Effect of Pulping, Bleaching and Refining Process on Fibers for Paper Making - A Review

[1]Madhuri Pydimalla
Assistant Professor, Department of Chemical Engineering, CBIT Engineering College, Gandipet, Hyderabad 500075, India

[2]Keerthana Reddy
Undergraduate, Department of Chemical Engineering, CBIT Engineering College, Gandipet, Hyderabad 500075, India

***Abstract*—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. The challenge involved in paper making is to remove lignin from middle lamella and cell walls so as to separate the pulp fibers and make them flexible. This paper presents a concise overview of Indian pulp and paper industry, importance of pulping, bleaching and refining of fibers for paper making. Significance of chemical constituents of biomass such as lignin, cellulose, hemicellulose, extractives, ash, for papermaking is explained. Status of different types of raw material used in Indian pulp and paper industry is presented. Reflections on different types of pulping processes such as Kraft pulping, Mechanical pulping, Chemical thermal mechanical pulping along with the necessary reactions have been provided. Also, Elemental chlorine free and Total chlorine free bleaching sequences are presented which yields a brightness of appr 80% ISO/SBD.**

Keywords—Pulping, Bleaching, Refining, Lignin, Fibers

I. INTRODUCTION

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. The use of paper and paper products is an indicator of the intellectual prowess of a nation. It influences multiple spheres of our daily life. Paper finds importance as a medium for communication and knowledge assimilation [1]. 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. It is expected that the demand for paper would grow to 23.51 Million tonnes /year by 2025 [2]. 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 use Subabul wood, Karnataka mills use seasonal bagasse, Punjab mills uses wheat straw) and recycled paper to make different grades of paper.

The paper industry is classified into four segments, Printing and Writing (P and W), Packaging Paper and Board, Specialty Papers and Newsprint [3]. The pulp and paper industry produces different grades of paper including writing and printing paper, corrugated material, packaging board, newsprint and tissue. Writing and printing paper accounts for about 26% of global paper production while corrugated material and paperboard packaging have a combined contribution of 51%. The newsprint and tissue account for 7% and 8% respectively. The chart depicts the variation of paper consumption across the segments in both global and Indian scenario (Fig. 1).

There are several challenges faced by the Indian paper industry like availability of quality raw material, technological obsolescence, high cost of energy & power and environmental concerns. Among these, the biggest challenge is scarce availability of quality raw material. The Indian paper industry therefore relies on different raw materials viz. wood, agro residues and recycled fibers to meet the demand. To counter the issue of wood deficit, Indian paper companies have started initiatives like monoculture tree plantations, agro forestry etc. The paper industry also relies on the import of waste paper to meet its demand for production of paper and paperboards [4].

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). As lignocellulosic biomasses are used for pulp and papermaking, their proximate chemical composition, pulping, bleaching and refining significantly influence pulp and paper production. Hence the main aim of this paper is to present a concise review on the status and chemical composition of raw materials, pulping, bleaching and refining methods.

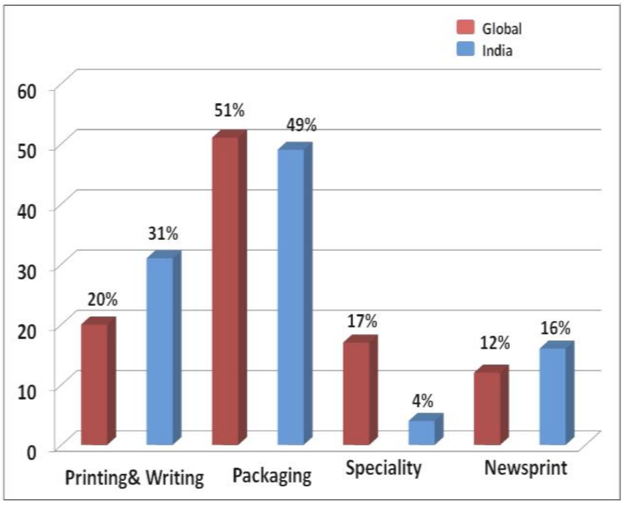

Fig. 1. Segment wise consumption of paper in India and World. [Source: Industry, IPMA - Indian Paper Mills Association, 2018]

II. 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) (Fig. 2). 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. Cellulose is a polysaccharide that gives strength to paper as it's microfibrils are smaller in diameter (*5-30 nm wide*) and oriented in fiber direction. Cellulose with degree of polymerization values (weight average) reaching up to 3500 *(native cellulose in-situ*) and requires a temperature of 320ºC and pressure of 25MPa to become amorphous in water [5]. 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 [6].

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 [7]. It has a great influence on the swelling behaviour of the fiber [8]. 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. 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 hemicellulose and cellulose. It confers mechanical strength to the wood cell wall. It is a thermoset polymer having three-dimensional network structures, but it is non-crystalline and acts as a binding agent to hold the cellulose fibers together [9]. It consists of C_6-C_3 phenylpropanoid units arranged in irregular 3-D network which makes lignin highly resistant to degradation. Removal of lignin is the main aim of the pulping and bleaching processes. Determination of lignin content in raw materials and pulps are regularly carried out to obtain their performance in processes. Hardness, bleachability, and other pulp properties, such as colour, are also associated with the lignin content [10].

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 interfere with the pulping process by causing foaming and corrosion [11] [12]. 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. The aim of paper manufacturing processes is to obtain pulp having negligible lignin content with high quality cellulose. 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 [13].

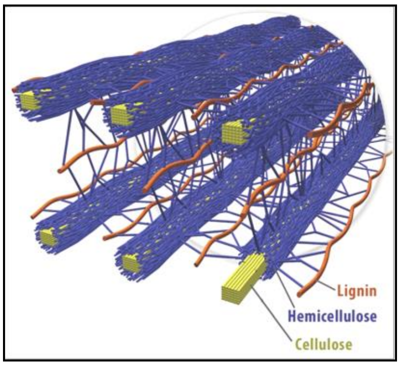

Fig. 2. Spatial arrangement of cellulose, hemicellulose & ligin in the cell walls of wood [14].

III. RAW MATERIALS FOR PAPER MAKING

A. 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 [7]. 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. The biggest difference between the species is hardwood contains more cellulose, hemicelluloses and less lignin than softwood (Table I). High yield, less lignin content are necessary to attain a compromise between cost and quality. In view of this, Indian pulp and paper industries are mainly focusing on wood species that have less lignin content and faster growth rate.

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) (Fig. 3). 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 (Eucalyptus 70.3; Subabul 75.2) and (c). % of ash content (Eucalyptus 0.66; Subabul 0.65) as per the report published by CPPRI, India [4].

B. Non-wood Species

The use of non-wood fibers for papermaking has been widespread in countries lacking an adequate supply of wood resources. 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 [15] [16] [17] (Fig. 4). It is characterized by high cellulose (40-50%), high hemicelluloses (xylan: 28-30%), but lower lignin contents (19-21%) compared to

International Journal of Engineering Research & Technology (IJERT)
ISSN: 2278-0181
Vol. 9 Issue 12, December-2020

Eucalyptus. These features enable *S.officinarum* to meet the quality requirements for newsprint and fine paper manufacture. 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 this alternative 'fiber sources' to meet the possible shortfall of wood for papermaking.

Table I: Chemical Composition of Softwoods and Hardwoods [5]

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

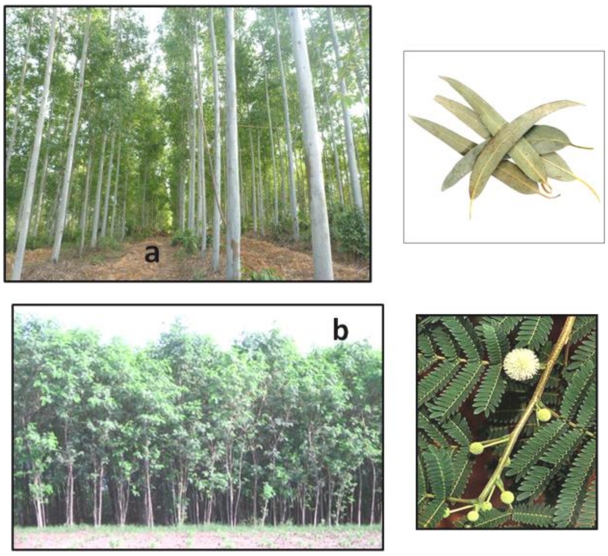

Fig. 3. (a). Eucalyptus plantation at Uttar Pradesh, India; (b). Subabul plantation at Tamilnadu, India.

Fig. 4. Sugarcane bagasse

IV. ULTRASTRUCTURE OF WOOD CELL, PULP AND PAPER

The raw material (wood/non-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. 5). Lumen diameter is around 10-20 µm and cell wall thickness varies between 2-10 µm [18]. The main aim for paper manufacturing is removal of lignin from middle lamella and cell walls by retaining sufficient percentage of cellulose and hemicellulose. Lignin removal from middle lamella is attained during pulping process, whereas removal of lignin from cell walls in multiple stages is carried out in bleaching process [19]. Refining or beating is carried out to remove kinks and this makes the pulp fibers more flexible. After bleaching and beating, the lumen (empty space in the middle of the fibre) is almost collapsed. Good paper can only be formed by pulp fibers which have collapsed lumen and low lignin content.

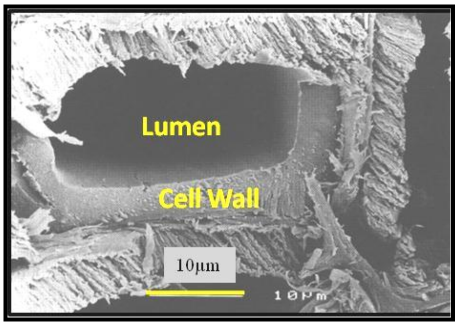

Fig. 5. SEM image of wood cross-section [20]

V. PULPING PROCESS

In pulping process wood is converted to fibers (Fig. 6) i.e wood or any other fibrous raw material is reduced to a fibrous mass by rupturing the bonds systematically within the wood structure [21]. During the pulping process, the chemical structure of cellulose also changes. The degree of polymerization value (weight average) of cellulose decreases from 3500 to 600–1500 when wood is transformed into Pulp [5]. The pulp is manufactured from wood or non-wood materials using *Chemical, Mechanical and Chemical Thermal mechanical pulping (CTMP) methods.*

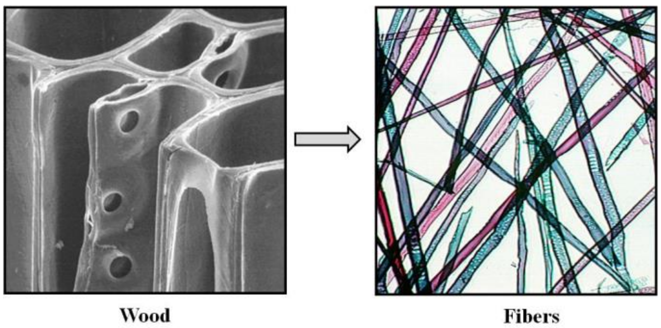

Fig. 6. Micrograph of wood and pulp fibers

A.Chemical pulping or Kraft cooking

Most of the world's chemical pulp is produced by ***kraft process***. The word Kraft in German language means strength. It implies that the paper made by kraft process (heterogeneous process) is superior in strength as compared to other processes [22] [23]. The main reason for it's dominance is its versatility in dealing with different raw materials coupled with superior pulp quality and the mature recovery of cooking chemicals [24]. 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 [5] [19]. 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.

$$NaOH + Na2S + Wood \longrightarrow Na\text{-}org. + S\text{-}org. + NaHS \quad .....(1)$$

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.

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

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

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 of ether bonds. These broken molecules or fragments dissolve in white liquor and ultimately leads to systematic degradation of lignin [5]. The kraft delignification process is divided into three distinct phases i.e. the initial, bulk and residual delignification phases [25]. The initial phase or impregnation stage is controlled by diffusion which is affected only by the total cross-sectional area of accessible pores [26]. In this phase the selectivity is low and only 20% of total lignin (mainly from middle lamella; low molecular weight lignin) is removed [27]. In bulk phase the cooking 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) is removed [28]. 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.

B. Mechanical pulping

The principle of mechanical pulping is to separate fibres from each other by mechanical energy applied to the wood matrix causing gradual breakage of bonds between the fibres and thereby releases single fibres, fibre bundles and fibre fragments [5] [29]. The objective is to 'maintain the main part of the lignin' in the raw material in order to achieve high yield with acceptable strength properties and brightness. Mechanical pulps have a low resistance to aging which results in a tendency to discolor. The three main mechanical processes commonly used are *Stone groundwood (SGW), Refiner mechanical pulping (RMP) and thermo-mechanical pulping (TMP).*

The SGW pulping process involves taking a log and pressing it against a rotating surface to grind off small pieces (Fig. 7). The groundwood pulp is then often cooked to soften it. This pulp is used in newsprint and other low cost book grades where it contributes bulk, opacity, and compressibility. The RMP process involves defibration of chips in a disc refiner under increased steam pressure. The process involves two refining stages in series, producing a longer fibrated pulp than conventional groundwood. The pulp is bulkier, stronger and contains fewer fines. The mechanical properties are also better but the pulp is darker in colour than SGW [7].

The TMP process involves high-temperature steaming before refining; this softens the inter fibre lignin and causes partial removal of the outer layers of the fibres, thereby baring cellulosic surfaces for inter fibre bonding. TMP pulps are generally stronger than groundwood pulps and is used as a furnish in printing papers, paperboard and tissue paper. Currently, mechanical pulps account for 20% of all virgin fibre material. The overall yield of mechanical pulping is generally in between 90-95%.

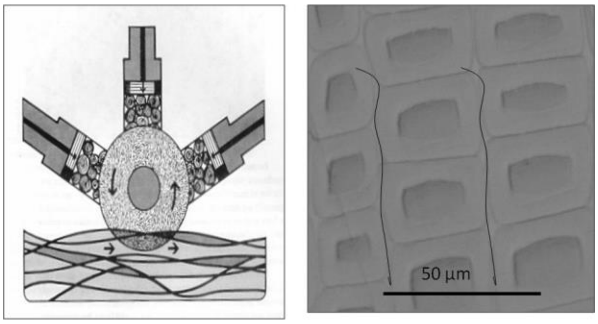

Fig. 7. Stone Ground Wood Process
[Note: The logs are pressed into the turning stones thus releasing fibers]

C. Chemical Thermomechaical Pulping (CTMP)

Chemical pre-treatment was introduced to overcome some of the above problems associated with mechanical pulping. The process starts with the penetration of 2-5% sodium sulfite and chelating agents at a pH of 9 to 10. The mixture is heated for 5-10 mins at a temperature of 120-130°C and is subsequently refined. The yield is in the range of 86-90%. The chemical pretreatment of the chips permits sulfonation of lignin, which causes swelling and weakening of the lignin matrix and consequently separation of fibres from the wood resulting in a higher and longer fibre content, and a much lower fines content than TMP. The CTMP pulps show good strength properties, higher brightness before bleaching. CTMP is best suited for absorbent grades and food packaging. The Pulps are weaker than chemical pulps, but cheaper to produce (about 50% of the costs of chemical pulp). They are obtained in the yield range of 85–95%.

International Journal of Engineering Research & Technology (IJERT)
ISSN: 2278-0181
Vol. 9 Issue 12, December-2020

VI. Bleaching Of Pulps

The objective of bleaching of pulp is to increase its brightness by removal or modification of colored components in pulp (Fig. 8, Table II). The chromophoric groups of lignin are principally responsible for colour [19]. 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 [30] [31] [32] [33]. 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 [34] [35] [36]. The distinguishing factor between the two processes is the use of chlorine dioxide, which is used in ECF but not in TCF. With the replacement of elemental chlorine (Cl_2) by chlorine dioxide (ClO_2) in bleaching sequences, the pulp and paper industry has reduced considerably the formation and discharge of chlorinated organic material into the aquatic environment [37]. 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 cause depolymerisation and create new hydrophilic groups. In India, CEH, CEHH, CHEH are used for lower brightness pulps; CEHEH, CCHEHH, CED, CEHD, CEHED are used for medium brightness pulp (up to 85% GE brightness) and CEDED, CEHDED, CCHEDH, CDEODED, OCDEHD are used for high brightness (around 90 or 90 plus) are among the most commonly used bleaching sequences.

As a new environmentally benign bleaching method, the use of enzymes has made an impact on the industrial bleaching. The biobleaching process is based on the action of the microorganisms and/or enzymes. 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 [38]. 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.

Table II: Approximate brightness ranges of unbleached pulps [5]

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

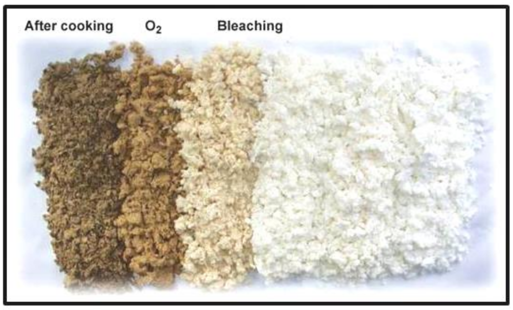

Fig. 8. Pulp bleaching process
[The dark colour of the pulp is mainly due to residual lignin. This is removed gradually during bleaching]

VII. Refining Of Pulps

Refining involves a mechanical action which is aimed to induce the internal and external fibrillation as well as delamination of the cell wall. In refining, both mechanical and hydraulic forces are employed to alter the fiber characteristics [7]. Fibers become more flexible by collapsing the lumens, thus creating ribbon like elements of great conformability [5]. During refining, fibers randomly and repeatedly undergo tensile, compressive, shear and bending forces [39]. The common device used for beating in pulp industries is PFI mill (Fig. 9). 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. The advantage of the PFI mill is that it only requires a small amount of pulp to carry out the complete refining. Hardwood pulps are quite easy to refine but sensitive to high loads involved in the refining process [40]. Softwood fibers require coarser fillings and higher refining intensity than those required for short and thin hardwood fibers. The effect of refining on paper properties is immense. Density and tensile strength increase due to improved fiber-to-fiber bonding.

International Journal of Engineering Research & Technology (IJERT)
ISSN: 2278-0181
Vol. 9 Issue 12, December-2020

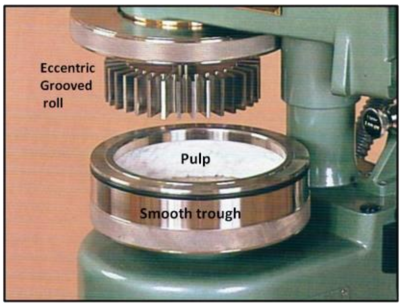

Fig. 9. PFI Mill showing pulp inside the trough [41]

Therefore it can be summarized that, pulp obtained from different raw materials (hardwood, softwoods, non-woods etc) after surpassing pulping, bleaching and refining processes are used to make different types/ grades of paper i.e. unbleached paper after pulping process, refined paper after cooking and refining/beating process, bleached paper after cooking, refining and bleaching process etc. The quality of the finished stock essentially determines the properties of the paper produced.

VIII. CONCLUSION

Lignocellulosic biomasses that includes woods (Hardwood and Softwood), agro residues (bagasse, wheat straw) are used for pulp and papermaking. The Proximate chemical composition, pulping, bleaching and overall papermaking process are significantly influenced by the raw material used for pulp production. In this article, a brief outline on status of Indian paper industry, various raw materials, pulping, bleaching and refining processes used for pulp and paper manufacture is presented. The effect of their physical and chemical components on pulping, bleaching and refining is also surveyed. In nutshell, this review outlines the evaluation concepts of pulp fibers for attaining high strength papermaking.

REFERENCES

[1] Kulkarni, H. D. (2013). Pulp and paper industry raw material scenario - ITC plantation a case study. IIPTA, 25(1),79-90.

[2] Jain, R. K. (2015). Compendium of census survey of indian paper industry. CPPRI, 3- 22.

[3] Dutt, D. Environmentally friendly and cost-effective method for manufacturing absorbent grade paper. Cellulose Chemistry and Technology. 47, 783–792 (2013).

[4] Subrahmanyam, S. V., Sharma, A. K., Godiyal, R. D., Janbade, V. T., & Gupta, H. K. (2000). Effect of physical and chemical composition of bagasse pulp on the development of strength properties. CPPRI Research Report no. CPPRI /RR-37.

[5] Smook, G. A. Handbook for Pulp and Paper Technologist. Vancouver: Angus Wilde Publications Inc. (1992).

[6] Madakadze, I. C., Radiotis, T., Li, J., Goel, K., & Smith, D. L. (1999). Kraft pulping characteristics and pulp properties of warm season grasses. Bioresource Technology, 69(1), 75-85.

[7] Karlsson, H. Fiber Guide: Fiber Analysis and Process Applications in the Pulp and Paper Industry. AB Lorentzen and Wettre Sweden (2006).

[8] Akhtar, R. S. (2001). Studies on pulping and bleaching of poplar deltoids. Institute of Paper Technology, Ph.D. Thesis, University of Roorkee, Uttarakhand, India, 18.

[9] Bailey J. E and Ollis D. F. Biochemical Engineering Fundamentals. McGraw-Hill (1986).

[10] Schoening, A. G., & Johansson, G. (1965). Absorptiometric determination of acid-soluble lignin in semichemical bisulfite pulps and in some woods and plants. SvenskPapperstidn., 68(18), 607.

[11] Meerts, P. Mineral nutrient concentrations in sapwood and heartwood - a literature review. Ann Sci. 59, 713–722 (2002).

[12] Levitin, N. (1970). The extractives of birch, aspen, elm and maple: Review and discussion. Pulp and Paper. Magazine Canada, 71(16), 81.

[13] Paulsson, M., and Parkas, J. Review: Light Inducing Yellowing of Lignocellulosic Pulps - Mechanisms and Preventive methods. BioResources. 7, 5995– 6040 (2012).

[14] Brandt, A., Grasvik, J. and Welton, T. Deconstruction of lignocellulosic biomass with ionic liquids. Green Chemistry. 15(3), 550-583 (2013).

[15] Pekka, N., Pekka, K. and Harri, A. Global competitiveness of the Indian paper industry. (2002).

[16] Verma, D., Gope, P. C., Singh, I. and Jain, S. Processing and properties of bagasse fibers. Biomass Bioenergy Process. Prop. 63–75 (2014).

[17] Rajesh, K.S., and Rao, M. N. R. Bagasse-the promising alternative for the future. IPPTA. 6, 151–158 (1998).

[18] Fengel, D., and Wegener, G. Wood: Chemistry, Ultrastructure,Reactions (1989).

[19] Britt, K. W. Handbook of Pulp and Paper Technology. USA: Van Nostrand Reinhold Company. (1970).

[20] Zimmermann, T., Sell, J. and Eckstein, D. SEM studies on tension-fracture surfaces of spruce samples. HolzalsRoh-und Werkstoff. 52, 223-229(1994).

[21] Smook, G. A. (2001). Overview of pulping methodology: handbook of pulp and paper technologists. Angus Wilde publication, 2nd edition, 36-43.

[22] Gartley, B. (2002). Ozone delignification at domtarespanola, paper presented at the PAPTAC Bleaching Committee, 21-23.

[23] Ibarra, D., Camarero, S., Romero, J., Martínez, M. J., & Martínez, A. T. (2006). Integrating laccase mediator treatment into an industrial-type sequence for totally chlorine-free bleaching of eucalypt kraft pulp. Journal of Chemical Technology Biotechnology, 81(7),1159–1165.

[24] Gullichsen, J. and Fogelholm, C. J. Papermaking Science and Technology: Chemical Pulping A19 (Fapet Oy, 1999).

[25] Epelde, I. G., Lindgren, C. T., & Lindstrom, M. E. (1998). Kinetics of wheat straw delignification in soda and kraft pulping. Journal of Wood Chemistry and Technology, 18(1), 69–82.

[26] Sjostrom, E. Wood Chemistry - Fundamentals and Applications. Academic Press,(1993).

[27] Lapierre, L., Bouchard, J., Berry, R. M., & Lierop B. V. (1995). Chelation prior to hydrogen peroxide bleaching of kraft pulps an overview. Journal of Pulp and Paper Science, 21(8), 268-273.

[28] Khandeparkar, R., & Bhosle, N. B. (2007). Application of thermo alkalophilic xylanase from arthrobacter sp. MTCC 5214 in biobleaching of kraft pulp. Bioresource Technology, 98(4), 897-903.

[29] Biermann, C. J. (1996). Pulping fundamentals: handbook of pulping and papermaking. Academic Press, 2nd Edition, 55-100.

[30] Parthasarathy,V. R. ,Klein, R., Sundaram,V. S. M., Jameel, H., & Gratzl, J. S. (1989). Hydrogen peroxide reinforced oxygen delignification of southern (loblolly) pine Kraft pulp and short sequence bleaching. In TAPPI pulping conference: proceedings (USA). TAPPI Press Atlanta, 539.

[31] Berry, R. M. (1991). Oxygen delignification, tech kraft pulp bleaching courses, tech, sect. CPA, Montreal, 101.

[32] Clark, T.A., Steward, D., Brice, M., McDonald, A.G., Singh, A.P. and Senior, D.J. 1991. Improved bleachability of radiata pine kraft pulps following treatment with hemicellulosic enzymes, APPITA J., 44: 383-389.

[33] Thomas, R., Singh, S.P. and Subrahmanyam, S.V. 2007. A study on oxygen delignification of Melocannabaccifera (muli bamboo) kraftpulp, Bioresour. Technol., 2(3): 430-441.

[34] Nie, S., Yao, S., Wang, S., and Qin, C. Absorbable organic halide (AOX) reduction in elemental chlorine-free (ECF) bleaching of bagasse pulp from the addition of sodium sulphide. BioResources. 11, 713–723 (2016).

[35] Ibarra, D., Camarero, S., Romero, J., Martínez, M. J. and Martínez, A.T. 2006. Integrating laccase mediator treatment into an industrial-type sequence for totally chlorine-free bleaching of eucalypt kraft pulp, Journal of Chemical Technology Biotechnology, 81:1159–65.

[36] Roncero, M.B. and Vidal, T. 2007. Optimization of ozone treatment in the TCF bleaching of paper pulps, Afinidad, 64: 420–428.

[37] Straton, S. C., Gleadow, P. L. and Johnson, A. P. 2004. Pulp mill process closure: a review of global technology developments and mill experiences in the 1990s, Water Sci. Technol., 50: 183-194.

[38] Afrida, S., Watanabe, T. and Tamai, Y. Acacia kraft pulp bio bleaching. BioResources. 12, 8272–8285 (2017).

[39] Bajpai, P. Technological developments in refining. (PIRA International) pp 140-141 (2005).

[40] Chauhan, V. S., Kumar, N., Kumar, M., Chakrabarti, S. K. and Thapar, S. K. Effect of separate and mixed refining of hardwood and softwood pulps on paper properties. J. Korea Tech. Assoc. Pulp Pap. Ind. 43, 1–10 (2011).

[41] Popil, R. E. Physical Testing of Paper. Smithers Group Company UK (2008).