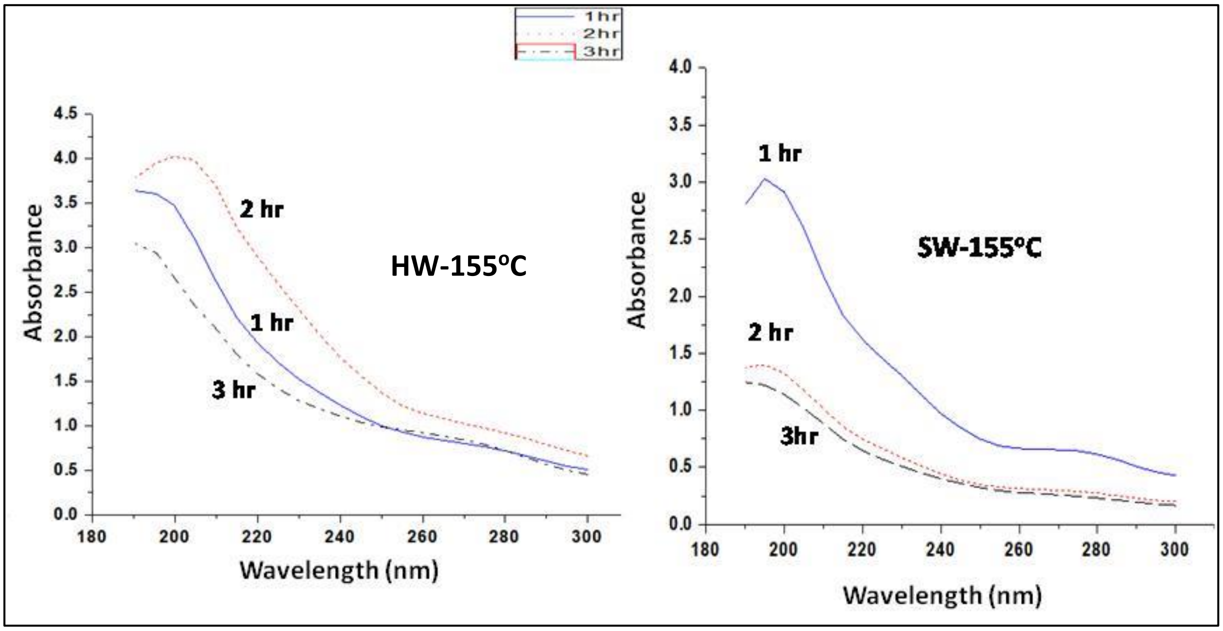


Fig 5.17: UV analysis for black liquor distillates. Black liquor was collected after 1 hour, 2 hours and 3 hours of cooking at 155°C, 3hrs.

Here samples were soaked for some time prior to cooking. In comparison with 140°C, an increase in absorbance for both sapwood and heartwood distillates can be noted. This observation can be attributed to the fact that., main delignification takes place during the BD (bulk delignification phase), which starts at about 150°C during which lignin is degraded as a result of the alkaline cleavage of the β-O-4 aryl ether linkages from CML and partly from cell wall layers. Thus accumulation of volatile fractions and presence of fines (few) that have accumulated in the black liquor during the soaking followed by cooking process could be the reasons for obtaining the peaks with higher absorbance than 140°C distillates.

5.4. CONCLUSIONS

- The UV-Visible spectroscopic data of sapwood and heartwood black liquor revealed significant lignin peaks for all three cooking temperatures (140°C, 155°C and 165°C). The peaks were obtained at 200 nm for all samples of heartwood black liquor, but the absorbance was highest at 2 hours sample, which indicates that most of the lignin is removed from wood cells within 2 hour of the cooking process. For sapwood, highest absorbance is for 3 hrs sample indicating that lignin degradation is gradually increasing with time.

- From bagasse UV analysis, depithed bagasse exhibited high peak concentrations than whole bagasse, between wavelength 190-205nm indicating aromatic groups and phenols. The absorbance obtained for 140^{o}C, 1hr is similar to the absorbance obtained for 165^{o}C, 1/2 hr which clearly indicates that increase in temperature can reduce the cooking time by 1/2 hr.
- Fractional distillation analysis indicated that heartwood distillates are darker than sapwood (for all three cooking temperatures) at every interval confirming higher extraction of chromophores. Also, the black liquor distillate samples have shown difference in absorbance between first distillate (darker, 30mins) and second distillate (lighter, 40mins) proving that the intensity of colour is characteristic of absorbance in UV analysis.
- The UV analysis of distillates have shown peaks at wave length around 195-205nm (for both SW and HW samples at all temperatures) representing poly unsaturated and aromatic compounds. The absorbance of SW was found to be comparatively higher than HW and the intensity of peak concentrations were higher in case of 165^{o}C than 140^{o}C.
- With respect to temperature and time, it can therefore be stated that, for a fixed cooking temperature (165^{o}C) SW cooking is to be performed for 3hrs and in case of HW, 2hrs of cooking time is sufficient i.e., as increasing the cooking time beyond 2 hrs in case of HW had no additional benefit. Also the results with respect to other cooking temperatures (140^{o}C and 155^{o}C) implies that use of lower temperatures with higher cooking time leads to better yields.
- Therefore it can be concluded that fractional distillation followed by UV spectrophotometer can be used as a tool to predict the extent of delignification during cooking.

CHAPTER -6

Effect of Bleaching on Pulp and Papersheet Characteristics

6.1. INTRODUCTION

Bleaching of pulp is the treatment of cellulosic fiber with chemicals to increase the brightness. A major proportion of bleached chemical pulp is produced by the kraft process. Lignin remains a primary constituent of pulp even after 3 hrs of kraft cooking process *(Reeve 1996)* i.e kappa number is in the range of 8-16 even after 3 hours of cooking. Lignin imparts a brown colour to the pulp (hence its name “brown stock”) and unless removed, will continue to darken with age (note the yellowing, darkening, and enbrittlement of newspaper exposed to sunlight). Bleaching performed to remove the lignin gives higher brightness to the paper and leads to a more durable and stable paper. Bleaching also removes hemicellulose and extractives. Lignin and hemicellulose are nearly removed in the production of dissolved grade pulps. The crystallinity index (crystal structure of cellulose increases because lignin is removed, lumen is collapsed and microfibril orientation increases in washing process) increases after the bleaching process *(Roncero et al. 2003).* A critical factor in choosing a bleaching chemical is the ‘‘selectivity”. Selectivity refers to the capacity of the chemical to attack lignin while doing minimal damage to the cellulose fibers. Unbleached pulp (brown stock) contains high levels of lignin, therefore less selective chemicals e.g., oxygen and chlorine are generally used in the initial stages of the bleaching cycle. Chlorine dioxide and hydrogen peroxide are highly selective, thus they react rapidly with lignin but also have minimum effect on cellulose. Hence these chemical agents are generally used in later stages of bleaching when the lignin content is considerably low in pulp fibers. Overall the tendency of paper industry is to bleach more pulp as the demand for bleached paper is increasing. Nearly 39 percent of the domestic paper and paperboard currently produced is from bleached pulp.

The pulp obtained from bleaching is subjected to refining process before using it to make different grades of paper sheets. The pulp is beaten or refined, to increase the tensile strength of the papersheet. During beating, delamination of the fiber wall takes place; breaking down the internal structure of the fibrils, allowing the fibers to swell in subsequent wet processing. Internal and external fibrillation is also caused by beating and these phenomena help to create large contact areas between microfibrils. The interaction of the sheet with water and moisture is increased by beating thereby reducing the dimensional stability of the product. This property is of great importance for both packaging materials and printing papers.

Paper is a sheet of non-woven fibrous based material, which is formed by an interaction of individual pulp fibers to form a network structure (*Fischer et al. 2017).* It is stated by many researchers that chemical pulp (kraft process) produces strong fibers. Due to better bonding between the fibers after bleaching and refining, paper with higher strength properties is normally expected. Hydrogen bonds are generally believed to be the dominating bonds exist in a paper network. Hydrogen bonds exist between glucose units in the cellulose molecule, between fibrils in the fiber wall and between fibers in the fiber network (*Retulainen et al. 1998*). Hence the paper strength mainly depends upon the cellulose content in pulp *(Madakadze et al., 1999).* Paper testing is an important quality analysis in pulp and paper industry because of the demands placed upon it for a wide range of applications. To meet this increasing demand and competition, paper makers have continually developed and improved their products vis-a-vis strength properties.

Therefore, the objectives of this chapter are categorized as follows:

- To understand the influence of bleaching (ECF) on Subabul wood (rawwood, heartwood, sapwood) and bagasse (depithed) pulps with respect to various properties such as brightness, % cellulose content, % lignin content, etc.
- To compare the strength values of unbleached and bleached papersheets. The variation in strength data with respect to pulps (subabul wood and bagasse) is also assessed.

6.2. MATERIALS AND METHODS

6.2.1. Bleaching and Analysis of pulp fibers

The ***Subabul Rawwood (RW) pulp*** obtained from kraft cooking (165ºC, 3hrs) having a brightness value of 19.4 and pulp viscosity of 27 c_p is subjected to Elemental Chlorine Free (ECF) bleaching process. Bleaching of pulp and measurement of pulp brightness and viscosity was carried at Central Pulp and Paper Research Institute, Saharanpur, India and bleaching sequence of $O\text{-}D_0\text{-}Eop\text{-}D_1\text{-}Ep\text{-}D_2$ was followed. In this sequence, O corresponds to oxygen stage, D_0 stands for first chlorine dioxide stage, Eop stands for first alkaline extraction stage reinforced with oxygen and hydrogen peroxide, D_1 stands for second chlorine dioxide stage, Ep corresponds to first alkaline extraction stage reinforced with hydrogen peroxide and D_2 stands for third chlorine dioxide stage. Bleaching parameters for all stages are described in Table 6.1. Here consistency is the ratio of *oven-dry weight of pulp* to the *weight of pulp + water*. The effect of bleaching on the pulp is evaluated by measuring Klason lignin content (TAPPI T222 and TAPPIUM250), % Cellulose content (reference: chapter 3), Water retention value (WRV; TAPPI standard- UM 256), % Ash content (TAPPI standard-T211), FTIR, Optical microscopy, TGA, Brightness (ISO 2474) and Viscosity (SCAN C 15:62). The results are compared with unbleached pulp to understand the impact of bleaching process i.e. effective removal of residual lignin from wood cell walls.

Table 6.1: Raw Subabul wood pulp (kraft cooked at 165°C, 3hrs) bleaching conditions

Parameter	**O**	**D_0**	**Eop**	**D_1**	**Ep**	**D_2**
pH	11-12	2.4	11	2.5	11	3-4
Pulp consistency, %	10	5	10	10	10	10
O_2 Pressure, kg/cm^2	5-6	-	2.5	-	-	-
Temperature, (^{o}C)	105	55	68	80	66	80

Subabul heartwood and sapwood pulp (kraft cooked at 165°C, 3hrs) having a brightness of 30.1 and 32.4 respectively was subjected to ECF bleaching at Avantha Centre for Industrial Research and Development, Yamuna Nagar, India. A two stage oxygen delignification followed by $D_oE_{op}D$ (D_o stands for first chlorine dioxide stage, E_{op} stands for first alkaline extraction stage reinforced with oxygen and hydrogen peroxide, D stands for second chlorine dioxide stage) bleaching sequence was applied to the pulps as described in Table 6.2. The effect of bleaching on the pulp was evaluated by measuring Klason lignin content, Kappa number (TAPPI T 236), Brightness (ISO 2474), Viscosity (SCAN C 15:62) data and also by performing SEM morphological studies (Thermofischer scientific APREO-S). The results were compared with the unbleached heartwood and sapwood pulps to understand the impact of the applied bleaching sequence. The ***Depithed bagasse pulp*** (kraft cooked at 165°C, 1hr) was also subjected to ECF bleaching sequence. A single stage oxygen delignification followed by $D_oE_{OP}D$ bleaching sequence was applied to the pulps as described in Table 6.3. The bleached pulps of all three categories (rawwood, sapwood/heartwood, bagasse) were subjected to refining before making handsheets.

Table 6.2: Subabul heartwood and sapwood pulp (kraft cooked at 165°C, 3hrs) bleaching conditions

Particulars	**Heartwood**	**Sapwood**
Oxygen delignification stage		
First stage: Consistency -10%, Temperature – 85°C, Time - 30 min, O_2 - 4.5 kg/cm^2 *Second stage: Consistency -10%, Temperature – 95°C, Time - 45 min, O_2 - 3.5 kg/cm^2*		
NaOH dose (%)	2.7	2.3
D_O stage *(Consistency -10 %, Temperature -55 °C, Time - 45 min)*		
ClO_2 added (%)	1.12	1.00
End pH	2.3	2.2
Residual ClO_2 (ppm)	16.9	14.8
E_{OP} stage *(Consistency - 10%, Temp. - 80°C, Time -120 min,* H_2O_2 *- 0.7%, O_2 - 0.6 %)*		
NaOH added (%)	1.7	1.6
End pH	10.9	10.8
Residual H_2O_2 (ppm)	6.8	6.8
D stage *(Consistency - 10.0%, ClO_2 - 0.5% Temperature - 75°C, Time - 180 min)*		
End pH	4	4.1
Residual ClO_2 (ppm)	21.6	21.6

Table 6.3: Bleaching parameters for depithed bagasse (kraft cooked at 165°C, 1hr)

Parameter	O	D_0	Eop	D
pH	11-12	2-2.5	11	3-4
Pulp consistency, %	10.5	10	10	10
O_2 Pressure, kg/cm^2	5	-	2.5	-
Temperature (^{o}C)	95	65	75	80
Retention time (min)	90	60	75	120

6.2.2. Refining of pulp using PFI mill and Lab Valley Beater

The bleached pulps were subjected to *beating/refining* process before handsheet making to loosen the fiber cell wall, so that the fibers are more flexible, adequately aligned and adjusted while making a paper *(Motaung et al. 2016).* The refining also flattens the fibers, removes the kinks thus increasing the fiber surface area and also increases the bonding between the fibers while making the handsheets. The structure and bonding of paper depends on fiber properties such as surface fibrillation (increase due to beating), fiber density and zero span tensile strength of pulp. There are indications that fiber/fiber joint strength also increases with beating due to changes in the physical structure of the fiber surface (fibrillation) that makes new surfaces available for molecular bonding *(He 2011).* The unbleached and bleached pulps are refined using Lab Valley Beater (GEC-P40313-A; Fig 6.1). The oven dried pulp of ~100 g along with water of ~3 lit (for free flowing of pulp) is fed into the beater basket from top. The beater roll blades are made of carbide material. The gap between the beater plate and the beater roll is reduced by increasing the weights on the pan so that very fine pulp is attained as shown in Fig. 6.1. As the motor rotates, the V-belt drive induces agitation/vibration, due to which the pulp moves forward in the beater basket (due to slight sloping) and passes through the gap between the beater roll and beater plate. It should be noted that one is a beater roll (rotating blade) and the other is a beater plate (stationary blade) fixed to the basket in an inclined position. Wet pulp undergoes shearing action due to which cell wall is disintegrated, lumen is collapsed and also slight change in colour is observed as shown in Fig. 6.2 due to the removal of small quantities of lignin (dark brown slurry). After the repetitive beating (process is run for ~ 45 minutes) the refined pulp is discharged from the outlet drain as shown in Fig 6.1.

The unbleached depith and whole bagasse (DPB and WB) pulps are subjected to refining using super mass collider (MKCA6-2J; Fig 6.3) which increases the fiber flexibility by causing little damage to the cell wall. Pulps of ~5g are soaked in 1 litre of water for 1hr and subjected to ultrafine wet grinding (refining) in which the SiC ceramic wheels are separated by a distance of 10 µm. This distance was selected because collapsed fiber has thickness of 5-10 µm. Both DPB and WB pulp slurries were run through the ultrafine wet grinding in 3 cycles. Here also, one wheel is stationary and the other is rotating and it is possible to refine the pulp (inducing damage to the cell wall) without compromising the fiber length reduction. The special grooves in ultrafine grinder allows pulp to refine more in the fiber direction, so that aspect ratio is maintained high unlike in Lab valley beater.

[The refined samples (having collapsed cell wall) are then passed over to the handsheet maker. The refining of bleached heartwood and sapwood pulps was performed by Avantha Centre for Industrial Research and Development, Yamuna Nagar, India using a PFI mill (TAPPI T 248) to predict the usability of a pulp (initial shopper Reigler value (°SR) of HW and SW: 15.5 and 16; final °SR is 30.5 and 30 i,e almost 100% increase in pulp freeness value after beating in PFI mill; The °SR value describes the amount of drained suspension and it is the degree of the drainage properties of the pulp, which has been diluted in water. One °SR corresponds to 10 ml of water]

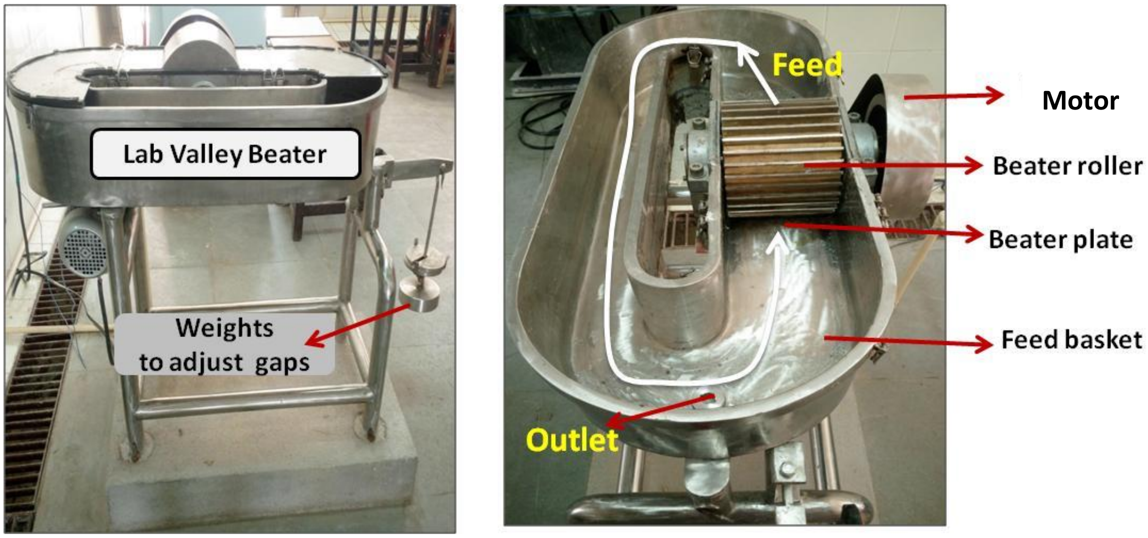


Fig 6.1: Lab Valley Beater used for refining pulp fibers.

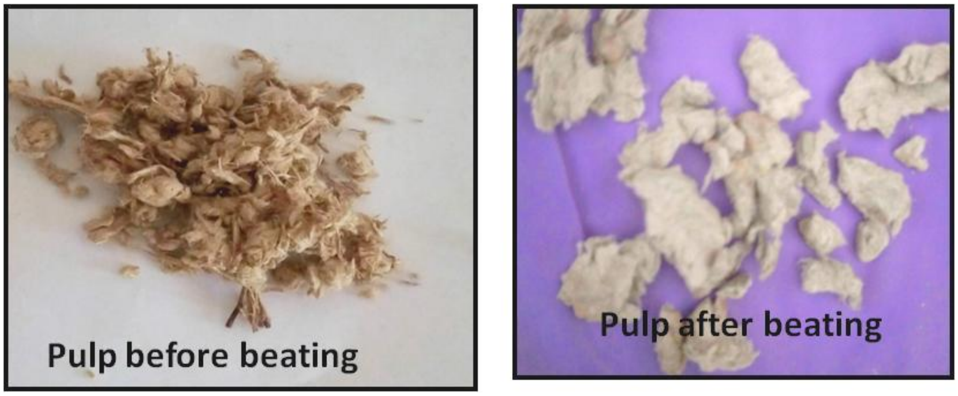


Fig 6.2: Kraft pulp fibers before and after refining/beating process

[During refining external fibrillation, internal changes in the wall structure, delamination, internal fibrillation, removal of nodes, kinks, micro-compressions in the cell wall, dissolving or leaching out colloidal material into the external liquor, etc., occurs due to which factors such as brightness, opacity, drainage resistance, tensile strength etc are affected (Lumiainen 1990). The brown color of pulp is due to chromophoric complexes formed with the lignin molecule, presence of resin and extractives (Saad and Ibrahim 2014) which are detrimental to unbleached pulp brightness. In the process of refining, the pulp slurry undergoes fiber disintegration and the surface bound lignin complexes, extractives etc are skinned off (due to abrasive action) and hence the resulting pulp is slightly lighter in colour (light brown) whereas the collected strained water is brownish]

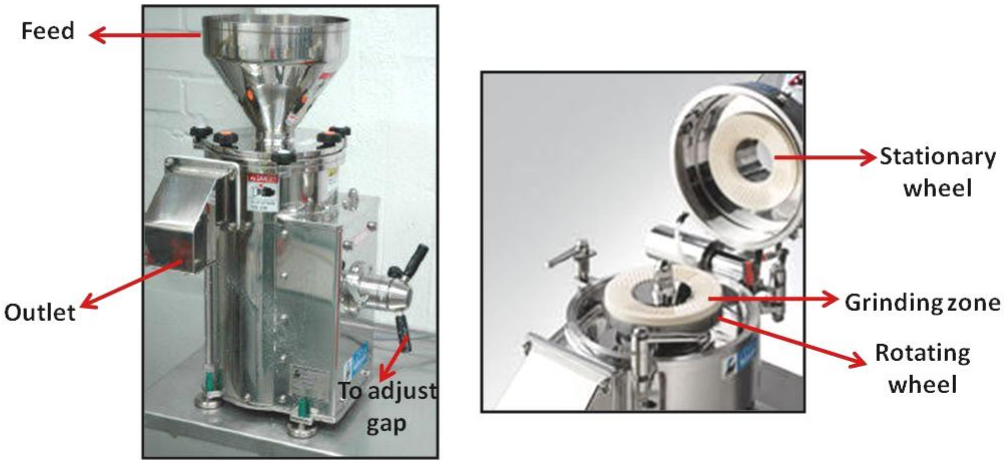


Fig 6.3: Super Mass Collider used for refining of bagasse pulp fibers

6.2.3. *Handsheet making and testing using unbleached and bleached pulp fibers*

The ***handsheet formation*** starts with filtration process where a suspension of flexible pulp fibers from the refining, overlay one another in random fashion forming a nonwoven sheets. A specific quantity of approximately 70 g of beated pulp (having more number of collapsed fibers) is mixed with 2-3L of water and fed to handsheet maker from top by closing all the levers to avoid water draining from the bottom which will help in attaining a uniform handsheet as shown in Fig. 6.4. The Handsheet maker (GEC-P40303-A) shown in Fig 6.4 has 3 levers. One at the top of the mesh and water container; the second one is at the cylindrical system for the filtrate to drain off; and the third is for cleaning and controlling the pressure. It has a stainless steel mesh (screen of 140 mesh size with ~100 µm opening diameter) through which the filtrate pass through when the slurry is added from the top. A mixer rod (Fig 6.5) is used to mix the contents in feed mixture and to have uniform consistency before filtration. The drain valve is then slowly opened while the mixing of slurry with stirrer is still continued. After complete filtering of the water, the top lever is removed to release the vacuum. Then the grid plate/mesh on which the fibers are settled is separated and placed over the steel plate. The water content/unbound moisture in the sheet is reduced to minimum level using a heavy roller pressing and also smooth and uniform wet sheet is attained as shown in Fig 6.5. After separating the handsheet from the grid plate, it is dried at 90^{o}C for 2-3 hrs to remove the bound moisture. The sheets thus prepared are circular and ~16cms in diameter and 1.5-2.5mm thick. The prepared handsheets are then tested for: Thickness, Grammage, Tensile strength (TAPPI T494; TAPPI T205), Erichsen cupping test and Fractography studies.

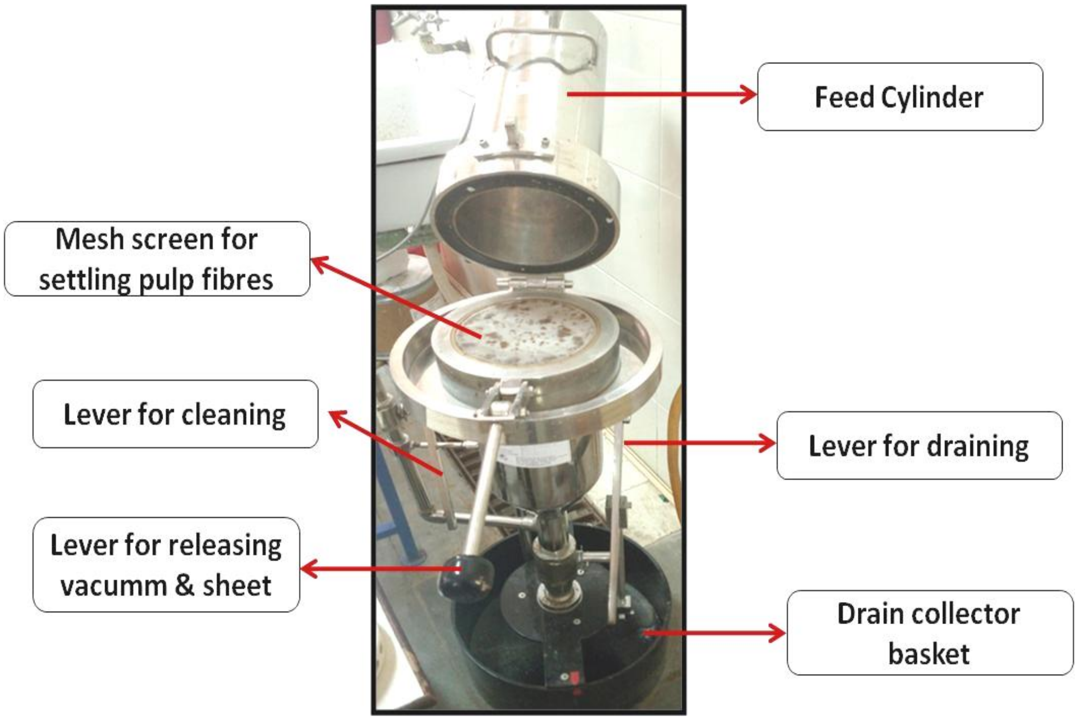


Fig 6.4: Handsheet Maker

Fig 6.5. Accessories used in handsheet making
[left : 1. Perforated stirrer; 2. Sheet roller for draining excess water/unbound moisture 3. Drier plates; 4. Drier rings stackable for drier plates, perforated all around with 15mm holes to allow conditioned air flow through.
right: Handsheet before drying]

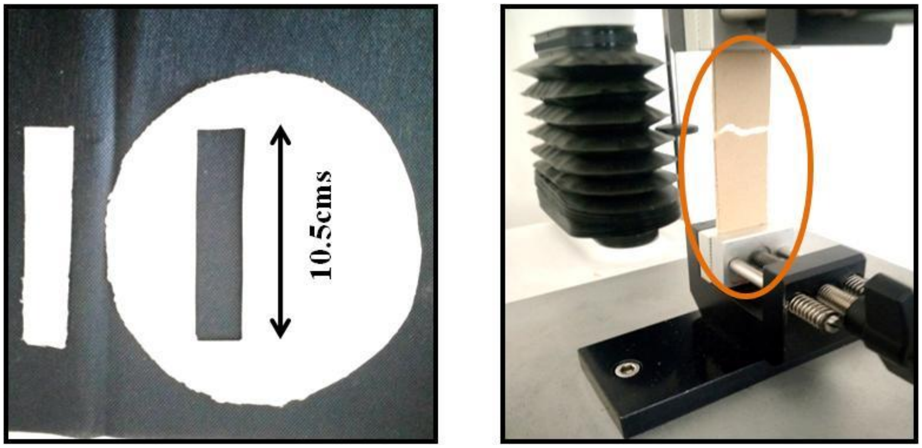
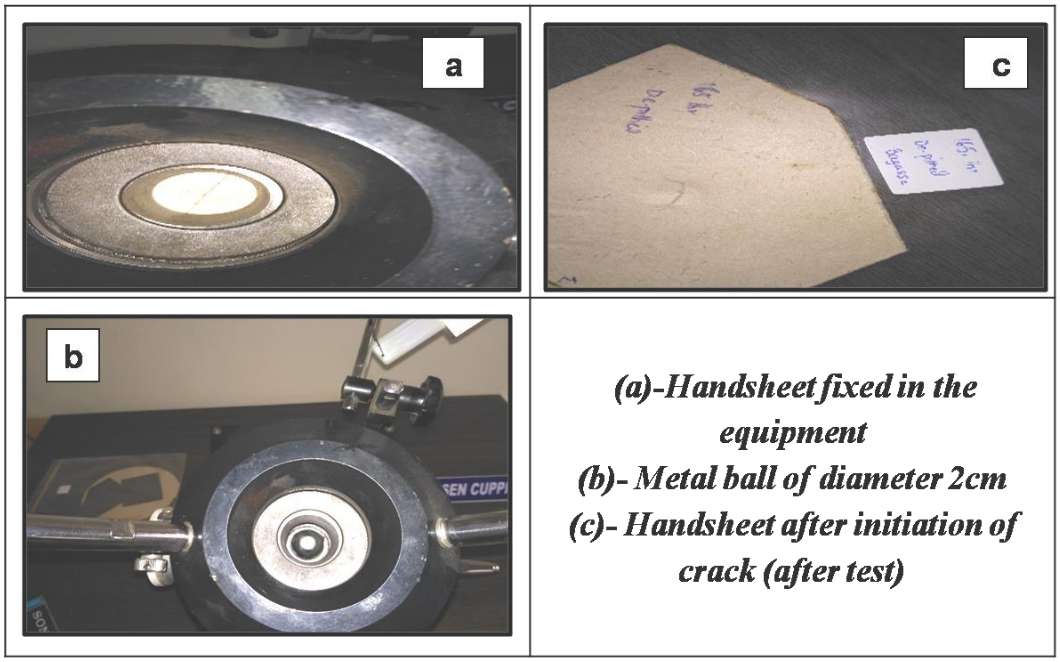


Fig 6.6: Tensile testing of handsheet
[left: specimen of 10.5cm length; right: ductile fracture-the image was taken immediately after testing)]

Tensile testing: Test specimen is cut into specific length and width (10.5cm, 2.5 cm) using a surgical blade (Fig 6.6). The specimen is loaded into the tensile testing apparatus with gauge length of 7.5 cm. Specific parameters such as load of 5 KN, pre-test speed of 10mm/sec, test speed of 1 mm/sec, post-test speed of 10mm/sec are maintained. As the test starts, the top grip moves away as per the specified speed. Specimens showed elastic recovery up to a certain strain, after which they exhibited plastic strain and eventually specimens were broken. The raw data of force, distance, time are collected during testing and properties i.e. tensile strength, modulus of elasticity, strains were measured from stress-strain curves plotted post testing. Here grips are coated with rubber and jaw breaks were not considered in testing.

Erichsen cupping test: It is used widely as a measure of strength in many kinds of papers, primarily as an indication of the suitability of certain fibers and the extent of beating and refining. It tells how much pressure paper can tolerate before rupture. While interpretation is empirical, the bursting strength serves as a quick check on the utility of papers which do not have an absolute tensile requirement. The samples were subjected to Erichsen cupping test (Fig 6.7). The handsheets were subjected to a burst (drawing) test by a steel ball having diameter of 2cm. The test provides an empirical value of how deep the metal ball could penetrate the handsheet before the crack starts to appear. It is a drawing test used for metals and it is different than burst test used for paper.



(a)-Handsheet fixed in the equipment
(b)- Metal ball of diameter 2cm
(c)- Handsheet after initiation of crack (after test)

Fig 6.7: Erichsen cupping test setup for burst strength determination

Grammage: It is the areal density of the paper. It is calculated by the formula given below. Mass of each sheet is measured using 3 digit weighing balance and it is divided by the area covered by sheet as the handsheet is circle in shape.

$$\text{Grammage} = \frac{\text{Weight of sample (g)}}{\text{Area (m}^2\text{)}}$$

Thickness: The thickness of a papersheet determines primarily its bending stiffness. The dominating method for the determination of paper thickness is to measure the distance between two parallel sides of the sheet. The thickness of the obtained sheets is measured using a vernier callipers. The thickness is carried out randomly at five different points on the sheet surface and the average of these values is taken as the final thickness of that specific handsheet.

Fractography: This analysis gives a proper morphological characterization of pulp fibers present in a handsheet. A small paper strip of ~3cms in length and 1cm in width is cut from the tensile fractured specimen using a surgical blade. Small strips of ~1.5-2 cm double tape is cut and placed on the glass slide over which the test specimen is glued. The imaging was carried out using stereo microscope *(OLYMPUS SZ17*) in reflectance mode.

6.3. RESULTS AND DISCUSSION

6.3.1. Characterization of bleached pulps (Rawwood, Heartwood and Sapwood)

Fig 6.8 displays a ***digital and optical photographs*** of unbleached and bleached pulps *(Subabul rawwood)*. The ECF bleaching process has a very pronounced effect on the brightness of the fiber as shown in the Fig 6.8. The images indicate the effectiveness of kraft cooking (Fig 6.8a) and ECF bleaching sequence (ODoEopD$_1$EpD$_2$) used to obtain the white colour pulp (Fig 6.8b). The unbleached pulp fibers exhibited intact individual fibers (unseparated fibers), uncooked chips, impurities (resins) and brown colour due to the presence of lignin chromophores. The bleached fibers are collapsed and entangled to each other due to the higher percentage of cellulose and damaged cell walls. The bleaching chemicals attack the light absorbing chromophoric groups of lignin (quinones). Most of bleaching chemical reagents are oxidants and they provided more stable pulp brightness. Therefore, the white colour appearance of attained bleached pulp indicates that most of the lignin fragments and non-cellulosic components such as extractives etc were removed. The ***optical images*** of the unbleached kraft pulp (Fig 6.8c) exhibited heterogeneous appearance with strong tendency of agglomeration (fibers entangled to each other), with fewer individual fibers. The bleached kraft pulp shown in Fig. 6.8d contains loose and collapsed fibers with noticeable fiber fractures and twists at random points. Bleached fibers formed a strong network structure with intermingled libriform fibers and tracheids of smooth individual fibers, but it is free from vessels. Therefore the visual information confirms the effectiveness of the applied bleaching sequence.

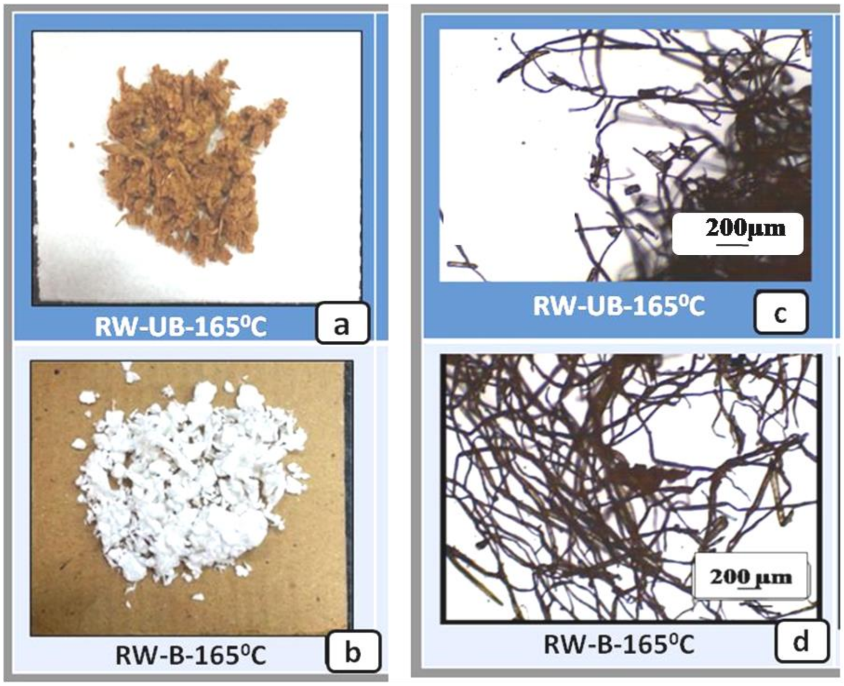


Fig 6.8: (a) and (b). Images of pulp obtained after kraft cooking;
(c) and (d). Optical images of pulp fibers
(RW-Raw wood, UB - Unbleached, B- Bleached)

Fig 6.9 shows ***SEM micrographs*** of the bleached sapwood (a and b) and heartwood (c and d) pulps. From the images, it is observed that the pulp fibers were more separated with wrinkles, axial micro compressions, twists and kinks visible on the surface of the fibers which eases the paper making. Another observation revealed by the SEM micrographs is the existence of pores indicating conducting vessels and parenchyma cells in sapwood pulps and unbroken vessels in heartwood pulp. Some physical changes such as a lumen collapse, smooth fiber surface can be observed after the fiber undergoing the bleaching treatment. Changes in the fiber occur due to the removal of surface impurities, lignin and hemicellulose. Fines which have length below 200 µm and vessels which have width above 35 µm are also visible. Fines have a negative impact on dewatering capacity and printing of the paper is influenced by vessels. The bleached pulps also presented better dimensional stability due to the formation of hydrogen bonds in cellulose. The micrographs thus visually conclude that effectiveness of $D_OE_{OP}D$ bleaching sequence and the resulting fiber and vessel dimensions are given below:

Sapwood: Fiber diameter: 7.5-11.5 µm; Vessel length: 226.5 µm and diameter: 154.4 µm.

Heartwood: Fiber diameter: 13.2-16.7 µm; Vessel length: 71.7 µm and diameter: 37.9 µm.

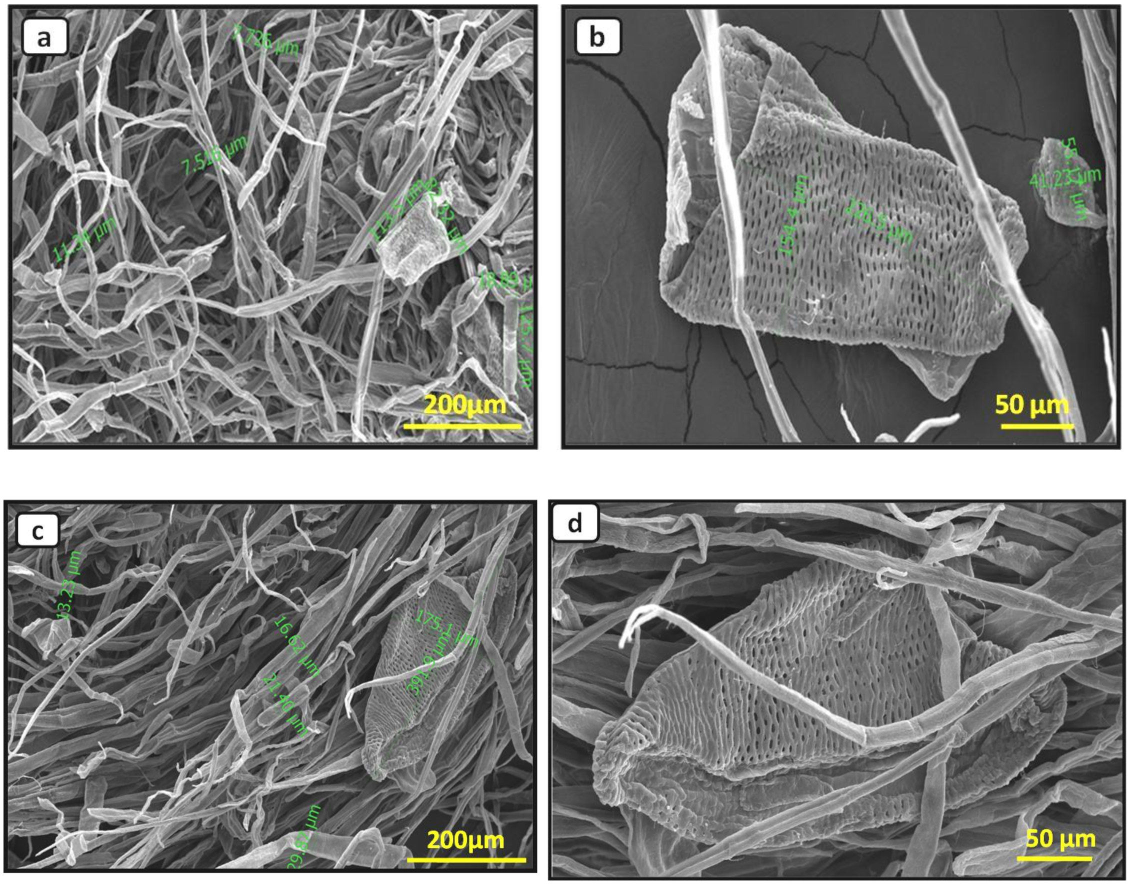


Fig 6.9: (a and b): SEM images of bleached sapwood pulp;
(c and d): SEM images of bleached heartwood pulp.
[(a). Loose sapwood fibers after bleaching process;
(b). Note the clear visibility of conducting vessels and parenchyma cells;
(c). Note the clear visibility of unbroken vessels and loose thicker fibers]

The unbleached and bleached (RW, HW and SW) ***pulp analysis results*** are presented in Table 6.4 and 6.5. The data obtained for unbleached pulp in comparison with bleached pulps exhibited significant differences, indicating the effectiveness of selected process conditions.

Table 6.4: Rawwood and Rawwood pulp characterization data

Sample	Residual lignin %	Kappa Number	Cellulose Content (%)	Water retention value-WRV	Ash %	Brightness (%ISO)
Rawwood (RW) chips	28.2 ±0.2	190±1.3	54.20± 0.3	0.43±0.1	0.94±0.2	-
Rawwood (RW) Unbleached Pulp	1.64± 0.3	11±2.1	74.2± 1.2	15.3±0.2	36.2±2	19.4
Rawwood (RW)Bleached Pulp	0.8± 0.1	5±0.6	92± 0.1	21.2±0.2	1.2±1.5	85.2

From ***Klason lignin*** result, bleached pulps have exhibited negligible lignin% (with high brightness: 85.2) and kappa number (which is an indication of the residual lignin content in pulp) is also low**.** The applied bleaching process removed chromophore compounds such as lignin, resins, metallic ions, and non-cellulosic carbohydrates using chemical reagents used in bleaching. The residual lignin in pulp generally contains less β-O-4 linkages, condensed carbon-carbon and lignin-carbohydrate linkages which are oxidized and solubilised at various stages of ECF bleaching process, thus resulting in negligible lignin% for bleached pulps. The bleached rawwood pulp with negligible lignin% exhibited higher percent of ***Cellulose*** (Fig 6.10) that corresponds to complete removal of extractives, acetyl groups and uronic acids from hemicelluloses as well as degradation and dissolution of α and β-aryl ether linkages in the phenolic units at middle lamella and also primary and secondary cell wall areas and thus enhancing the relative cellulose content of pulp fibers.

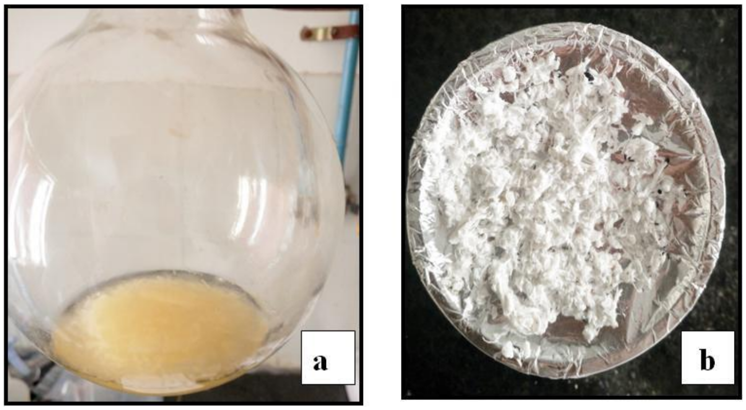


Fig 6.10: (a). Bleached pulp sample during reflux; (b). Pulp sample after drying.
[Both images were taken as part of the cellulose content determination]

The ***Water Retention Value*** (WRV) is an empirical measure of the capacity of pulp fibers to hold water. WRV can be used as an indication of the degree of swelling of the fibers. The bleached pulp exhibiting internal fibrillation widens the small internal pores and delaminates the cell wall, which is referred as 'Swelling", occurs concurrently with development of external fibrils, which also serve to hold additional water. Thus the bleached pulps with high porosity and cellulose content and negligible residual lignin and hydrophobic resins in the fibers could retain more amount of water than unbleached pulp. ***Ash*** is an indication of amount of inorganics present in the sample. During the incineration process, the combustion of cellulose-lignin composite structure continue to take takes place until 900ºC whereas decomposition of cellulose alone ends at 400ºC, because it burns continuously due to the absence of interfaces. In this study temperatures were restricted to 525ºC and ash content was found to be low (0.9 %) for raw wood. Bleached pulp contains only cellulose, negligible lignin or other aromatic extractives and absence of lumen (collapsed fibers) due to which ash content is very low for bleached pulps (1.2 %). For bleached pulps, the % of interfacial pore area becomes very low which allows complete degradation of cellulose/hemicellulose/lignin leaving only inorganics. For unbleached pulps (the lignin content is comparatively high) the % of interfacial pore area becomes very high which allows slow evaporation of extractives, slower degradation of lignin fragments and giving enough heat and time so that cellulose can oxidise and form cyclic rings which can be noticed by observing black coloured pulp (reference: Fig 3.9). Due to this ash content was found to be high (36.2 %) for unbleached fibers.

Table 6.5: Heartwood and Sapwood pulp properties

Particulars	**Lignin (%)**	**Kappa number**	**Brightness (% ISO)**	**Viscosity (cP)**
Unbleached heartwood (HW) pulp	1.7	11	30.1	15.6
Bleached heartwood (HW) pulp	0.13	2	88.4	10.5
Unbleached sapwood (SW) pulp	1.5	10	32.4	18.0
Bleached sapwood (SW) pulp	0.11	0.7	88.6	11.3

The unbleached pulps (RW, HW, and SW) have exhibited lower ***brightness*** (<30, Table 6.4 and 6.5) values mainly due to lignin whose colour originates from different oxidised structures. Oxidative mechanisms are believed to convert part of the lignin's phenolic groups to quinone-like substance that are known to absorb light. O-quinones have the strongest impact on the colour of lignin. Heavy metal ions (e.g., iron and copper), extractive materials from resinous woods (mainly heartwood) are also known to form coloured complexes with the phenolic groups. The bleached pulps have exhibited higher brightness values in the range of 85-88%. The bleaching of fibers with chlorine dioxide and oxygen involve radical reaction mechanism that targets phenolic and non-phenolic structures (lignin) resulting in brightening effect, oxidation and chlorination of lignin. Alkaline hydrogen peroxide bleaching can change the chemical, physical, and optical properties of pulp significantly. It is used for delignification or brightening. HOO^{-} ion is the active agent in hydrogen peroxide bleaching. The bleaching of fibers with peroxide (nucleophilic bleaching chemical) involves cleavage of carbon-carbon bonds. It reacts with lignin through the carbonyl group.i.e. it reacts with chromophoric lignin structures and cause depolymerization of lignin and boosts the brightness of the pulp.

The ***viscosity*** (intrinsic) is a control parameter of cellulose pulp quality. The decrease in molar mass of the wood polymers during chemical degradation is normally estimated by measuring the *intrinsic viscosity* of dissolved *pulp* fibers. It is an indirect measurement of the mean value of the degree of polymerization (DP) of cellulose measured through dissolution of a pulp sample in a solvent e.g. cupric ethylene diamine. In general, cellulose in wood has DP of 5000-10,000, but cellulose in wood pulp has an average DP of 600-1200 and regenerated cellulose DP is in between 100-200. Lignin is a high molecular weight polymer. Lignin and extractives in wood protect the fiber from mineralization phenomena. Hence its degradation and dissolution during pulping and bleaching caused reduction in viscosity because lignin is embedded as thin layers in cell wall composite. Bleaching also affects the chain length of cellulose and hemicelluloses as well as the bulk cell wall structure. Thus, pulp bleaching makes the cellulose chain more susceptible to degradation, which could lead to breakage of chain length of cellulose molecules. The lower viscosity values for bleached pulps (50% lower compared to unbleached pulps) could be due to the above reasons and also due to dissolution of amorphous fraction of the cellulose consisting of shorter chains during the last stages of bleaching process.

Fourier transform infrared (***FTIR***) spectroscopy is employed to study the functional groups of both unbleached and bleached fiber and to monitor the effect of fiber treatment on structure and chemical changes of the lignocellulosic fiber. Fig. 6.11 shows the IR spectra for unbleached and bleached pulp (*reference: rawwood pulp is taken into consideration for comparison*). The absorption bands in the finger print region of 900-1800cm^{-1} is related to various functional groups of lignin. The absorption bands in the 1600–1400 cm^{-1} region in the spectra is attributed to the presence of aromatic or benzene rings in lignin. The bands in the region 1300–1000 cm^{-1} involves the (C–O) stretching vibrations of primary and secondary aliphatic alcohols in cellulose, hemicellulose and lignin and primary and secondary aromatic alcohols in lignin. The aromatic C-H in plane deformation around 1160, 1114, 1055 cm^{-1} is present both the spectra's. The bands around 2130-2135 cm^{-1} representative of C=C stretching and 1470-1455 cm^{-1} indicating OH in-plane bending in cellulose are prominent in bleached pulp. A broad peak can be observed at region 3600–3200 cm^{-1} indicating the presence of hydroxyl (OH) group in both pulps. The absorbance peaks around 2900–2800 cm^{-1} were attributed to stretching of the C–H group. From the spectra, the % transmittance of bleached pulp is higher than unbleached pulp. The peaks appearing strikingly for bleached pulp at 1430 cm^{-1} represents the crystalline region of cellulose and 1610 - 1640 cm^{-1} corresponds to water absorbed in cellulose. The vibration peak detected at 899 cm^{-1} for unbleached pulp is assigned to C-H out of-plane ring stretching in cellulose due to the glycosidic bonds, which are symmetric in polysaccharides.

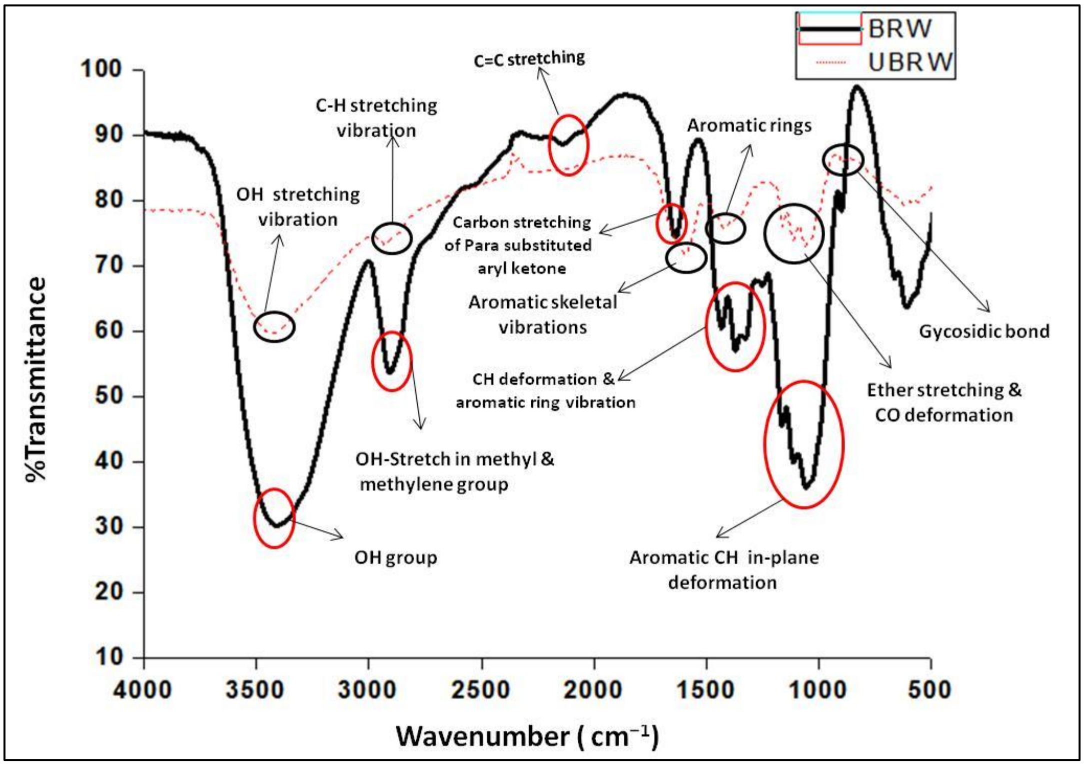


Fig 6.11: The absorption bands from FTIR analysis of rawwood pulp obtained from kraft cooking at 165ºC, 3 hrs *[BRW- bleached rawwood; UBRW- Unbleached rawwood]*

In ***TGA*** (*rawwood pulp is taken as reference for comparision*), it is widely accepted that the primary thermal decomposition of cellulosic materials occur between 200ºC to 400ºC (*Fisher et al. 2002*) and the initial decomposition takes place in the amorphous regions (*Mostashari et al. 2007*). From the data shown in Fig 6.12, it is observed that, there is a slight decrease in unbleached rawwood pulp weight below 100ºC which corresponds to water vaporization or removal of volatile organic extractives. The main degradation step (T_{max} corresponds to huge weight loss) is found between 300ºC to 350ºC for bleached rawwood pulp and for unbleached rawwood pulp it is between 250ºC to 300ºC. Also the thermal stability of the bleached pulp is found to be very low between 380ºC to 600ºC compared to unbleached pulp. The kraft cooking and bleaching process have degraded the amorphous lignin matrix from middle lamella and cell walls respectively leaving collapsed cellulose fibers of moderate crystallinity. Hence bleached fibers were thermally stable until 300ºC but sharp reduction in its weight from 95% -18% for increase of temperature from 300-380ºC i.e. the second sigmoid (in case of bleached pulp) could be due to absence of lignin and also absence of composite structure with micron size pores acting as heat shields.

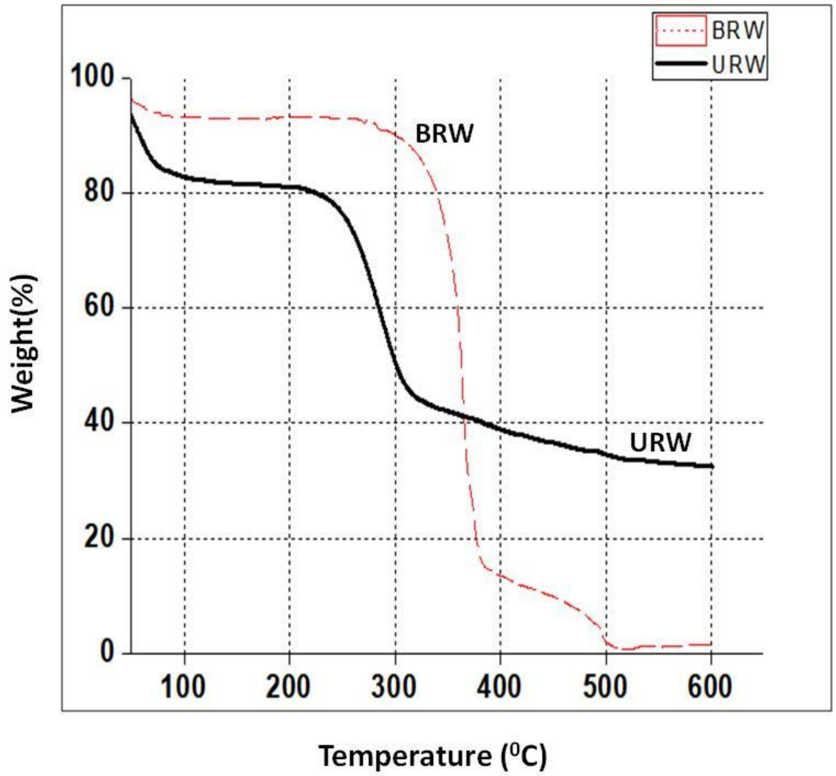


Fig 6.12: TGA of bleached and unbleached rawwood pulps obtained from kraft cooking at 165°C, 3hrs ***(BRW- bleached rawwood, URW- unbleached rawwood)***

Similarly overall weight loss of 38% (second sigmoid) in case of unbleached pulp could be due to the presence of thermally stable composite structural units of residual lignin which forms complexes with polysaccharides especially in cell walls. These unbleached pulps has changed its color at around 320°C, mostly availing charcoal structure with huge number of C-C bonds which makes these pulp thermally stable until 600°C. The unbleached pulp at 380°C to 600°C temperature range are exhibiting very little amount of weight loss due to presence of impurities, low molecular weight extractives and inorganic fragments.

6.3.2. Characterization of unbleached and bleached handsheets

Fig 6.13 and 6.14 represent SEM images of bleached handsheets. After bleaching, beating and pressing, the fiber shape changed from tubular to flat, indicating full collapse of the lumen as the fiber walls became more flexible. The binding property of pulp fiber is of utmost importance for the longevity of the paper handsheet. Higher contact areas between the fibers are achieved with flat shapes than tubular shaped fibers. In addition to fiber flattening, voids between fibers were filled due to fines created during processing. Finally a paper resembling a thick film having nonwoven web like structure filled with long fibers, short fines and ray cells was formed.

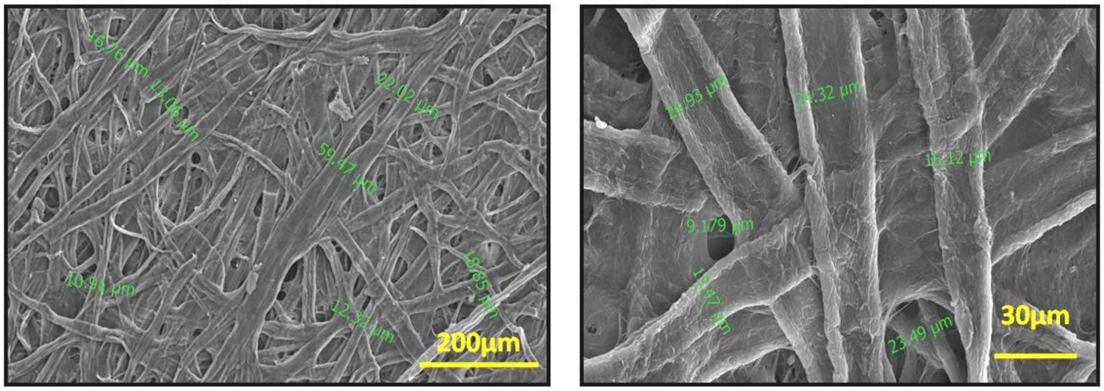


Fig 6.13: SEM images of bleached heartwood handsheets
[Note: collapsed pulp fibers]

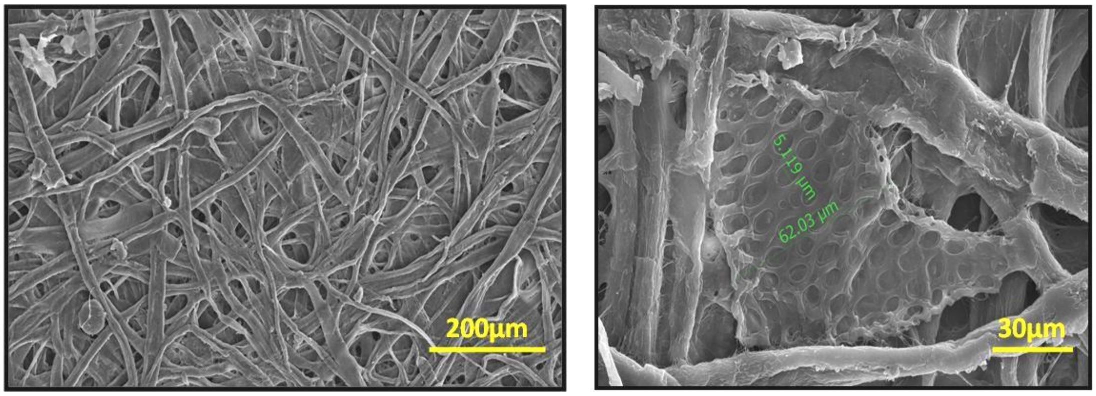


Fig 6.14: SEM images of bleached sapwood handsheets
[Note: collapsed pulp fibers and conducting vessel]

Thickness: For a given basis weight, thickness determines how dense a paper is. From the results (Fig 6.15) it is observed that the thickness of HW paper is higher than SW paper. The higher bulk presented by *papersheets* could be addressed to thicker cell wall fibers (forms bulky sheets of low tensile strength) due to lower cell wall shrinkage or collapsibility during refining process because of presence of aromatic constituents., contributing to the bulkiness of handsheets. Also a very slight increase (0.61 mm for wood and 0.12 mm for bagasse) in thickness for bleached sheets in comparison with unbleached papersheets can be observed from the plot. This could be addressed to dissolution of hydrophobic material (such as extractives and low molecular weight lignin) and the introduction of new short, flexible fibers or fines and more carboxylic groups into the fiber structure during the bleaching process. At high fines contents, the sheet thickness is slightly higher than expected on the basis of fibers, because fines totally cover the fibrous structure/network due to their low lengths (<200 µm).

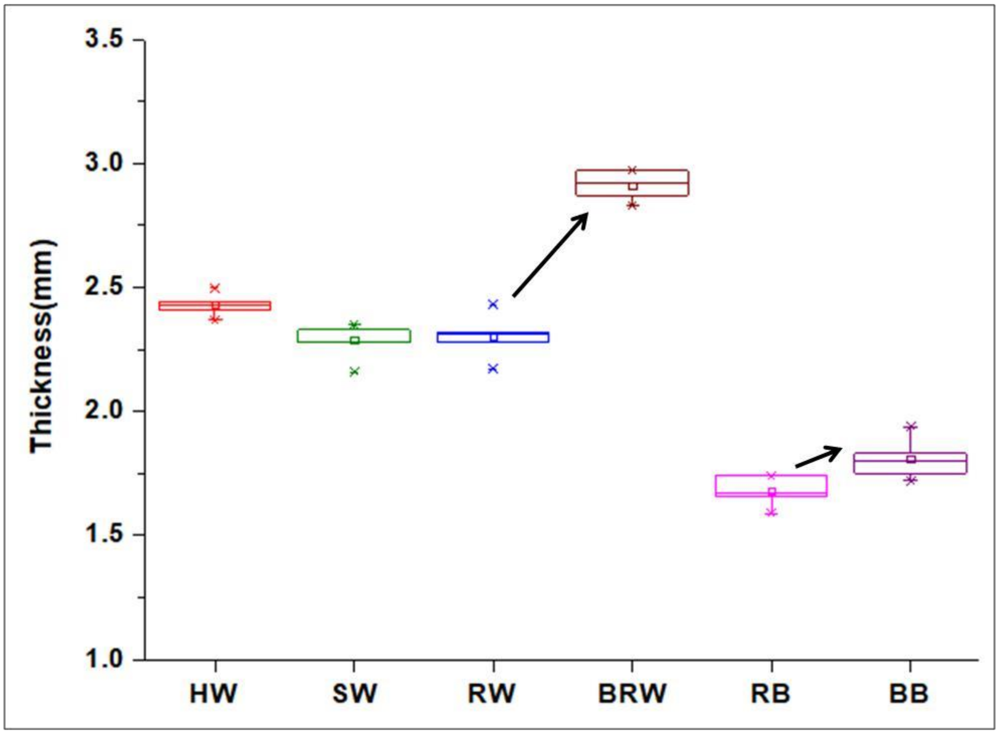


Fig 6.15: Box-and-whisker plots revealing thickness of bleached and unbleached handsheets processed @165ºC.
[HW-Heartwood; SW-Sapwood; RW- Rawwood; BRW- Bleached rawwood; RB- Raw bagasse; BB-Bleached bagasse;]

Tensile strength: Mechanical properties (strength, modulus) are important for printing papers, packaging papers, boards and other papers. The tensile properties of handsheet describe the strength of the individual fibers, their arrangement and the extent to which they are bonded to each other. The attained results illustrated a clear distinction in the strength properties of paper from whole vs depithed bagasse, heartwood vs sapwood, unbleached vs bleached and also between higher (165ºC) vs lower (155ºC) pulping temperatures.

Unbleached bagasse handsheets: The extent of inter fiber bonding is considered as the most important factor contributing to tensile strength properties of paper and an increase in moisture content of the paper will decrease the tensile strength (*Karlsson 2006*). So, the handsheets were dried carefully and measured for their basis weights as it is required in the calculation of tensile strength index (Nm/g) values shown in Table 6.6. For depithed bagasse (DPB) sheets, basis weight was found to be 272 g/m^2 (140ºC) and 240 g/m^2 (165ºC). For whole bagasse sheets, basis weight was found to be 274 g/m^2 (140ºC) and 247 g/m^2 599 (165ºC). The σ–ε plots shown in Fig. 6.16 indicates that whole bagasse pulp samples have exhibited higher strain compared to depithed bagasse pulp. Also, it can be seen that whole bagasse papersheets have higher tensile strength and higher modulus and for 165ºC specimens the difference is noticeable i.e. 200% increase in tensile stress, 100% increase in strain, 50% increase in modulus. The non-linear behaviour of the stress-strain curve of whole bagasse papersheets indicates the inelastic (plastic deformation or plasticity) character of papersheets, which implies higher tensile strength compared to the depithed bagasse papersheets. This could be due to the fact that, the pith containing large number of parenchyma cells and vessels was able to form the network structure with the fibers resulting in high strength sheets. The pith parenchyma cells are thin-walled, highly perforated with large surface area and can act as fillers (*Rainey et al. 2016*). If these cells are not well bonded just below the surface of the sheet then the mechanical strength of paper is adversely affected i.e. it is picked-up during printing.

Whereas, the depithed bagasse sheets consisting of thick walled fibers with low fiber coarseness resulted in a more opaque sheet suitable for writing and printing. Temperature also had a positive impact on the whole bagasse sheets where as it showed a negative impact for depithed bagasse sheets as shown in Table 6.6. The degree of separation was higher for depithed bagasse pulp samples cooked at 165ºC (residual lignin content: 1.08±0.04%). However the treatment of fibers resulted in curliness and sharp change in axial direction of fibers (Chapter 4, Fig 4.3) leading to lower tensile strength. Changes in the axial direction of fibers such as angular folds tend to form paper with low elastic modulus (*Page et al. 1979; Seth and Page 1988*). Despite the longer fibers, presence of short length fines may have reduced contact area and contributed to this effect (lower tensile strength).

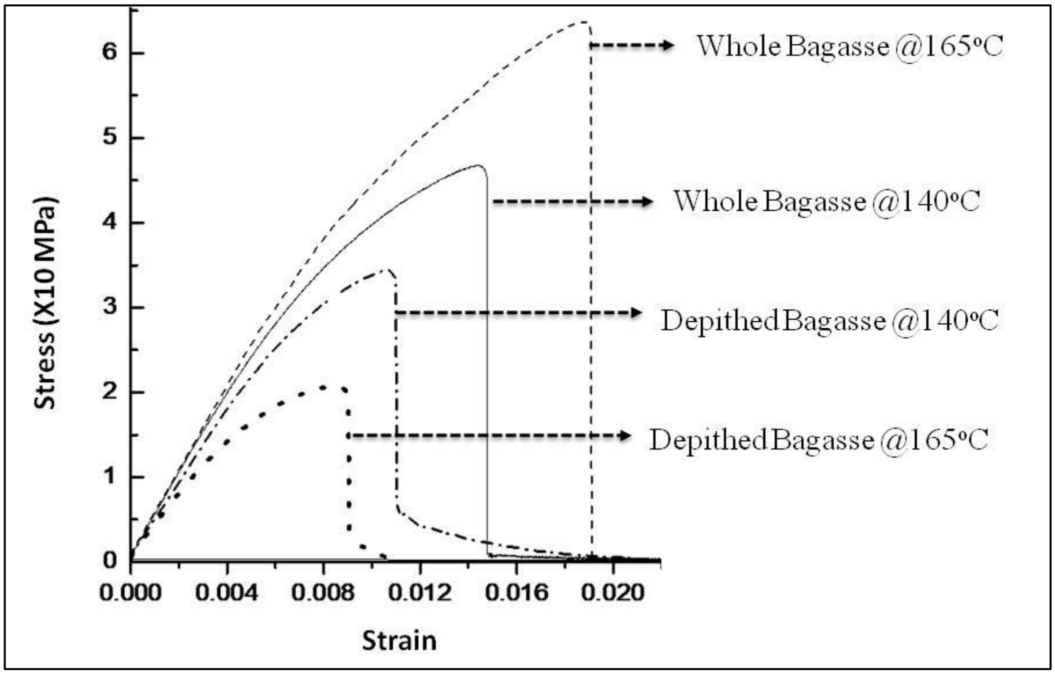


Fig 6.16: Tensile stress-strain plots of handsheets made from unbleached bagasse pulp. Note the strain ranging from 0.8 % to 2 % and strength ranging from 20 to 60 MPa

Table 6.6: Mechanical properties of bagasse handsheets made from unbleached pulps

Bagasse handsheet	Cooking Temperature (ºC)	Tensile strength (N/mm²)	Tensile strength index (Nm/g)	Tensile strain (%)	Tensile modulus (KN/mm²)	Erichsen cupping test depth (mm)
Depithed bagasse	140	34.1±7.4	10.63+2.7	1.1±0.30	4.09±0.03	4.00
	165	20.4±1.3	7.95±0.5	1.0±0.33	3.10±0.02	3.65
Whole bagasse	140	46.7±5.7	7.21±1.4	1.4±0.27	4.61±0.02	5.00
	165	63.6±10	13.77±1.6	1.9±0.28	4.96±0.03	4.45

Unbleached heartwood and sapwood handsheets: In heartwood papersheets, only elastic deformation is observed, with 1% deformation as shown in Fig 6.17. Hence it can be stated that the fibers are brittle in nature due to presence of high residual lignin content (reference table 3.1; 2.8% for 165ºC cooking). Normally low lignin content in the material indicates less brittleness and therefore exhibits high strength and strain. For sapwood papersheets, the plot shows an increasing tendency of plastic deformation (upto

2%) and it could be due to more cellulose content. Due to high cellulose contents, it can be concluded that the sapwood pulp fibers have exhibited higher tensile strength than the heartwood pulp fibers (Table 6.7).

The cellulose aggregates increase in size with increase in temperature (from initial delignification phase 140ºC to bulk delignification phase 165ºC), which is due to thermally induced rearrangement of cellulose molecules. Hence, with respect to temperatures, not much difference is observed between sapwood handsheets., but a slight difference between heartwood handsheets is due to reduction of fiber length due to 7 % residual lignin reduction.

Tensile properties of heartwood and sapwood handsheets are shown in Table 6.7. The tensile strength is an important paper property which measures the resistance to deformation and structural integrity of paper. High tensile strength reflects the ability to withstand high amount of stress before the deformation. This important property was found to be higher for sapwood papersheet than heartwood papersheets indicating that fiber strength is proportional to cellulose content. Sapwood pulp has high cellulose content (~80%), higher amount of short fibers which lead to evenness of the sheet and small pore size resulted in superior opacity to the sheet. In heartwood papersheets, the fibers are rich in lignin and making them stiffer, which causes coarseness, non- uniform mass distribution and hence it negatively influenced the tensile strength.

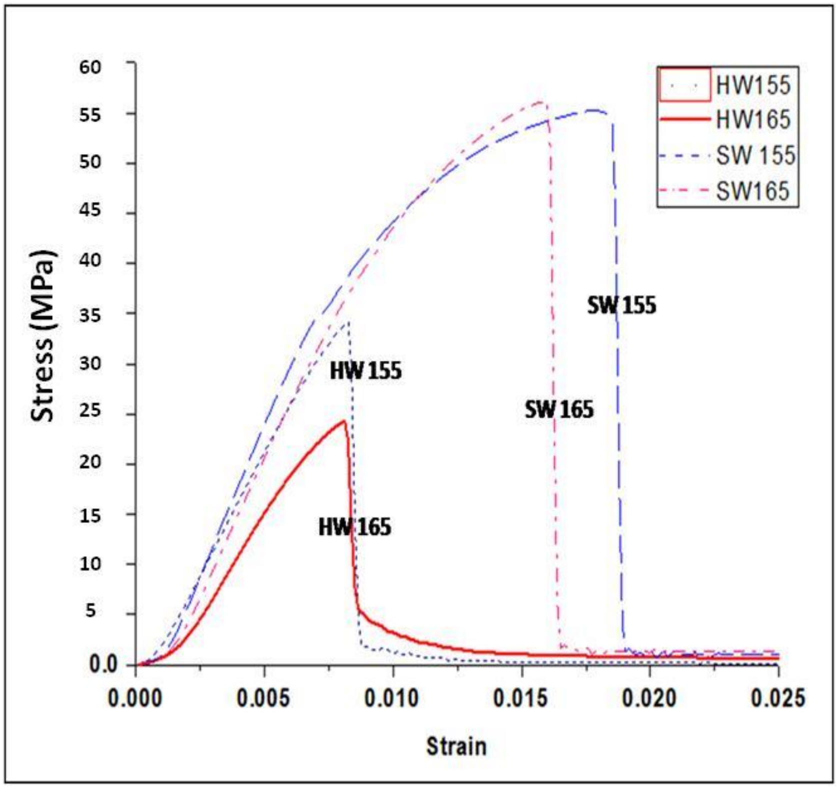


Fig 6.17: Tensile stress-strain plots of handsheets made from unbleached heartwood (HW) and sapwood (SW) pulp.

Table 6.7: Mechanical properties of heartwood and sapwood handsheets made from unbleached pulps

Handsheet	**Cooking Temperature (°C)**	**Tensile Strength (MPa)**	**Tensile strength Index (Nm/g)**
Heartwood	155	33±11	19.72±1.3
	165	23±8	12.78±5.2
Sapwood	155	54±4	32.64±3.8
	165	56 ±16	29.82±2.5

Bleached vs unbleached handsheets: Similar plots comparing between unbleached and bleached papersheets are shown in Fig 6.18 (a, b and c). An interfiber bond or fiber-to-fiber bonds is an important characteristic that determines the strength property of a papersheet, where fibers are so close to each other that the intermolecular hydrogen bonds as well as vander waals forces or molecular entanglement can occur (*Retulainen et al. 1998*). Therefore the chemical composition of the fiber, physical state of the fiber surface, may play an important role in inter-fiber bonding. Although surface fibrillation of fibers occurs in unbleached pulp fibers (due to pulping and refining) the mechanical interlocking of fibers is detrimental because of presence of residual lignin. Due to the hydrophobic nature, the presence of lignin (in unbleached pulps) in the bonded area may constitute a barrier to the formation of hydrogen bonds between cellulose molecules.

During the bleaching, the removal of lignin and the exposure of cellulose would result in more generation of hydrogen bonds between adjacent fibers in papersheet and increases its tensile strength. Hence due to the above reasoning, the unbleached pulp sheets has lower tensile properties (low strength, low elongation, low modulus) compared with bleached pulp sheets. The other reason why unbleached papersheets has low strength and low strain is pore formation in continuous lignin matrix due to cooking.

From the above phenomena, it can be concluded that, residual lignin content can decrease the tensile strength. This has been supported by the tensile strength results for bleached samples (Table 6.8, 6.9 and 6.10) which has approximately 95% cellulose and has therefore exhibited high tensile strength when compared to unbleached pulps (approximately 75-80% cellulose). Higher lignin removal results in lower yields and lower viscosity thereby increasing the cellulose accessibility and promoting the cellulose crystallites to have an increased propensity to co-crystallize (*Sun et al. 2014*).

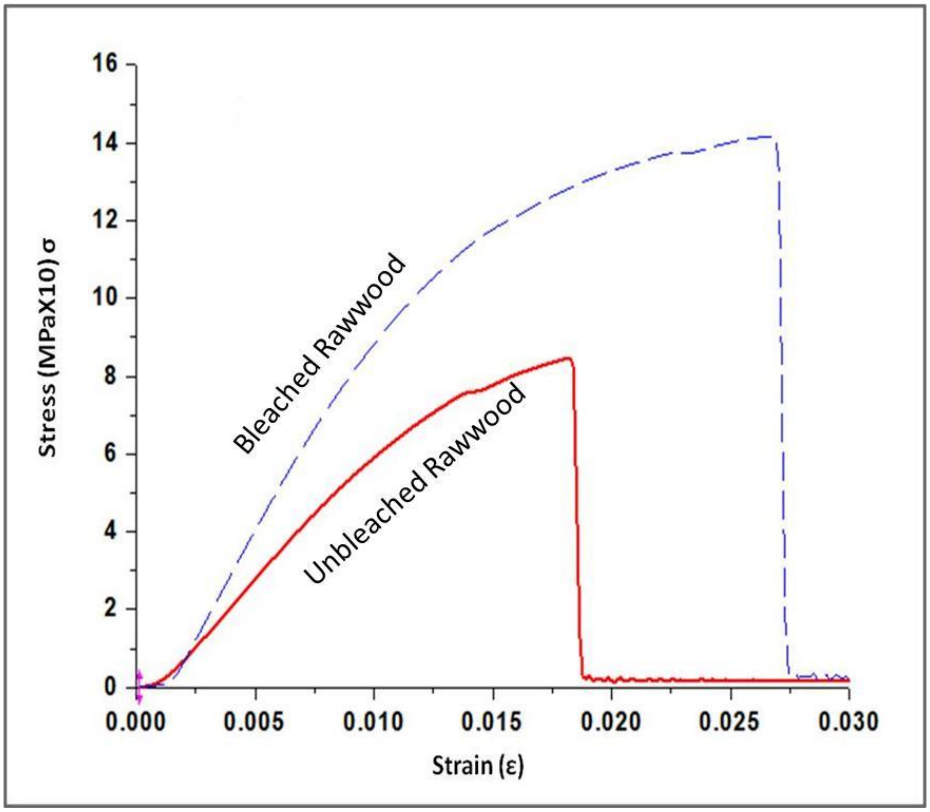


Fig 6.18: (a). Tensile stress-strain plots of handsheets made from unbleached and bleached rawwood pulp obtained from kraft cooking @165^{o}C, 3hrs

Table 6.8: Mechanical properties of handsheets made from bleached and unbleached rawwood pulp *(kraft cooking at 165^{o}C)*

Rawwood Handsheet	Tensile strength (MPa)	Tensile Strength Index (Nm/g)
Unbleached	84±21	45.7±1.6
Bleached	141±20	54.2±8.1

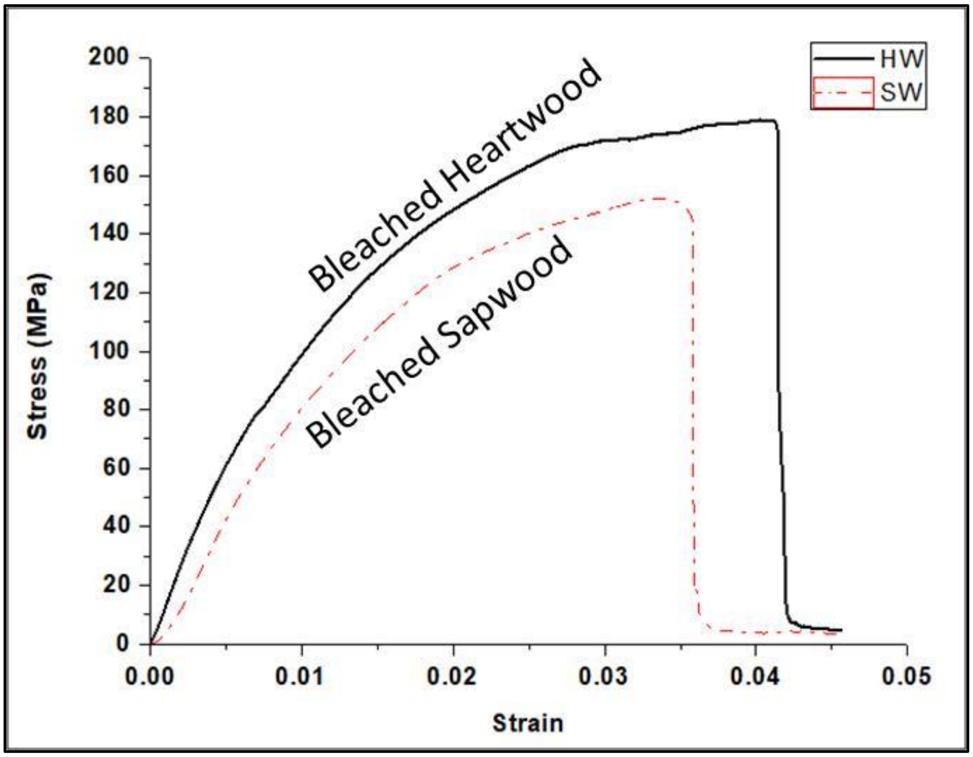


Fig 6.18: (b). Tensile stress-strain plots of handsheets made from bleached heartwood and sapwood pulp (obtained from kraft cooking @165°C, 3hrs)

Table 6.9: Mechanical Properties of handsheets made from bleached and unbleached heartwood and sapwood pulp ***(kraft cooking at 165°C)***

Handsheet	Tensile strength (MPa)	Tensile Strength Index (Nm/g)
Bleached heartwood	178.9±11	96.3±4
Unbleached heartwood	23±8	12.8±5.3
Bleached sapwood	152.5±9	82.4±5
Unbleached sapwood	56±16	29.8±2.5

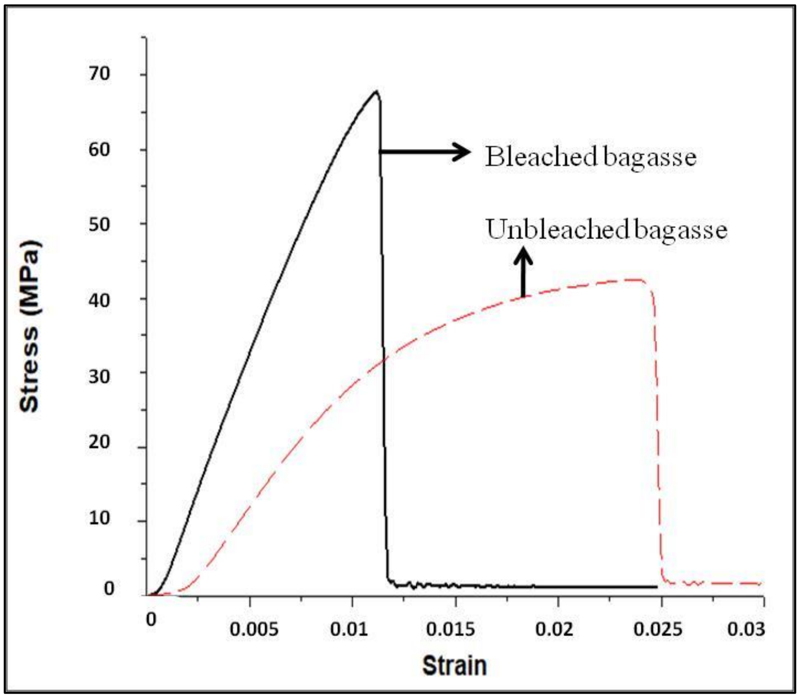


Fig 6.18: (c). Tensile stress-strain plots of handsheets made from depithed bagasse (obtained from kraft cooking @165ºC)

Table 6.10: Mechanical Properties of handsheets made from bleached and unbleached depithed bagasse pulp *(kraft cooking at 165ºC)*

Bleached Handsheet	Tensile strength (MPa)	Tensile Strength Index (Nm/g)
Bleached bagasse	67.7±8	35.3±9.6
Unbleached bagasse	42.1±16	25.9±1.7

Erichsen cupping test: The burst strength is calculated for unbleached whole and depithed bagasse (attained from two different temperatures i.e 140 and 165ºC). From Fig 6.19, it can be stated that the whole samples developed a crack at a greater depth compared to the depithed samples upon impact by the steel ball. These results can be corroborated from the microscopic images shown in Fig 6.20. It can be seen that the crack developed among the depithed samples was deep and greater de-alignment of fibers can be seen compared to the whole samples though crack length was small. Therefore it can be concluded that the burst strength was highest for paper sheet made from whole fibers which were obtained at 140ºC cooking temperature. This is in support to the tensile test results where the presence of pith resulted in greater strength but lower conformability due to fibers being trapped in the pith vessels.

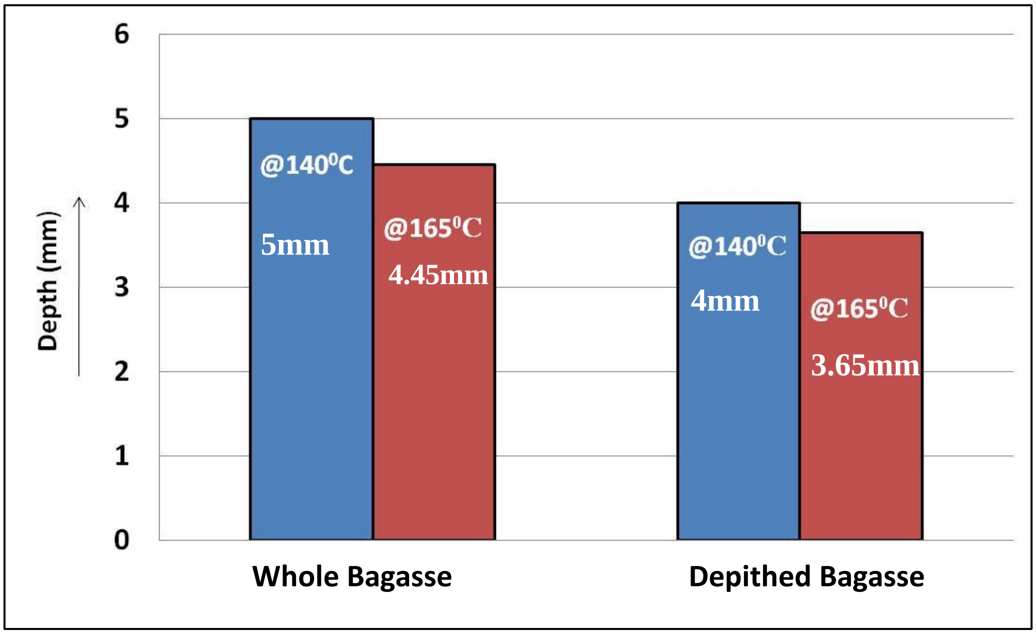


Fig 6.19: Measured during Erichsen cupping testing of bagasse handsheets

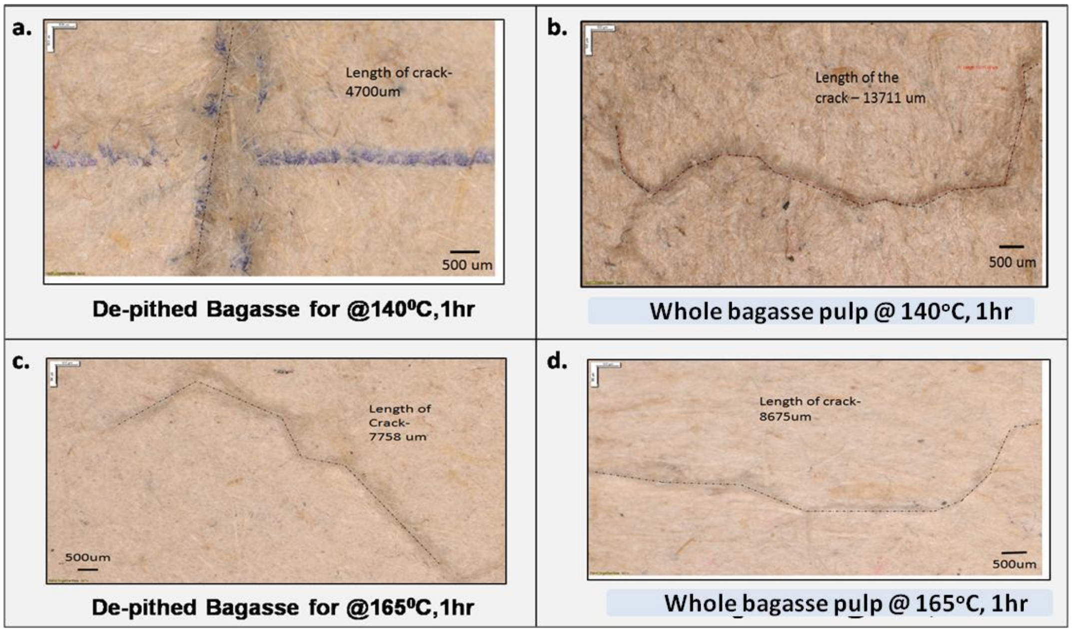


Fig 6.20: Optical images of bagasse handsheets after Erichsen cupping test. Note the misalignment of surface fibers in case of sheet made from depithed bagasse pulp processes at 140^{o}C.

Grammage: Paper is generally sold by weight but the buyer is interested in area of paper. The basis weight/area (grammage) is what determines, how much area the buyer gets for a given weight. In papermaking, basis weight is important from production rate point of view. Hence, grammage is calculated for all bleached and unbleached handsheets prepared from rawwood, heartwood, sapwood and bagasse pulps. When we compare grammage values at given temperature it is observed that, the average value for heartwood pulp sheet was found to be higher compared to sapwood pulp sheet. When grammage values are compared with respect to temperature, the papersheets from kraft cooking at 165^{o}C was found to be lower compared to 155^{o}C (Fig 6.21). Similarly, bleached handsheets have exhibited less grammage value than unbleached papersheets (Fig 6.22). The fibers which are free from lignin (*Banavath et al. 2011*) promotes greater contact area/inter fiber bonding between fibers and lead to existence of more densely packed fibers in the sheet, hence fines or moisture content of the sheet is low and subsequently grammage is low. The fibers whose cell wall is filled with certain amount of residual lignin, prevents inter fiber bonding of fibers and sheet generally has low water absorption capacity or lower water retention value. Hence, the high grammage values can be attributed to the material which has lower absorption capacity due to high residual lignin content. As we have taken equal amount of beated pulp (70 g) for making handsheets, it has liquid (water) and solid component (pulp). The water retention value of the pulp is directly proportional to the liquid to solid ratio. Hence the sample which has less amount of solid mass exhibits less grammage of the handsheet after drying. *[The area of all handsheets are equal i.e. approximately 200cm^2].*

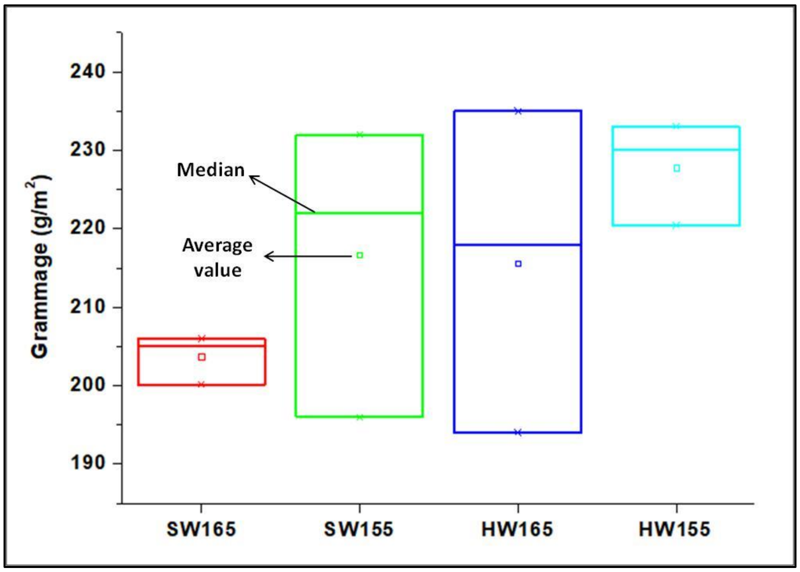


Fig 6.21: Grammage analysis of unbleached heartwood (HW) and sapwood (SW) handsheets ***[cooking temperatures were 165ºC and 155ºC]***

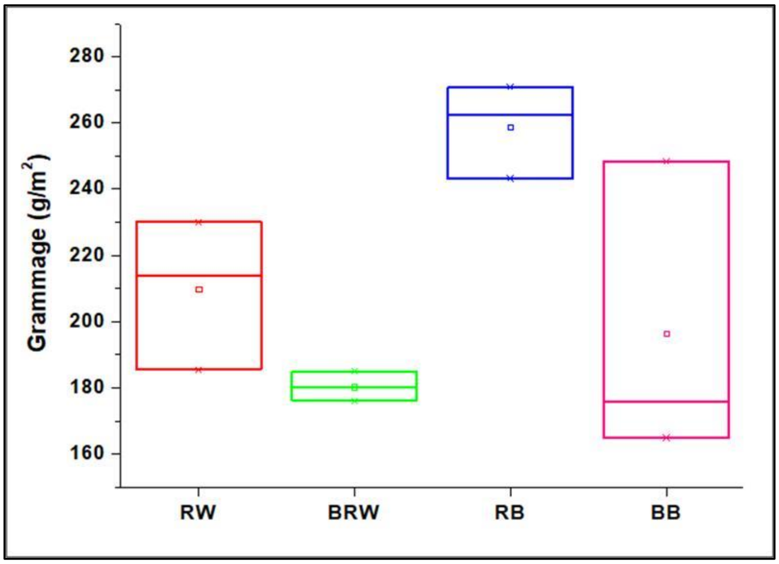


Fig 6.22: Grammage analysis of bleached and unbleached handsheets. (kraft cooking @165ºC) ***[RW- rawwood; BRW- Bleached rawwood; RB- Raw bagasse; BB- Bleached bagasse]***

6.3.3. Microscopic analysis of fractured sheets

The fractography or fracture morphology of papersheets is shown in Fig. 6.23, 6.24 and 6.25. The tensile strength of bagasse can be corroborated from the stereomicroscopic images (Fig 6.23) of the fractured samples where in the presence of pith seem to hold the fibers together during the tensile test resulting in lower pull out of fibers. Among the depithed samples, there was a greater amount of fiber pull out at lower stress itself under similar conditions. The unbleached tensile fracture specimen showed coarse fiber pull outs in comparison with bleached papersheets (Fig 6.24). A similar behaviour is also observed in heartwood papersheets (Fig 6.25) in comparison with sapwood (for a specific temperature) papersheets.

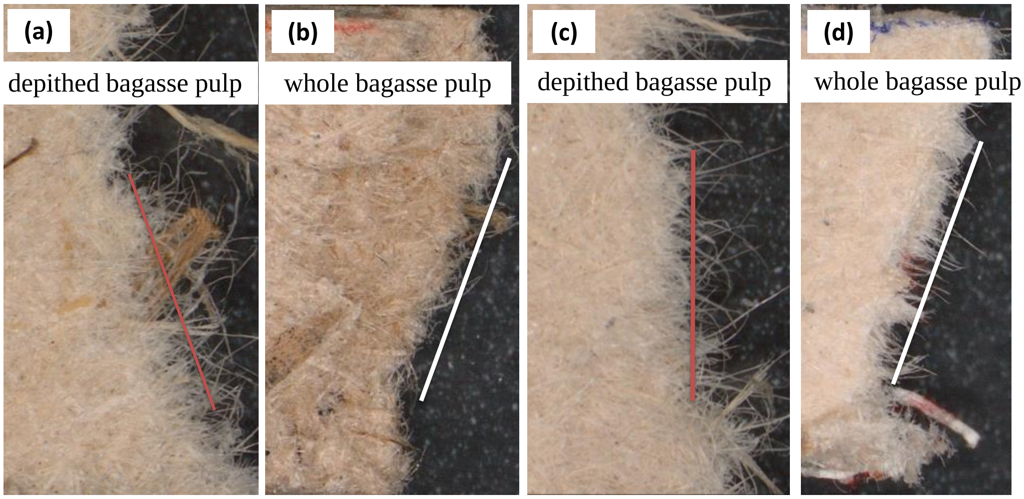


Fig. 6.23. Microscopic images of tensile fractured handsheets made from unbleached bagasse pulp. Note the angle of fracture (-20^o, +20^o, 0^o, +20^o).
a: Depithed bagasse pulp @140^{o}C; b: Whole bagasse pulp @140^{o}C;
c: Depithed bagasse pulp @165^{o}C; d: Whole bagasse pulp @165^{o}C

The fractured specimen shown in Fig. 6.25 showed coarse dimple fracture *[occurs through the formation and coalescence of microvoids along the fracture path]* which confirms the loss of materials ability to undergo significant plastic deformation before rupture. The resistance of paper to fracture depends on the inter fiber bonding in the rupture zone. Pulling the fibers away from the papersheet network depends on the length of the fibers (short fibers give dense network) and inter fiber bonding strength. During tensile testing the crack propagates across the sample, fibers tend to be pulled out, due to weak hydrogen bonding. The papersheet in which the fibers start to break instead of being pulled out is considered to be intact mainly due to higher inter fiber bonding strength. It takes less time and energy to break a fiber than to pull it out (at least for long fibers) therefore, the tearing strength decreases, as fiber bonding strength increases. Therefore it can be concluded that the differences in intrinsic viscosity, morphology, and structure of the individual fiber cell walls as well as the network structure (nonwoven) of the paper have contributed to the fractographic variations of different specimens.

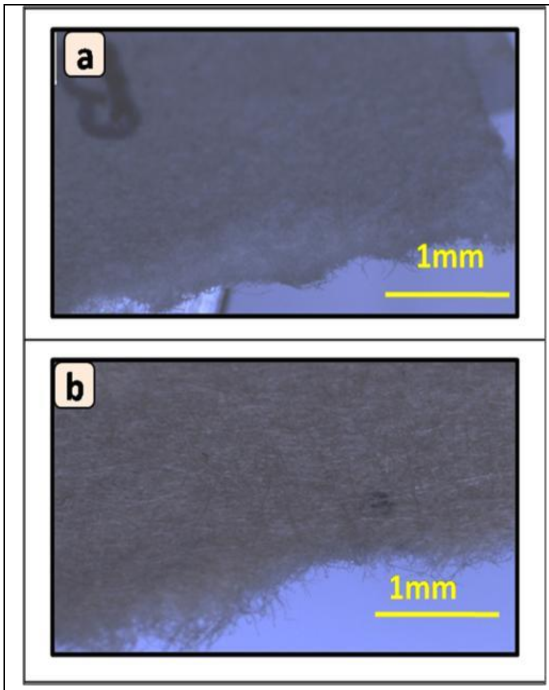


Fig 6.24: Microscopic images of tensile fractured handsheets made from rawwood bleached pulp (a) and unbleached pulp (b)

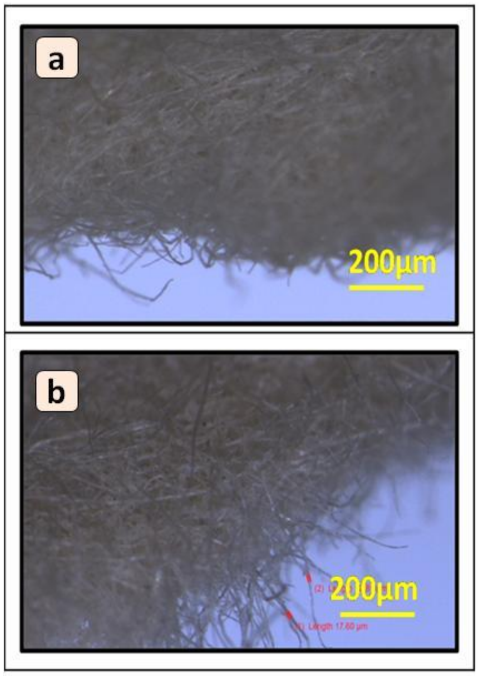


Fig 6.25: Microscopic images of tensile fractured handsheets made from unbleached sapwood pulp (a) and heartwood pulp (b)

6.4. CONCLUSIONS

The refining/beating process increased the °SR value and decreased the fiber length with increasing number of revolutions thus resulting in shorter, smoother and flexible fibers. The bleached pulp has exhibited higher brightness (85.2%), higher cellulose content (92%), higher water retention value (21), lower pulp viscosity (14.8 cP) and lower residual lignin content (0.8%) compared to unbleached pulp indicating the effectiveness of selected ECF bleaching. The bleached pulps also exhibited higher thermal stability than unbleached pulps until 300°C. Afterwards thermal stability of bleached pulps rapidly decreases to lower value (weight loss of >95%) by 500°C, whereas unbleached pulps remains partially stable (weight loss of <70%) until 600°C indicating the applicability of unbleached pulps in thermal packaging due to the existence of micro pores. These positive outcomes again indicate the effectiveness of selected ECF bleaching sequence. As fiber strength is proportional to cellulose content, the strength properties of paper sheet have confirmed greater tensile strength for sapwood (~80% cellulose) in comparison with heartwood handsheets. The dissolution of lignin fragments during bleaching elevates the hydrogen bonds between adjacent fibers in papersheet and resulted in higher tensile strength in comparison with unbleached sheets. In case of bagasse, the handsheet properties were greatly affected by the presence of pith. The handsheets made from pith were much stiffer compared to the ones prepared from depithed pulp. The greater tensile and burst strength of whole bagasse handsheets indicate that it could only be used as a packing material or in preparation of cardboard papers. The dimensions and strength of the individual fibers, their arrangement, and the extent to which they are bonded to each other etc., are all important factors contributing to test results. This hypothesis is confirmed by microscopic/SEM and fractographic analysis.

CHAPTER 7

CONCLUSIONS

The innovation/novelty of this thesis includes *"pulp characteristics obtained from sapwood and heartwood and also pulp characteristics obtained from whole bagasse and depithed bagasse"*. Plantation grown wood species (smaller in diameter) are mostly used as raw materials for paper making in India. Separating the whole wood log into heartwood and sapwood and performing the cooking process separately is currently not being practiced. Pulp and paper industry always consider the entire wood log for pulping, because of huge raw material crisis and minimal side effects of bark during kraft cooking. One of the innovations of this thesis work is separation of wood log into sapwood and heartwood before cooking and bleaching. This technique was in fact practiced during 1960's and 1970's; wherein **sapwood (SW)** was used in paper making and **heartwood (HW)** was used as structural timber. Hence, the objective of the research work was to perform the cooking process separately by considering SW and HW chips. Extensive pulp and black liquor characterization was carried out to find the differences between SW and HW by optimizing the cooking temperature and time.

From experimental analysis, it was observed that high temperatures are not required for SW cooking process. The required pulp properties for paper making obtained at 165^{o}C, 3hrs of cooking for HW (which is generally followed in the industry) can be obtained at lower temperatures i.e. 155^{o}C, 3hrs for SW. This implies that by separating SW and HW and then performing the pulping process, it is possible to cook the SW chips 10^{o}C lower than HW chips.

Then, the influence of cooking time was investigated by collecting black liquor samples during the pulping process. Because of the digester setup, removing pulp every 1hr or 1/2hr was not possible, but black liquor from bottom of the digester using the valve was collected at regular intervals of time. From black liquor analysis, it was observed that for a fixed temperature, the lignin is getting separated from the middle lamella and cell wall within 2 hrs of cooking in case of HW chips. Whereas in SW chips, the lignin separation is slowly increasing with respect to time and continued until 3 hrs (165^{o}C). HW lignin has a very dense network structure especially in middle lamella, so initiation of lignin degradation is a bit difficult (requires a higher temperature), but it propagates rapidly because of formation of multiple pores in lignin matrix. Based on black liquor and pulp characteristics, higher temperature with less cooking time

(165^{o}C, 2hrs) is optimal for HW chips. Whereas for SW chips, lower temperatures with higher cooking time is found to be optimal (155^{o}C, 3 hrs).

Another innovation/novelty of the research work involves the determination of the influence of HW and SW chip sizes during pulping process. As the chip size decreases, more surface area is available, higher impregnation and greater removal of lignin is possible in less span of time. Hence decrease in chip size provided a good result i.e. lower residual lignin content and high cellulose content. The research study also discusses the differences between SW and HW. In HW chips, lignin is tightly bonded to hemicellulose and cellulose fibrils. It is found that HW pulps has high lignin content, low water retention value, and low ash content irrespective of the sizes. So, it is recommended to use SW than HW in kraft cooking.

A detailed study using non-wood species was also carried out, as Indian paper mills use bagasse seasonally (available for 6 months in a year). Normally paper making from bagasse is done after depithing process. The objective of the study is to observe the differences between whole bagasse pulp and depithed bagasse pulp and their effects on papersheet. From mechanical characterization it was observed that, the depithed bagasse sheets exhibited 69 % lower tensile strength compared to whole bagasse sheets, even though whole pulp has lower cellulose content and lower WRV. In packaging applications, where the strength is the main criteria and not the ink absorption, whole bagasse can be used. Also, it can be concluded that the cooking can be done within 1hr (unlike wood which requires 3hrs cooking time) because the structure of bagasse cells is very loose and porous.

The influence of cooking time investigated by collecting black liquor samples during the pulping process indicated that the absorbance obtained for 140^{o}C, 1 hr is similar to the absorbance obtained for 165^{o}C, 1/2 hr, which clearly indicates that increase in temperature reduces the cooking time to 1/2 hr in case of bagasse. Another intresting aspect is found from thermal analysis of pulp. Whole bagasse pulp having the short parenchyma cells (which forms glue like substance as it starts degrading or softening with increase in temperature) formed a protective layer and became more thermally stable. Hence sheets made from whole bagasse pulps can be used for thermal packaging applications where high strength and thermal stability is required. The above important characteristic of whole bagasse is not reported in the literature.

For the equipment design (Rotary digester) two/three temperatures were selected and pulping process was carried out. The objective was to observe the effectiveness of process parameters in case of wood/bagasse. Surprisingly it was found that the cooking temperature had a significant effect during the pulping process i.e. with increase in temperature a reduction in lignin content, increase of WRV and cellulose content was noted. This (cooking at 165°C- 170°C) is being practiced in industry and not an innovation/novelty of the work. The new finding is basically separation of HW and SW; optimizing the time and temperature i.e. cooking SW chips at lower temperature and HW chips at lower cooking time.

In comparision with bleached wood pulp sheets, the bleached depithed bagasse sheets has shown almost 60% less tensile strength index. From mechanical testing of unbleached and bleached wood pulp sheets, the bleached sheets exhibited 80-85 MPa higher tensile strength. The sheets made from 165°C pulps (have low lignin and high cellulose content) showed better strength properties. This is because the strength of the paper is proportional to cellulose content and length of pulp fibers. So that they bond with each other to make a good nonwoven web. Similarly whole bagasse exhibits better tensile properties due to pith cells. Based on pulp characteristics it is recommend to use sapwood (165°C, 3 hrs) and depithed bagasse (165°C, 1 hr) for making printing grade paper. Based on tensile strength index, it is recommend to use unbleached sapwood sheets (165°C, 3 hrs) and unbleached whole bagasse sheets (165°C, 1 hr) for packaging grade applications.

SCOPE FOR FUTURE STUDIES

1. The current research work is limited to only two wood species (Eucalyptus and Subabul). Hence this process can be tried with other wood samples (neem, mango, oak, salwood etc) available in India and explore the characteristics of sapwood and heartwood separately for different applications.
2. This work is also limited to characterization of one type of sapwood/heartwood, however this work can be extended to include mixed sapwood/heartwood pulps (eg: SW/HW of eucalyptus, rubber etc) at different proportions and analyse the properties for suitable applications including non print types (ex: packaging applications).
3. This lab scale work can be scaled up to industrial level with minimum or no modifications of existing set up and further optimization of kraft cooking parameters (time and temperature) can be done for heartwood and sapwood to obtain similar results.
4. The characteristics of papersheet obtained from sapwood and heartwood pulps can be explored to find suitable applications.

5. The characteristics of papersheet obtained from whole bagasse pulps can be explored towards realisation of better packaging products.
6. Properties of unbleached heartwood and sapwood papersheets can be explored for different printing, writing & packaging applications.

LIST OF PUBLICATIONS

1. Characterization of Eucalyptus Heartwood and Sapwood Pulp after Kraft Cooking. **Journal of the Indian Academy of Wood Science**, 13(1), 8-15; SCOPUS indexed, 2016.
2. Pulp and Black Liquor Characterization of Subabul Wood after Kraft Cooking. **IPPTA (Indian Pulp and Paper Technology Association) - The Official International Journal**; 28 (2); 130-142. 2016.
3. Characterization of Subabul Heartwood and Sapwood parts after Cooking and Bleaching. **Cellulose Chemistry and Technology**, SCOPUS Indexed (Accepted in March 2019).
4. Influence of Temperature on Kraft Pulping of Whole and Depithed Bagasse. **Sugar Technology**, SCOPUS Indexed, 2019. DOI: 10.1007/s12355-019-00719-8

CONFERENCE PROCEEDINGS:

1. ***Delignification of Heartwood and Sapwood***. Indo-US Conference on Advanced Lignocellulosic Biofuels. IICT Hyderabad, Nov.10 thand11th, 2014.
2. ***Characterization of Subabul Pulp after Kraft Cooking and Bleaching.*** Chemference, IIT Hyderabad, 5 th and 6 th Dec. 2015.
3. ***Characterization of Subabul Heartwood and Sapwood after Kraft Cooking***. Proceedings of the International Conference on Advances in Chemical Engineering, NITK Surathkal, Karnataka, Dec 20-22 th, 2015.
4. ***Black Liquor Characterization of Subabul Heartwood and Sapwood after Kraft Cooking***. CHEMCON, IIT Chennai, 27-30th Dec, 2016.
5. ***Analysis of Subabul Wood, Pulp and Black Liquor obtained from Kraft Cooking***. Emerging Environmental Challenges-An Engineering Approach (EEC), BITS Hyderabad, Feb 16th, 2018 **(Received best oral presentation award)**
6. ***Kraft Cooking of Bagasse and Pulp Properties.*** Recent Advances and Challenges in Chemical Engg and Applied Chemistry, Anurag Group of Institutions, March 26th and 27th , 2018 **(Received best oral presentation award)**

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	PI: Treatment of Nitrogeneous waste water using microalgae and its utilization for biofuels and value added products - BITS-Pilani, CORE project, Waste, Water and Energy
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