Some basic aspects of high yield pulping

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SUMMARY

This paper deals with some of the fundamental aspects of high yield pulping. The thermal and adhesive properties of wood constituents and their impact on pulping is extensively reviewed. The role of 'glass transition point' of lignin and its variation due to moisture, in high yield pulping is pointed out.

The mechanism of ground wood pulping and its alkali strengthening characteristics are explained. The recent scientific developments and scope for improvement in this pulping process are also highlighted. Thermo mechanical pulping (TMP), chemi-thermomechanical pulping (CTMP), particularly sulfonated thermomechanical pulping (STMP) process are reviewed. The effects of thermal softening (TMP) and hydro-philicity of sulfonated lignin (CTMP) on pulping are explained. The morphological characteristics of fibers obtained by these are compared.

The Forest conservation movement has attained a new height with the public interest and enlightenment of the importance of ecological balance. The paper industry is one of the highest consumer of forests and is making all out efforts to consume less raw material and produce more paper through high yield pulping technology.

The proximate chemical analysis[1,2,3,4] of various raw materials reveals that most woods contain around 30-40% non-cellulosic constituents which includes lignin, extractives etc. The average pulp yields of kraft process, which is most commonly used in India are around 45% with approximately 3% lignin. Even with the revolutionary research with anthraquinone[5,6] or polysulfide[7,8] we could enhance it by only 2-3%. Thus we are losing a valuable carbo-hydrate fraction to the tune of 20-30%. This is of prime importance in view of forest conservation process economy and industrial output. Further due to high load of organics, colour, BOD and COD of the effluents, extensive and modern effluent treatment plants are required. The problem can be considerably reduced by high yield pulping.

The technical advantage of kraft pulps are mainly I) higher strength and II) capacity to reach a high brightness. The strength aspect is very important in case of packaging papers, but as far writing and printing papers are concerned, it is quite possible to get adequate strength properties out of high yield pulps[9,10].

LIGNIN AND CARBOHYDRATE BOND

Almost all the high yield pulpings are lignin preservative. Hence, it is desirable to understand the behaviour of lignin under the high yield pulping conditions. The thermal properties of the constituents of wood are of particular interest and importance. Lignin has a polyphenolic, three dimentionally branched network. The lignin and carbohydrate components exist in intiamate association, through two major forces, one based on absorption and chemi-absorption and other as covalent bonds Due to these bonds the selective removal of lignin during pulping or elsewhere is quite difficult. Invariably some amount of carbohydrate fraction is also lost in these operations. Lignin thus acts as a superb laminating agent, which penetrates fibers in such a way that delamination is very difficult.

Panda[11] reported that out of total alkali charge of 15% (as Na_2O) only 4-5% is used for delignification. The rest is consumed for dissolution of carbohydrates and other acids generated. This also proves the inaccessibility of lignin. If this lignin can be made accessible by any means, probably we may get a better pulp yield at a desired level of delignification.

Another problem with delignification is its hydrophobicity. Lignin is having a very slight hydrophilic

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character probably derived from its hydroxyl group content, (1.15 per phenyl propane unit[12]. But this is not at all sufficient to bind the lignin with solvents and delaminate it from the fiber. Thus the dielectric constant of water can not influence the carbohydrate-lignin bond.

Another question is why the lignin is considered to be undesirable in the pulp ? No definite conclusive answer has been pinpointed. Almost all the objections against lignin are based on its mechanical properties i.e. I) it binds wood fibers together and restricts fibrilation II) its three dimentional structure and less hydrophilic nature III) it produces physical bulking. If these mechanical undesirabilities could be overcome and if it can be reduced to a two dimentional structure by partial degradation or plasticization, through some process which could modify the structure of lignin, so that more and more of it can be kept in the pulp.

THERMAL PROPERTIES OF WOOD CONSTITUENTS

The attainment of high yield pulps has called for the recognition of a number of physical and chemical aspects of wood and its constituents. Specially thermal properties, like the glass transition point phenomenon which is of immense importance in understanding the theory of high yield pulping. Amorphous polymers exhibit a state of transition at the glass transition temperature and the mechanical behaviour of the polymer changes a lot. The glass transition state causes increased mobility of polymer molecules with the increase in its temperature. Below this temperature, the polymer molecules are held together strongly by forces like covalent bonds, hydrogen bonds and vanderwall's forces. At this temperature the chain acquires sufficient energy for large scale movement with respect to each other and the polymer becomes soft. When a low molecular weight diluent is absorbed by the polymer, the glass transition temperature is usually lowered, because the molecules of the diluent force apart the chains of the polymer and thereby decrease the energy required to develop large scale motion (glass transition).

Wood, as stated, is a mixture of three polymeric species, cellulose and lignin. Cellulose is partially crystalline, whereas the other two species are amorphous. Goring[13] has conducted extensive studies on the thermal softening, adhesive properties and glass transition properties in isolated lignin, hemicellulose and cellulose.

Cellulose was found to soften at high temperature (>230°C). Sorption of water by cellulose had negligible effect on the softening temperature probably due to the crystalline nature of cellulose. Softening temperatures, both dry and moist of several isolated lignins and hemicelluloses are listed in Table-I. Lignin showed quite a wide range of thermal softening temperature lowest being for spruce dioxine lignin (because of its low molecular weight—4300). Dry xylan and glucomannan softened between 165°C and 185°C. The softening temperatures of lignin and hemicelluloses were decreased by the presence of water. Thus water acts as a diluent and lowers glass transition temperature.

TABLE--I SOFTENING AND BONDING TEMPERATURES OF WOOD COMPONENTS

Sample	Dry °C	Moist °C
Spruce Periodate Lignin	193	116
Spruce Dioxene Lignin I	127	72
Aspen Dioxene Lignin	134	78
Pine Glucomannan	181	56
Birch Potassium Xylan	167	54
Kraft Pulp	245	239
Regenerated Cellulose Film	244	237

In a more interesting experiment Goring determined the adhesive properties of lignin and homicelluloses to determine the tack temperatures. When pressed dry, lignin is found to develop bonding properties at around 130°C. This temperature was lowered by 60°C in the wet state. In case of hemicelluloses bonding occured above 17 °C in dry condition. In wet state bonding occured at all temperatures. The strength developed at 50°C is double than that at lower temperatures. The strength developed with hemicelluloses is greater than that developed by lignin.

GROUND WOOD PULPING

This process involves the wet grinding of wood into a fiorous mass by means of a large revolving grind stone. Logs of wood are held with pressure against the surface of the stone, such that the fibers are at right angle to the stone movement[14], and the stone grinds the wood into fibers. A stream of water is sprayed on the stone to carry the pulp away and absorb the heat generated.

There are two stages of the grinding process, (I) Wood fibers and fiber bundles are formed or brushed from the log by the action of grinder stone, (II) the fiber and fiber bundles produced in the first stage are refined and reground to some extent. Both the stages however proceed simultaneously.

The heat which is generated in the first stage is considered to be important, since it softens lignin. But according to Atack[15] though temperatures as high as 180°C have been measured in the grinding

zones of commercial grinder, there is little evidence that fiber separation from parent wood occurs through middle lamella. Long ground wood pulps are not predominantly lignin encased and ground wood pulps of equivalent quality can be produced from similar wood samples at the same specific energy level and at the temperatures ranging from 100—180°C. According to him, since wood fiber in the grinding zone attain temperatures above lignin softening point for only a few milliseconds span, it would appear that most of the lignin does not effectively soften in this short time. This view is supported by previous investigations[16] which with the help of cross section of ground wood pulp, showed that break down of wood in the ground wood process does not involve any preferred region. Micrographs clearly showed failure in the cell wall as well as in middle lamella.

It was observed that pulp wood having thinner cell walls gave exceptionally high quality of pulp by break down to fine thread like stands which appeared to arise from S_2 layer, where as wood having thick walls gave poor quality pulp. This confirms that the amount of lignin and density of wood are more important parameters than the grinding temperatures.

Ground wood pulps are composed of individual fibers, broken fibers, fines and coarse fiber bundles compared to pulps obtained by other processes. The pulp does not hydrate during beating but tends to break up indicating the unexposed nature of S_2 which usually fibrilate during beating and hence the pulp is lower in strength. Brauns[17] reported that in lignin there were five free hydroxyl groups per unit molecular weight of 840, which may be compared with three hydroxyl groups per molecular weight of 162 of cellulose. So lignin would have lesser bonding sites available than those of between cellulose surfaces. This also accounts for the low strength of ground wood pulps.

Though ground wood pulps have lower strength properties, they have certain advantages eg. low cost, good printing quality, high bulk and opacity etc. Apart from these advantages it requires lesser energy compared to other mechanical pulping process. GWP is the oldest mechanical pulping process However, to produce newsprint with desired qualities out of 100% GWP furnish is still an elusive goal to papermakers and researchers. More efforts are to be made in this area to achieve this goal. Some researches carried out to improve the quality of GWP are worth mentioning.

Foote and Parsons[18] described a method to upgrade the strength properties of GWP. It is reported that sbstantial increase in strength properties could be obtained by treating GWP for several hours in a solution containing 3% of alkali. But this process requires considerable time. Hence, Becher etal[19] invented a Jet alkali process, where GWP will be treated continuously at high temperature and pressure in presence of alkali and lignin reactive chemicals. This has given great improvement in the strength properties. GWP at a high yield of 95-98% was found to approach 100% bleached soft wood pulp in tensile strength, the maximum strength being obtained with 3% sodium sulfite. The effect is mainly due to the increased swelling and plasticization of fiber constituents. Another important development in upgrading of GWP is pressurised ground wood pulping[20]. In this process the grinders were operated at 1 kg/cm^2 pressure. The strength properties improved considerably compared with conventional GWP—tear by 60%, tensile by 15% and wet strength by 50%. The properties are quite comparable with pulp from TMP.

THERMO MECHANICAL PULPING (TMP)

TMP involves the steaming of raw wood chips at relatively low pressure and refining after the lignin has softened. In the first step of TMP, preheating of the chips is done just to soften the lignin, so that fiber separation is easier. Atack[15] reported that steaming at 130°C for 3 minutes leads to complete fiber separation. In fact the fiber separation through middle lamella region will be favoured at high temperature (above lignin softening temperature). In addition, it is also necessary to fracture the secondary wall of the individual fiber to get it fibrilated. At higher temperature i.e. well above the glass transition temperature of lignin, the softened lignin reverts to glassy state and becomes an obstacle in further refining. In addition to this some lignin condensation may also take place in the plasticized state, because of the prevailing acidity[21]. The three stages of presteaming (below, at and above glass transition temperature) and their effect on fibrillation fiber encasement with lignin were illustrated by Higgins[21] with the help of scanning electron micrographs. Hence, as a compromise to softening and further fibrilization, the steaming is done at glass transition point. Kurdin[22] found that the strongest TMP were produced just below the glass transition point. Chips heated to temperature just below the glass transition point of lignin can be cooled and the lignin will remain soft indefinitely, so that refining can be done at atmospheric pressure.

During refining the fibers are stress cycled by the refiner for a large number of times at values less than the breaking point. The fiber wili be subjected to compression and decompression. Eventually due to

fatigue failure, the outer layer of the fibers will be peeled off exposing the S_2 layer. This exposure is beautifully micrograph by Atack[15]. This exposure of polysacchiride rich S_2 layer facilities the response to subsequent beating or refining and permits internal and external fibrillation without the expenditure of large amounts of energy. In TMP pulps the debris content is greatly reduced and the fibers are relatively longer than GW. The fiber fractions upto +50 screen contains full fibers with smooth surfaces. The other fractions contain ribbon like, flexible lamella which are important to fiber contact, improved internal bonding, high strength and smoothness. Brightness of TMP pulps is less than that of ground wood pulps.

CHEMI THERMO MECHANICAL PULPING (CTMP)

TMP can produce a stronger pulp than GW or RMP, but the high strength can be obtained only at lower darinage levels. At the same time long stiff fibers produced in TMP do not bond properly to each other. In order to overcome these difficulties, CTMP has come into the picture. Mild chemical treatment of the chips in the CTMP before refining, makes it possible to increase the softness of the chips still maintaining a yield above 90% and produce a fiber with a very high flexibility. Out of all chemicals tried, sodium sulfite was found to be more effective. The pH of the system will usually be maintained between 9 to 10 with NaOH.

Lignin can be made to swell in water by substitution with polar groups such as carbonyl and sulpho groups. The introduction of these groups make lignin more hydrophilic. Lignin can be sulphonated with hydrogen sulphite ions in acidic, neutral or alkaline solutions.

Atack[23] found that the softening temperature of lignin deminishes linearly with increasing sulphonic acid content. Taking this into consideration, Higgins[21] carried out his CTMP experiments at 100°C. Thus the presence of sodium sulphite and low temperature will ensure the maintenance of reasonable brightness. Higgins[21] has also reported that the best pulps prepared at their CSIRO division by CTMP process from Eucalyiptus (Freeness-158 ml CSF; Bulk-1.47 cm^3/g; Breaking length-8.6 km; Burst Index—5.2 $KPam^2/g$ and Opacity—92%).

Mutton etal[24] sulphonated wood chips with Na_2SO_3 at 140°C for 30 minutes and the resultant refined pulp was shown to have superior properties than TMP. Comparative strength properties of SGW, TMP, CTMP and SBK are given in Table-II, and give a fair idea about the pulps from various mechanical processes. From the table it can be

TABLE—II COMPARATIVE STENGTH PROPERTIES OF VARIOUS HIGH YIELD PULPS

Particulars		SW	TMP	SCMP	SBK
Yield on wood	%	95	94	92	43
CSF	ml	90	150	350	550
Breaking length	km	3.2	4.0	6.0	8.0
Burst Index	MN kg	1.3	1.7	3.4	6.0
Tear Index	Nm^2/kg	5.0	8.0	8.8	14.0
Long fiber (> 48 mesh BaurMc Nett)	%	40	55	72	80
Fines (< 100 mesh Baur Mc Nett)	%	50	35	19	8

observed that freeness of the pulps increased from SGW to SCMP. Yield of SCMP is also quite comparable with those of other highis yield pulps. Long fiber fraction is considerably higher in SCMP. These facts infer that there is less fiber damage and more fibrillation in SCMP. Thus the lignin in SCMP has become more soft and can take more lead during refining without fiber cutting. Thus the peeling off of the primary and outer secondary wall isfacilitated exposing the cellulose rich S_2 layer for easy fibrillation. Thus a pulp of better strength properties resulted.

Another interesting study is that of Jansan and Mannstrom[25], where they subjected the chips to two stage chemical treatment, before them. In the first stage a mild alkali treatment is given which stabilizes the hemicelluloses to different degradations. This is partly because, acetyl groups are split off and this results in an increased tendency for the hemicelluloses absorbed on the solid phase. In the second stage the lignin in chips is sulphonated with Na_2SO_3 there by increasing the hydrophilicity and all other beneficial effects in the beating and paper making characteristics.

Axial compression of wood at room temperature prior to TMP or CTMP or RMP increased the level of bonding in all these three pulps[26]. The specific energy required in refining is considerably decreased by this process. Photomicrographs of the wood after compression showed that S_1—S_2 fiber wall separation was initiated by the compression at several sites along each fiber.

CONCLUSION

The-increasing demand of paper and paper products and fast depletion of natural resources forced the paper technologists and researchers to

come forward with newer ideas to use resources efficiently and judiciously The high yield pulping processes are attracting a great deal of interest through out the paper industry. The extensive researches and process developments made so far in this direction suggest the following important aspects.

(1) There is considerable scope for improving the quality of ground wood pulp. The pulp properties can be improved by treating it continuously with some doses of alkali and/or lignin reactive chemicals under pressure and temperature.

(2) In thermo mechanical pulping, various processing parameters i.e. response of good variety, efficient utilization of refiners and other equipments, consistency, chips dimension as well as TMP in combination with other pulps are to be evaluated systematically.

(3) TMP process should be carried out just below the glass transition point of lignin to get maximum advantage of this process in terms of energy saving and better pulp quality.

(4) The use of sodium sulfite in the presteaming stage has proved to be most efficient and effective in CTMP.

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