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A Review on Pulping, Bleaching and Papermaking Processes

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Abstract
This paper presents a concise overview of pulp and paper production process, chemical constituents of the paper making biomass, pulping and bleaching processes. Processes related to raw material preparation, washing of pulp, chemical recovery operations, stock preparation and papermaking are described. Significance of chemical constituents of papermaking biomass such as lignin, cellulose, hemicellulose, extractives, ash, water solubility and alkali solubility towards papermaking is explained. Reflections on different types of pulping processes such as soda, soda-AQ and Kraft pulping along with the necessary reactions have been provided. Various sequences of conventional, elemental chlorine free and total chlorine free bleaching along with use of enzymes in bleaching is portrayed. In addition, status of different types of raw material used in Indian pulp and paper industry is also presented.

Keywords- Raw Material, Chemical Composition, Pulping, Bleaching, Pulp and Paper.

1. Introduction

Pulp and paper industry in India are one of the main industrial sectors and has its own socio-economic importance. The use of paper and paper products is indicator of the intellectual prowess of a nation and is often considered as a yardstick of its development, influencing multiple spheres of our daily life. Amongst various uses, the use of paper finds importance as a medium for communication and knowledge assimilation (Kulkarni, 2013). As one may expect, therefore production of paper and paperboard is expected to grow in future with literacy and industrial. A large number of capacity expansion and modernization initiatives in the paper sector are already planned by the paper mills to meet the growing demand, however there are several challenges confronted by the Indian paper mills like availability of quality raw material, technological obsolescence, high cost of raw material, energy and environmental concerns. Among these the scarce availability of quality raw material is one of the main constraints faced by paper sector. India is deficient in wood based raw materials, this is because of forest based wood cannot be lumbered as per the present policy. The Indian paper industry therefore relies on different raw materials viz. wood from farm forestry, agro residues and recycled fibres to meet the demand. Presently the wood contributes towards 19%, agro residues 10 % and recycled fibres 71 % respectively (Anonymous, 2017).

As mentioned above, the wood supply to the industry is not possible from designated forests as per the provisions of the present forest policy. Very limited supply of trees from the forests hardwoods and few species of bamboo are available to the paper industry. The supply of various other hardwood species such as Eucalyptus, Poplar, Subabul and Acacia etc. are met through social and agro farm forestry. The supply of the agro residues is affected by harvesting cycles of the agricultural produce, which limits the availability of agro residues for paper industry. The availability of Bagasse, one of the major lignocellulosic agro residues are used by the paper industry is limited due to its use as an alternative fuel in sugar industry. Only 18% of surplus bagasse is available to paper mills for manufacture of paper and paperboard. The recovery of wheat straw is only 75% due to prevailing harvesting mechanism and 40 % higher cost of transportation of loose straw due to unavailability of scientific baling mechanism. Also, wheat straw finds extensive use as cattle fodder in various parts of the country, decreasing its availability to the paper sector. Indigenous waste paper into finds competitive use as packaging material. Further, recovery rates of wastepaper collection in India are very low i.e. only 30-35% as compared to 55-60% in developed nations. Moreover, the quality of post-consumer wastepaper collected in India is inferior as compare to imported wastepaper due to the absence of an effective wastepaper collection, sorting and grading system. Therefore, the paper industry relies on the import of wastepaper to meet its demand for production of paper and paperboards **(**Subrahmanyam et al., 2000).

Under these conditions, the Indian paper sector has increasingly been using non-conventional raw material for paper making, even as these substrates are not able to produce paper products having similar excellence as one may obtain using wood. In the world today, Asia is the only place where sustained growth of the paper making is being observed. Out of this, major growth is expected in India, with paper sector expected to exhibit at CAGR of 6-7% over the next decade. Thus, the demand of paper would grow to 23.51 Million tonnes /year by 2025 (Jain, 2015). Hence, paper industry in India must gear up to meet this growing demand by augmenting and ensuring steady supply of lignocellulosic raw materials including woody, non-woody and post consumer waste (paper and paperboards). Since many of the lignocellulosic biomasses are used for pulp and papermaking, it is to be noted that their proximate chemical composition, pulping and bleaching significantly influence the pulp production. Hence the aim of this paper is to present a concise review on the pulp and paper production process, chemical composition of raw materials, pulping and bleaching methods.

2. Pulp and Paper Production Process

The paper mills world-wide employ various processes to manufacture the final product. Major papermaking processes are: 1) Raw material preparation, 2) Pulping, washing of pulp and chemical recovery operations, 3) Bleaching of pulp, 4) Stock preparation and paper making, and 5) Finishing of product. Prior to pulping of the raw materials, while the woody raw materials are chipped and screened to get uniform sized chips, the agro residues are cut and washed, except bagasse, which is depithed and cleaned.

During cooking or pulping, the cellulose fibres get released from the lignocellulosic raw materials by chemical, mechanical and semi-chemical methods. Pulping methods using chemical agents are dominant as it produces a higher quality product than mechanical pulping process. The most popular method of pulp production is the kraft process, producing nearly 85% of all pulp worldwide and is also predominant in India. The agro based mills use soda pulping process, barring few large integrated pulp & paper mills, which used kraft pulping to delignify the cellulosic raw materials. Chemical charge, cooking time, temperature of cook and solid to liquid ratio are the major process variables during cooking. The yield and kappa number of pulps are two important variables, which are controlled and checked at the end of the pulping process by optimization. Pulp washing is utilized to separates the dissolved components from the lignocellulosic raw materials. This process is also known as Brown Stock Washing (BSW) (Biermann, 1966; Smook, 2001).

The filtrate containing spent pulping chemicals, generated from pulp washers is taken to the recovery section to regenerate cooking chemicals for pulping and for utilization of energy by incinerating organic residuals. The chemical recovery operation starts from the generation of "weak black liquor" after the washers (Jain et al., 2006).

Processing of agro based black liquor in chemical recovery is difficult as compared to wood black liquor. Viscosity of agro based black liquors is higher and the combustion behaviour is erratic. Presence of non-process elements like Potassium, Manganese and Calcium, high viscosity and poor thermal properties of agro residue black liquors are some of the problems that need to be addressed for efficient chemical recovery operations (Kleinert, 1966; Parthasarathy et al., 1989).

In the bleaching process, the industry is facing serious issues to reduce discharge of chlorinated organic compounds from bleach plants. Therefore, in the delignification process, the prior to bleaching has become the practice. O_2 delignification has surfaced as a popular pre-bleaching process. Thus, unbleached pulp is made to interact with bleaching chemicals like chlorine, chlorine dioxide, hydrogen peroxide, oxygen and ozone etc to obtain bleached pulp with desired brightness. Modern bleaching sequences involve multistage processes utilizing different chemicals and conditions in every stage. Usually washing is carried out in between the bleaching stages (Parthasarathy et al., 1989; Berry, 1991; Clark et al., 1991; Thomas et al., 2007). The common sequences employed in Indian pulp and paper mills are CEpHH, CEDED, DEpD etc. To meet ever more stringent wastewater standards, a few mills in North America and Scandinavia have gone to bleaching with Total Chlorine Free (TCF) sequences. The requirement to discard chlorine dioxide in bleaching sequences has resulted in growth of various bleaching sequences where oxygen, ozone, peroxide and other more environmental friend treatments such as enzymes, chelants and peracids are used. One of the challenges in bleaching of agro pulp is to achieve the required brightness deprived of losing fibre strength which ultimately affects the runnability of pulps on paper machine. It has been observed that strength of pulp can be retained by optimizing bleaching conditions thereby retaining the fibre strength (Kostamo et al., 2004; Ragner et al., 2005).

The bleached pulp is treated in the stock preparation to produce desired quality paper from the paper machine. In the stock preparation such as mechanical treatment on fibre is performed to make it usable for papermaking operation. The stock preparation begins with dilution of the high consistency pulp from HD storage tank and is completed with blending of papermaking furnish in the machine chest. In the mills using market pulp, stock preparation starts by feeding pulp bales into the hydra pulpers. Chemical additives like rosin, alum, fillers and dyes are added in the pulp stock to get required paper properties. Refining is one of the most important unit operations in stock preparation which involve mechanical methods to create the best possible papermaking features in connection with the paper product being manufactured. During papermaking, the refined stock pulp is converted into a wet web on paper machine which is further dried to get the paper or paper board (Biermann, 1966; Smook, 2001).

3. Chemical Constituents of the Paper Making Biomass

The chemical composition of a lignocellulosic raw material is important in paper making. The chemical composition of a plant decides its suitability for papermaking (Hartley, 1987; McDougall et al., 1993) and must be ensured prior to its pulping etc. Cellulosic fibre bundles present in the cell walls of the raw material are the main component for pulp and papermaking **(**Taiz and Zeiger, 1991; Philip, 1992; Cassab, 1998). The amount and composition of the cell wall differs from species to species. The final pulp characteristics depend upon the type of raw material and pulping method used **(**McDougall et al., 1993). Though the chemical composition of the lignocellulosic fibrous raw materials like wood or non wood raw material varies from species to species, on an average there is around 45% of cellulose, 20-28% of lignin, 5-10% extractives and 5-10% inorganic matters present in a fibrous raw material where the remaining part is the mixture of polymer non glucosic carbohydrates (hemicellulose).

3.1 Cellulose

Cellulose, $(C_6H_{10}O_5)_n$, is one of the major components of fibrous raw materials. The strength and life of paper depends upon level of purity of cellulose. Here, n represents the degree of polymerization of cellulose units. The number of repeating cellulose units varies in pulp samples depending on the chemical and mechanical treatment during pulping, bleaching. The un-degraded cellulose may be a linear chain of about 10,000 anhydro glucose units whereas in the degraded form it may contain about 500 – 3500 units depending on the treatment during processing **(**Kocurek,1989).

In cellulose molecule, the –OH group reveals different behaviours. The –OH groups of cellulose chain take part in hydrogen bonding. These hydrogen bonds result in the formation of ultra-structure of cellulose. Cellulose is hydroscopic in nature as the –OH groups of cellulose can also from hydrogen bond with the –OH groups of water. These water molecules or cluster of water molecules can be attached to the surface of the cellulose (Dobbins, 1970).

Fibre and paper strength as well as its longevity is dependent upon the cellulose purity. The paper prepared from the pure cellulose is more durable due to presence of high alpha cellulose in it. This is a crystalline form of cellulose having up to 95% purity. Cellulose can be classified as alpha, beta and gamma cellulose depending on its purity and degree of polymerization (DP). Cellulose content in softwoods and hardwoods varies from 65-75 %, whereas the alpha cellulose content ranges from 45-55%. The mechanical strength of the paper (especially tensile strength) is directly proportional to the cellulose content **(**Madakadze et al., 1999).

3.2 Hemicellulose

Hemicelluloses are non-fibrous hetero polysaccharides. Hemicelluloses with an average degree of polymerization of 150±30 are soluble in dilute NaOH. They are hydrolysed to form mannose, glucose, galactose and arabinose. The amount of hemi cellulose varies from 10-25% in the raw material depending on the species used. Hemicelluloses contents are higher in agro residues than the hardwoods and softwoods **(**Bisht, 1996). It is desirable to retain of hemicelluloses during the pulping process since it enhances the yield of pulp and make the fibre bonds stronger. However, in case of dissolving grade pulps the hemicelluloses are not desirable. Acid-prehydrolysis is carried out to reduce the quantity of hemicelluloses prior to pulping **(**Subrahmanyam et al., 2000). Whereas cellulose is long chain polymer, hemicellulose has much lower molecular weight. It has a low degree of crystallinity and dissolves to a large extent in the chemical pulping. The presence of hemicelluloses also results in the swelling of the fibre **(**Akhtar, 2001).

3.3 Lignin

Lignin is a polyphenolic compound. During cooking, lignin is selectively removed, thus releasing the cellulose fibres. Removal of lignin is the main aim of the pulping and bleaching processes used by paper industry. Based on the lignin content present in any raw material different pulping and bleaching process are performed. Therefore, determination of lignin content in raw materials and pulps are regularly carried out to obtain their performance in processes. Brightness of pulp and paper depends on the lignin content **(**Schoening and Johansson, 1965). The residual lignin present in the pulp influences the paper properties and gives high stiffness in paper. The amount of lignin present in the lignocellulosic raw materials determines the chemical dose, time and temperature during delignification. The higher lignin content in a raw material, the higher is the requirement of the chemical charge and longer is the cooking time for pulping process. In non-woody plants, chemical demand for pulping and bleaching is lesser due to lower lignin content **(**Hunsigi, 1989).

The primary precursors of lignin. It is formed in cell wall of plants, but not in those of mosses, algae and microorganism (Kawamura and Higuchi, 1964). Lignin is distributed with hemicelluloses as matrix and is probably linked by covalent bonds (Lai and Sarkanen, 1971) with inter-cellulosic microfibrils in the cell walls (primary and secondary) and the middle lamella of fibres **(**Fergus and Goring, 1970; Scott and Goring, 1970; Wood and Goring, 1971). It acts as a cementing material for fibres to improve hardening and mechanical properties of the xylem tissue **(**Higuchi, 1990). In nature, lignin is abundant, and comes second after cellulose in terms of weight. Lignin has high calorific value, therefore in terms of energy content it might be the single most abundant material on earth.

The lignin also varies from plant to plant and species to species. The distributions of different building blocks of lignin in different raw materials are briefly discussed below. In softwoods (gymnosperms) trans- p- coniferyl alcohol (guaiacyl propane unit) is the main pre-cursor, while in the hardwoods (angiosperms), trans- p- coniferyl alcohol and trans – p – sinapyl alcohol (syringyl propane unit) are major pre-cursors. In grasses and agro residues lignin the main pre-cursors are trans -p - coumaryl alcohol (p- hydroxyl phenyl propane unit) in addition to trans p-sinapyl and trans p- coniferyl alcohol **(**Creighton et al., 1944; Higuchi et al., 1967) and p- coumaric acid with esterified terminal hydroxyl group of side chain **(**Smith, 1955). However, presence of minor amount of other precursor (s) in softwood and hardwood lignins is also reported in literature **(**Bland et al., 1950; Leopold and Malmstrom, 1952; Bhandari and Bisht, 1989).

3.4 Extractives

The extractives represent waxes, fats, resins, gums and phytosterols in biomass in quantified terms. The nature of extractives varies from one raw material to the other. Woody raw materials show the presence of essential oils, resin acids and sterols while other nonwoody raw materials contain tannins and coloring matter. The alcohol benzene solubility of wood shows the presence of extractives affect the quality of pulp and creates problems in papermaking processes due to pitch problems **(**Levitin, 1970).

3.5 Ash (Inorganic content)

Ash represents presence of various inorganic constituents in raw materials. Amount of ash content depends on nature of raw material. Softwoods and hardwoods, bamboo and bagasse, wheat straw and other grasses exhibits 0.5-1.0%, 1.0-2.5% and 5.0-10 % respectively. The higher ash content is of more than 15% is reported in the case rice straw. The main reason for high inorganic content in agricultural residues is due to the presence of silica in the lumen and leaves of the plant (Lal et al., 2011).

3.6 Water and Alkali Solubility

Water solubility is a measure to enumerate presence of tannins, gums, sugars, colouring matters and starches in wood and pulp. It affects the pulp yield to some extent. Therefore, it desirable that in a raw material and pulp the water soluble should be as low as possible.

While the superior hot water solubility indicates an easier penetration of pulping chemicals, 1% NaOH solubility indicates that pulp is more susceptible to deterioration during storage. The water and alkali solubility reflect the possibility of fungal decay or degradation in the raw materials by heat or light (Morgan, 1931).

4. Pulping Process

Pulping is the process by which the bonds between fibres within the raw materials structure are systematically broken by chemical or mechanical treatment (Smook, 2001). In chemical pulping, chemicals are used to separate fibres from lignocellulosic structure, whereas in the mechanical processes physical (mechanical) action separates the fibres (Biermann, 1996). The chemical pulping is further categorized in three categories as alkaline pulping processes (kraft and soda pulping); acidic pulping processes and solvent pulping processes (organo solvent pulping). The reaction takes place at elevated temperature and pressure in presence of chemical where in lignin and certain carbohydrates present in the raw materials dissolve during pulping. However along with the lignin hemicelluloses also dissolve and cellulose degrades which are the limiting factors in alkaline pulping. The prevalent reactions of cellulose degradation are called peeling reactions. Peeling reaction of 1, 4 linked polysaccharides such as cellulose, glucomannans and xylan was explained by Kocurek (1989.

These reaction starts from the reducing end of the cellulose chain. The reactions are dependent upon alkali dose, concentration of chemicals, pulping time and temperature. Some stopping reactions are also reported in the literature (Fengel and Wegener, 1984). Rates of reactions (peeling and stopping) are determined by an intramolecular reaction which is dependent on the degree of ionization. The higher activation energy of stopping reaction (135 kJ/mol) as compared to that of peeling reaction (103 kJ/mol) implies that the stopping reaction increases with increase of temperature (Haas et al., 1967).

Various researchers have reported that alkaline delignification kinetics is categorized into three phases namely initial, bulk and residual delignification phases (Epelde et al., 1998). Initial phase is characterized with slow delignification. However, in this stage high carbohydrate dissolution and heavy consumption of alkali takes place. Nearly all the lignin is eliminated in bulk delignification phase. Residual delignification on the other hand is slow and its selectivity is poor. The yield loss and carbohydrate degradation take place in the residual stage and are detrimental to pulp quality. At optimum temperature, aqueous alkali hydrolyses β-0-4 linkages of native lignin and decomposition of lignin polymer chains leads to formation of decomposed products which are soluble and are thus removed **(**Kocurek, 1989**).**

4.1 Soda Pulping

Soda pulping is an alkaline process that takes place in two phase system, namely the solid phase and the liquid phase. The solid phase consists of the raw materials. The liquid phase involves the moisture presents inside the raw material and the pulping liquor outside the raw material take part in the reaction. The historical evidences show that the soda pulping is the first pulping method that was adopted industrially. It involved the use of Na_2CO_3 and NaOH for cooking (Gullichsen and Fogelholm, 2000). The soda process was found to be useful for low lignin containing fibrous raw materials like agro based remains where using sulphidity shows no advantage. The soda process has some basic drawbacks also such as: low pulp yield, relatively lower paper strength properties, longer cooking time, high temperature and chemical charges. Paper manufactured from soda pulps have high bulk, opacity, absorbency and printability, therefore they are best suited to the paper grades, where pulp strength requirements are not important. Soda pulps are too soft to be used alone and are strengthened by blending with longer and stronger fibres; they serve as the “filler fibres” when added to the paper furnish **(**Dutt, 1994).

4.2 Soda-Anthraquinone (AQ) Pulping

In order to address the low yield of soda pulps, anthraquinone (AQ) is used during soda pulping process. Its use accelerates the removal of lignin and protects aldehyde group of carbohydrates against alkaline peeling reaction. The soda-AQ pulp has been reported to have better bleachability, higher pulp yield and sometimes better paper strength properties. AQ acts as a redox catalyst at moderate temperature (around 50^oC or higher) and stabilizes the carbohydrates. This preserves the pulp yield (Laine and Stenius, 1997). The mechanism reported is that initially AQ is reduced to anthrahydroquinone (AHQ) by the polysaccharide end groups. AHQ then effectively cleaves the α-aryl ether linkages to form free phenyl propane units of lignin (hence accelerating delignification) and simultaneously gets oxidized to AQ. This way AQ completes a redox cycle was studies by Greenberg et al. (1992).

4.3 Kraft Pulping

The kraft pulping process dated back to 1879 when it was invented in Germany by Carl F. Dahl. The word Kraft in German language means strength. It implies that the paper made by kraft process is superior in strength as compared to other processes. However, it is important to maintain high sulphur ratio or sulphidity to get maximum strength. Acidic sulphite processes on the other hand deteriorate cellulose in excess of the kraft process. It is reflected in lower strength of fibres. Kraft pulping is also called sulphate pulping due to addition of salt cake (Na_2SO_4) to meet the sulphur losses. The sulphur is lost during washing, evaporation and incineration of black liquor. Therefore, in order to compensate the losses, Na_2SO_4 is added during chemical recovery along with thickened black liquor. It is reduced in to Na_2S during combustion in recovery boiler under reducing atmosphere. The kraft pulping process uses the reaction of raw materials with white liquor (NaOH and Na_2S). This process is over 100 years old but still dominates in the paper industry. Nearly, 70% of the world’s pulp is still being manufactured by this process.

Some of the important features of Kraft pulping which are advantageous are as under:

Suitability for any commercially available wood species (hardwood and softwood) or non-woody plants (wheat straw, rice straw and bagasse) to produce a stronger pulp than most other chemical and mechanical processes.

Wide variety of unbleached and bleached products can be produced from the same basic pulping process ranging from high strength linerboard to high chemical purity dissolving grade and specialty pulps.

The high efficiency and economically viable chemical recovery system regenerates pulping chemicals, generates process energy and steam for pulp mill operations.

Following disadvantages of the Kraft pulping process are also reported:

The strength loss reported due to fibre damage during kraft cooking ranges between 0 to 35%. The average strength delivery at the end of cook is reported to be about 75%. The mechanism involved for fibre damage is that the fibre walls get exposed to damage during cooking process. Further the mechanical impact after cooking when pulp is blown from digester to blow tank, decreases the strength of fibres due to rapture of fibre wall.

It is observed that the conventional pulping process is effective over 2mm thick chips. Over 5mm thick chip particles are poorly cooked in the chip centre. Therefore, it results into unevenly cooked chip particles.

In order to cook inside of chip particles, cooking chemicals and heat must be transferred into the chip particle. Heat transfer is faster than mass transfer in lignocellulosic raw materials. Therefore, mass transfer limits the delignification in the chip particle’s cross section.

Over the years, various modifications have been made in kraft process, taking into consideration the chemistry of conventional cooking for producing stronger and more uniform pulp, increasing pulp yield, reducing energy usage and meeting the current and future environmental restrictions. The four basic principles considered for modifications are reported as below (Colodette et al., 2011; Germgard and Norden, 1994; Gierer and Imsgard, 1977; Lima et al., 2003; McDonough, 1985; McDonough et al., 1985). At the initial stage of cooking, the concentration of hydroxyl (OH–) ions must be low and as uniform as possible. The concentration of SH^- ions must be the highest at the start of cooking cycle. The dissolved lignin and Na^+ ions concentration must be minimal at the completion of the pulping cycle.

The temperature of digestion must be decreased throughout the whole cooking cycle. Lot of research was carried out in kraft pulping process during 1980 when batch and continuous cooking processes were competing. At this time, batch cooking technology was trying to survive and compete with continuous cooking due to its higher energy consumption.

Kraft pulping process is a heterogeneous process **(**Bajpai and Bajpai, 1992; Ban et al., 2011; Gartley, 2002; Ibarra et al., 2006; Khandeparkar and Bhosle, 2007; Lyytikainen et al., 2011). In this process swollen lignin in the raw materials is dissolved and it splits. High temperature and pressure facilitate the liberation of phenolate and carbohydrate anions from solid lignocellulosic raw material matrix. The lignin molecules condense and from larger molecules at high temperature. The condensed lignin is more difficult to remove from the fibers (Granholm et al., 2010; Jamieson and Smedman, 1973). An important role of the sulphide or hydrosulphide ions in kraft pulping is to reduce condensation of lignin fragments by blocking reactive groups such as hydroxyl in benzyl alcohol (Germgard et al., 1985). The delignification can be divided into three distinct reaction phases **(**Greenberg et al., 1992; Gullichsen and Fogelholm, 1999a; Gupta et al., 2000; Kishore at al., 1995; Khandeparkar and Bhosle, 2007), initial, bulk and residual delignification phase. Even at a low temperature 140^{o}C, the delignification occurs as a result of cleavage of aryl ether bonds into the phenolic units. About 20-25 % of the total lignin is removed during initial delignification (Lapierre et al., 1995).

The alkali consumption in this phase is high and almost 50 % of the alkali is consumed for the hydrolysis of hemicelluloses and for the removal of the carbohydrates by peeling reactions (Clark et al., 1991; Mathur et al., 2001). During bulk phase, delignification increases with increasing hydroxide and hydrogen sulphide ions concentrations **(**Fu et al., 2005; Kutney et al., 1984; Kishore et al., 1995; Khandeparkar and Bhosle, 2007). In the bulk phase the heating taken place from 150^{o}C to 170^{o}C and cooking at 170^{o}C. This phase results in the dissolution of about 70% of the residual lignin **(**Kleinert, 1966; Greenberg et al., 1992). Bulk phase delignification represents first order kinetics regarding lignin dissolution and the lignin in residual phase is in modified form. It is altogether different from lignin initially present in the wood (Dence and Reeve, 1996). The carbohydrates are removed by the hydrolysis of glycosidic bonds and followed by peeling reactions. It causes reduction in viscosity of pulp and total yield. Peeling reactions are finally stopped by stopping reactions, where the reducing end group is converted into stable glucometasaccharanic acid through benzylic acid rearrangement. Since carbohydrates are not available for further peeling reactions therefore cleavage of carbon-carbon bonds occurs (Clark et al., 1991).

The reason for the poor selectivity of the residual phase of delignification is because of the structure of the residual lignin remaining in the pulp at the end of the cook. It has a low reactivity toward the pulping chemicals, thereby making fragmentation and dissolution difficult **(**Eiras and Colodette, 2003). The consumption of alkali is mainly due to the neutralization of the peeling reaction products (Mathur et al., 2001). Alternatively, several researchers have suggested that lignin dissolution is affected by the attachment of the residual lignin to carbohydrates molecules (Godsay and Pearce, 1985; Jaaskelainen et al., 2003). The most important alkali catalyzed reactions responsible for carbohydrate losses during kraft pulping process are known as “yield loss”. About 50-60% of hemicelluloses and 10-15% of celluloses are degraded during kraft pulping (Bajpai and Bajpai, 2001).

5. Bleaching Process

In India, various bleaching sequences are adopted which includes elemental chlorine and (ECF) bleaching. The use of elemental chlorine is being discussed and is being replaced by (totally chlorine free) TCF bleaching sequences; however, some mills are still using CEH, and CEHH bleaching sequences. Elemental chlorine being a major source of pollution, the bleach plants account for 60-70% of BOD and 80-90% color load of the entire mill (Rao, 1997). Various toxic chlorinated compounds including the chlorinated phenolics, dioxins, furans, chlorinated resin and fatty acids are generated in the effluents followed by these sequences (Jauhari and Maheshwari, 1974; Chinnaraj et al., 2000). The chlorine consumption of agro-based and wood-based mills is 130-200 kg/t and 60-100 kg/t of pulp respectively. It is estimated that 1 ton of bleached pulp production contributes to about 100 kg of color imparting substances and 2-4 kg of organochlorines form bleach plant effluents (Nagarathanamma and Bajpai, 1999). Various processes to lower the use of molecular chlorine are being used prior to bleaching. These are oxygen (O_2) delignification modified cooking processes. Use of cooking aids (Ragauskas et al., 1994) and chlorine dioxide are also being promoted.

Molecular oxygen in alkaline medium allows prolonged delignification with preservation of pulp yield. It shows good performance in presence of carbohydrate stabilizers such as ($MgSO_4$) (Mukherjee and Bandyopadhyay, 1993; Gullichsen and Fogelholm, 1999b; Rodriguez et al., 2007). Oxygen delignification stage prior to pulp bleaching cause reduction in demand of chemicals used for bleaching as well as the doses of NaOH during initial extraction phase. Oxygen delignification causes almost half reduction in pulp kappa with no adverse effect on pulp viscosity (Parthasarathy et al., 1989; Berry, 1991; Clark et al., 1991). This also results in loss of pulp strength (Biermann, 1996). It is interesting to note that ODL preserves the yield while the additional techniques of prolonged pulping are found to affect the yield negatively. The chemicals used in the oxygen stage and the resultant reaction products are sent to chemical recovery system for processing. ODL decreases the formation of chloroorganics such as absorbable organic halide (AOX) in bleach plant effluents. ODL also decreases BOD, COD and color of the effluents (Thomas et al., 2007).

Elemental chlorine free (ECF) and total chlorine free (TCF) bleaching has revolutionized the technological status of the pulp and paper mills. This ensures production of environmentally benign paper and mitigation of environmental emissions (Ibarra et al., 2006; Roncero and Vidal, 2007). With the replacement of elemental chlorine (Cl_2) by chlorine dioxide (ClO_2) in bleaching sequences, reduced formation and discharge of chlorinated organic materials into the aquatic environment has been observed (Stratton et al., 2004). A decrease of about 48-65% AOX in Kraft pulp bleaching has been reported by mills using ECF (Kostamo et al., 2004). Meeting the tough environmental demands of Best Available Technology (BAT), set up by the European commission seems to be quite possible through these modern bleaching sequences of ECF and TCF (Ragner et al., 2005).

Nowadays, the enzymatic bleaching using Xylanases (X) is being explored as a simple and economic alternative for cleaner pulp production (Fu et al., 2005). They have been found to be quite promising for chlorine-free pulp bleaching processes. Treatment with Xylanases has been reported to increase overall bleaching efficiency by improving subsequent stages (Roncero et al., 2003; Valls et al., 2010). Therefore, the applications of Xylanases in the prebleaching of pulps have been found to increase. Microbial xylanases in bleaching process have also been studied for Aspergillus oryzae (Christov et al., 1999). A niger (Zhao et al., 2006) and fumigatus (Bajpai, 2004). The exploitation of xylanases is possible to replace of 5–7 kg of chlorine dioxide per ton of kraft pulp and it may result in an average fall of 2–4 units in kappa number (Polizeli et al., 2005).The bio-bleaching process is based on the action of the microorganisms and enzymes. The use of xylanase allows production of pulps with high yields, elevated brightness and conserves bleaching chemicals (Bajpai, 1999; Kaur et al., 2010). It is broadly applied to bleach nonwood pulps (Bajpai and Bajpai, 1996; Chauhan et al., 2006; Ninawe and Kuhad, 2006). Some researchers have reported that the commercial xylanases are not suitable for pulp bleaching (Ayyachamy and Vatsala, 2007) but they have been found to be useful after purification. The use of enzyme has been known to reduce pollution load. However, an increase has been reported in effluent COD and color due to the hydrolysis of hemicelluloses (Vidal et al., 1997; Mathur et al., 2001; Roncero et al., 2005). In a study at 100% ClO_2 substitution, the extent of AOX reduction in effluent of xylanase pre-treated softwood pulp has been reported as 40% (Senior and Hamilton, 1993). In effluent, COD and BOD increase is reported by 32 % and 108 % after treatment of eucalyptus kraft pulp with commercial xylanase. The AOX was reported to reduce by 15 % after same treatment in comparison with control (Jain et al., 2006). The properties of many commercial xylanases have been found to be unsuitable for the bleaching process of pulp also (Ayyachamy and Vatsala, 2007).

6. Conclusion

Many lignocellulosic biomasses are used for pulp and papermaking. This includes woods (Hardwood and Softwood), agro residues (bagasse, wheat straw, rice straw), bamboo and grasses etc. Proximate chemical composition, pulping, bleaching and overall papermaking process are significantly influenced by the species of the raw material used for pulp production. In this article, a review of literature conducted on status of Indian paper industry, various raw materials, pulping methods and bleaching processes used for pulp and paper manufacture is presented. The effect of their physical and chemical components on pulping, bleaching and papermaking is also surveyed. In nutshell, this review outlines the evaluation concepts of pulp and papermaking process.

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