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Manufacturing of Paper by Sulphate (Kraft) Process

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ABSTRACT

This paper covers the scenario of Indian Paper Industry and different processes for the production of paper. In this study wood is take as raw material which is converted into pulp and primary form of Paper. Generally two (Mechanical and Chemical) pulping processes are used for manufacturing of pulp from wood. In the manufacturing process of pulp and paper firstly wood chips are cooked in digester and then washing, screening, bleaching operations are carried out and then forming, pressing, drying operations used for paper manufacturing.

KEYWORDS:

Paper and Pulp Industry, Growth of paper industry, Raw Material, Different Processes.

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INTRODUCTION

The word paper is derived from the “Latin” word “Papyrus” and from French “Papier” Paper is basically composed of vegetable fibres mattered together to form into sheets. “Papyrus” is a kind of grass material. Papyrus is an aquatic plant which grew in abundance in the delta of the Nile in Egypt. In an understandable language it means a sheet formed by the composition of vegetable, mineral, animal or synthetic fibers or mixtures with or without the addition of other substances into liquid vapour, or gas so that the fibers are intermeshed together.

Paper consumption is used as basic measure of civilization. Initially writings and carvings were made on stones, clay, copper, bras and palm trees, etc. The art of paper making was first developed in China where it was made from the bark and leaves of the mulberry tree. In 751 A.D. the Arabs took the Chinese as prisoners and from them the art of paper making reached to the Middle East and Europe.

As per history, the efforts to mechanize the Indian paper industry were first made by William Carey. He started a paper mill in 1812 at Serampore, West Bengal. He himself set up a steam engine in 1820 and he added first four-drinier type machine in 1832 and paving to the development of mechanized paper mills. The Upper India Couper Paper Mills, Lucknow (1882) and Punalur Paper Mills, Kerala (1883), Titaghur Paper Mills, West Bengal (1884), Deccan Paper Mills, Maharashtra (1887), Bengal Paper Mills, West Bengal (1891) and Imperial Paper Mills Corporation, West Bengal (1894) were pioneering units in the early Indian Paper Industry. The then British Government in India had given a preferential treatment to the indigenous paper production in 1880 to encourage and establishment paper mills. During the course of time the paper industry had been transformed into one of the major and key industry for independent India¹.

2. GROWTH OF PAPER AND PULP INDUSTRY:

The Indian Pulp & Paper industry impressive growth rates in the GDP at 8% CAGR. This translates into consumption of about 24 million tonnes and production 22 million tonnes by 1025 resulting in 17 Kg².

Table-1. "Growth of paper mills in India"

Year	No. Of Units	Installed Capacity (Million tonnes)	Production (MillionTonnes)	Capacity utilization (%)	Per Capita Consumption (Kgs)
1950	17	0.13	0.11	85	0.9
1970	57	0.77	0.75	99	1.9
1990	325	3.3	2.43	62	3.6
2000	380	3.94	4.87	99	5.5
2006	660	8.5	6.8	80	6.7
2007	667	8.5	8.3	100	8.3
2010	759	12.7	10.11	80	9.3

Source: IPPTA JOURNAL, VOL 25, No. 1, 2013

3. DIFFERENT PRODUCTION PROCESS OF PULP AND PAPER:

The manufacture of paper can be divided into two phases: the pulping and the paper making. In the pulping phase the cellulose raw material must be processed to free fibres with suitable properties for paper product. The paper making is the continuous process consisting of forming slurried pulp in sheet form then pressing, drying, calendaring.

3.1. Pulping:

The pulping process can be divided into three categories: chemical pulping, mechanical pulping, and semi-chemical pulping (combination of two above categories).

3.1.1 Mechanical pulping:

Mechanical pulp is produced by grinding or shredding the wood or non-wood materials to free the fibres. In addition heat and pressure may be applied to assist the process. Mechanical pulping provides low grade pulps with high colour and short fibres, but with a high yield converting 95% of the wood into pulp and produces minimal on-site air pollution and relatively water loads. There are six basic mechanical pulping processes are stone ground wood, refiner, thermo mechanical pulping, chemical mechanical, defibrated or exploded pulping, and recycled paper but the are first two^{3, 10}.

3.1.1.1 STONE GROUND WOOD PULPING:

The first grinders were built by Voith in 1852. In this method logs of wood are ground against a stone wheel to produce clumps of fibre. Stone ground wood does have some favourable characteristics: low energy costs and high fines content which is desirable for printing characteristics.

3.1.1.2 REFINER PULPING:

The first attempt to use disc refiners to produce mechanical pulps was made in the 1950's. This demonstrated that it was possible to produce pulp which was stronger than stone ground wood. Thermo-mechanical pulping (TMP) process was developed. This technique involves pre steaming of chips for a short period, typically about three minutes, at a 110-130°C and 150-210kPa and then performing the first stage of refining under pressure ⁴.

3.1.2 Chemical pulping:

Chemical pulping is done by digesting to free fibres from the wood chips, non-wood materials such as bamboo, straw, grass, cotton, in chemical solutions that help to dissolve the lignin binding material. Pulp yield is normally in the range of 35 to 57% and about 95% of the lignin is removed in pulping. Chemical pulps may be subdivided into Kraft (sulphate), sulphite, semi-chemical and soda.

Two major chemical pulping processes are currently in commercial use are kraft (sulfate) pulping, and sulfite pulping. The kraft process dominates the pulp and paper industry, accounting for 76 percent of the pulp produced for paper and paperboard in 1984 ^{4,11}.

3.1.2.1 SODA PULPING:

The soda pulping was the first chemical process applied in pulp manufacture. In the process, sodium hydroxide is used as cooking liquor with adding a mixture of soda ash (Na_2CO_3) and lime $\text{Ca}(\text{OH})_2$ to the digester. This process is most suitable for agricultural residues pulping ⁵.

3.1.2.2 SULPHITE PULPING PROCESS:

The sulphite pulping process is one of the major pulping methods. This process is most suitable for non-resinous softwood. In this method, the fibre-binding lignin is softened and dissolved to a considerable extent in a solution containing dissolved SO_2 , hydrogen sulphite ions with pH value between 1.5-12. Depending on the cooking degree, the yield varies from 45 to 65%, but normally the yield is about 50% for standard non bleached pulps. If the pulp is bleached,

another 4 to 5% of the original wood weight may be lost in the process. An advantage of the Kraft pulping process is the possibility of recovering both process chemicals and the heat content of the dissolved lignin. One drawback is that the process results in pulps with a high kappa number which thus require bleaching for many applications ³.

3.1.2.3 KRAFT PULPING PROCESS:

Kraft pulping, first used in 1879, is a modification of the caustic soda process in that sodium sulphite (Na_2S) is added to the cooking liquor. The presence of caustic soda in the cooking liquor is suitable for use of practically all wood species. Sodium sulphate is on duty of buffering, that digestion can be implemented at a lower OH^- ion concentration. Thus damage to the fibres is reduced and high strength pulps are produced. Generally, kraft pulp recoveries from softwoods are approximately 47 percent for unbleached pulp and 44 percent for bleached ^{6,9, 30, 31}.

3.1.2.4. SEMI- CHEMICAL PULPING:

Semi-chemical pulping uses a combination of chemical and mechanical (i.e., grinding) energy to extract pulp fibres. Wood chips first are partially softened in a digester with chemicals, steam, and heat. Once chips are softened, mechanical methods complete the pulping process. The pulp is washed after digestion to remove cooking liquor chemicals and organic compounds dissolved from the wood chips. This virgin pulp is then mixed with 20 to 35 percent recovered fibre (e.g., double-lined Kraft clippings) or repulped secondary fibre (e.g., old corrugated containers) to enhance machinability. The chemical portion (e.g., cooking liquors, process equipment) of the pulping process and pulp washing steps are very similar to Kraft and sulphite processes. At currently operating mills, the chemical portion of the semi-chemical pulping process uses either a non sulphur or neutral sulphite semi-chemical process. The nonsulfur process uses either sodium carbonate (Na_2CO_3) only or mixtures of Na_2CO_3 and NaOH for cooking the wood chips ^{7,8}.

3.1.3 Other Processes

According to ⁵ recognizing the difficulties of using established processes on a small scale, a number of alternative processes are being developed which are claimed to be specially suitable for small-scale operation either because they are non-polluting (in at least one case it is claimed that digestion liquor can be used as fertilizer) or because the recovery process is relatively simple. Examples of these Processes are:

Ammonia-based pulping.

Oxygen (air) and alkali processes.

Universal process (acid based).

Organosolv Pulping (Ester Pulping) ^{12, 28} .

Hydrotropic Pulping ^{18, 19}.

3.2. Paper making:

In the paper making process pulp is converted into paper. Normally, the process consists of four main steps: stock preparation, sheet preparation, water removal and sheet finishing. Pulp in the stock is heated and mixed. Some different chemicals and fillers like alum, clay, and starch are added to the pulp stock for enhancement of certain paper properties. Next, the pulp is evenly distributed over a travelling belt of fine wire screening, and carried to rolls. A small portion of the water contained in the pulp passes through the screen, while the longer fibre are laid down on the wire, pressed through a series of rolls then air dried in a steam-heated dryer section. After drying, the sheet may be surface treated and then finished. A considerable portion of the fine fibres and some filler also pass through the screen wire with water. Because of its colour, this wastewater is called "white water". The main sources of waste from paper mills are beaters and paper machines.

4. METHODOLOGY (PROCESS DESCRIPTION):

Kraft pulping involves treating wood chips and sawdust with a sodium sulphite and sodium hydroxide solution. The highly alkaline chemical and wood mixture is cooked with steam under pressure (digested) for between 1 and 3 hours. Digestion may be either a continuous process or treated in discontinuous "batches." Most of the lignin and some of the Hemi cellulose is dissolved, leaving the remaining cellulose fibres separated.

The cooking liquor containing the dissolved lignin and other extractives (black liquor) is routed to a chemical recovery plant where the lignin and organic wastes are burned to produce energy needed in the pulping process. Valuable extractives (e.g., turpentine, tall oil, and resin) are separated for sale as commodity chemicals. Process chemicals are recovered with only a relatively small loss in volume, and after replenishment with sodium salts, they are returned to the digester for reuse.

The brown pulp (brown stock) from the digester is washed, screened, and passed through a battery of cleaners. If the pulp is to be bleached, it is "thickened" by removing excess water and sent through a series of bleach operations. These can vary widely in the type of chemicals used and their sequence. Bleached pulp is then ready for the paper making process.

Both softwood and hardwoods can be pulped by the Kraft process. Fibber recovery is largely a function of the wood species used, the time and temperature of cooking, the degree of bleaching,

and the paper strength required. Generally, Kraft pulp recoveries from softwoods are approximately 47 percent for unbleached pulp and 44 percent for bleached.4 Hardwood recoveries range from 50 to 52 percent for unbleached Kraft pulp to 50 percent for bleached^{9, 13}.

4.1 Wood Preparation:

Wood is delivered to the Kraft mill in one of two ways: whole logs and sawmill chips (residuals from sawmills). The logs have their bark removed, either by passing through a drum debarked or by being treated in a hydraulic debarked. The drum debarked, which consists of a slightly inclined, rotating drum is best suited to small diameter logs. The hydraulic debarked, which uses high pressure water jets, can handle large diameter logs. The removed bark is a good fuel, and is normally burnt in a boiler for generating steam. After debarking, the logs are chipped by multi knife chippers into suitable sized pieces, and are then screened to remove overlarge chips. The *thickness* of the chips is the most important parameter, as this determines the speed and the thoroughness of the impregnation of the cooking chemicals into the wood chip. Neither debarking nor chipping are usually necessary for sawmill chips.

4.2 Cooking:

The "cooking process" is where the main part of the delignification takes place. Here the chips are mixed with "white liquor" (a solution of sodium hydroxide and sodium sulphide), heated to increase the reaction rate and then disintegrated into fibres by 'blowing'-subjecting them to a sudden decrease in pressure. Typically some 150 kg of NaOH and 50 kg of Na₂S are required per tonne of dry wood. This process is, like any chemical reaction, affected by time, temperature and concentration of chemical reactants. Time and temperature can be traded off against each other to a certain extent, but to achieve reasonable cooking times it is necessary to have temperatures of about 150 - 165°C, so pressure cookers are used. However, if the temperature is too high then the chips are delignified unevenly, so a balance must be achieved.

The kinetics of the Kraft pulping is quite well understood, but the reaction is heterogeneous and therefore difficult to examine. To determine when to interrupt the cooking, a model relating time, temperature and cooking chemical charge is used. The degree of delignification is the most important parameter for determining pulp quality, and is normally expressed in what is called a "Kappa number". This number is directly related to the amount of lignin still remaining in the cooked pulp.

There are two different cooking systems; batch and continuous. In batch cooking, chips and white liquor are charged to a pressure vessel and are then heated with steam to a set temperature for

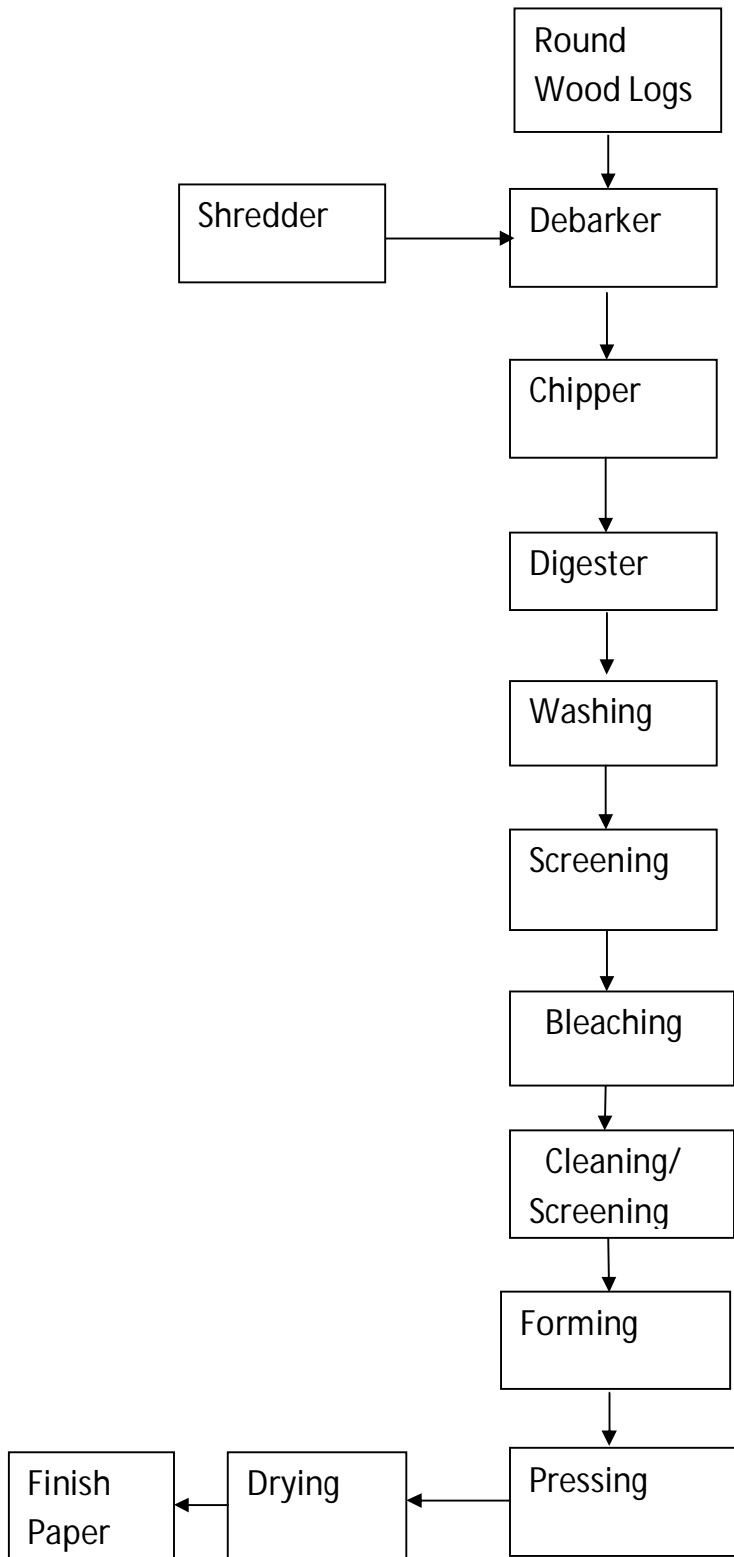
a set time. When the correct delignification has been achieved, the cook is "blown" (the pressure is suddenly released so that the cooked chips disintegrate into fibres). In the continuous process, chips and white liquor are fed continuously to the top of a tall pressure vessel. The chips move down the 'digester' by gravity (as a plug) to be finally blown from the bottom of the vessel. The cooking time cannot be varied in this case (it is set by the production rate) and only the temperature and the chemical charge can be controlled. Many developments have taken place during the last decade to improve the 'science' of Kraft pulping. The challenge has been to remove as much of the lignin as possible without degrading the cellulose and without losing too much yield. It is now well known that the concentrations of NaOH, Na₂S and dissolved lignin during the various phases of the delignification are of crucial importance for the pulp strength. Generally speaking, it is desirable to have a high sulphide concentration in the beginning of the cook, a low lignin concentration in the liquid phase towards the end of the cook, and an even alkali concentration during most parts of the cook. How to achieve this in practice under conditions of high temperature and high pressures has been a challenge, and much development is still going on.

4.3 Pulp Washing:

Because of the high amounts of chemicals used in the cooking wood in Kraft pulping, the recovery of the chemicals is of crucial importance. The process where the chemicals are separated from the cooked pulp is called pulp washing. A good removal of chemicals (inorganic and organic) is necessary for several reasons:

1. The dissolved chemicals interfere with the downstream processing of the pulp
2. The chemicals are expensive to replace
3. The chemicals (especially the dissolved lignin) are detrimental to the environment

There are many types of machinery used for pulp washing. Most of them rely on displacing the dissolved solids (inorganic and organic) in a pulp mat by hot water, but some use pressing to squeeze out the chemicals with the liquid. An old, but still common method is to use a drum, covered by a wire mesh, which rotates in a diluted suspension of the fibres. The fibres form a mat on the drum, and showers of hot water are then sprayed onto the fibre mat.



Flow diagram for pulp and paper manufacturing process 13

4.4 Pulp screening:

Apart from fibres, the cooked pulp also contains partially uncooked fibre bundles and knots. Modern cooking processes (together with good chip screening to achieve consistent chip thickness) have good control over the delignification and produce less "rejects". Knots and shives are removed by passing the pulp over pulp screens equipped with fine holes or slots.

4.5 Bleaching:

This process of bleaching (delignification and brightening) uses several chemicals and processes. number of processes and variants of existing processes that increase the efficiency of the process for removal of lignin or offer substitutes for bleaching with molecular chlorine have been implemented in the industry and have been reviewed. Pulp produced by the Kraft process is brown. This presents no problem for certain uses, e.g. for sack paper, most corrugated boxes, some bag paper etc. However, a major proportion of the Kraft pulp that is made is used for white or coloured papers such as writing and printing papers, and then the pulp needs to be bleached. Bleaching involves removing virtually all of the lignin that still remains after cooking, as the lignin contains the chromophoric groups which make the pulp dark. Strictly speaking, bleaching and cooking are both delignification processes, and modern developments have tended to blur the difference between the two processes. However, traditionally the name 'bleaching' is reserved for delignification that is taking place downstream of the cooking process. In practice, there are two separate "bleaching" process steps: oxygen delignification and final bleaching.

To measure the lignin content in pulp, a number called the "Kappa number" is used. The Kappa number is directly proportional to the lignin content of the pulp. Pulp from the digester has a Kappa number of 20-35 for softwood and 15-20 for hardwood (hardwood contains less lignin and can therefore be cooked to a lower Kappa number). Oxygen delignification removes about half of the lignin remaining after the cooking process, so that the Kappa number of the oxygen delignified pulp is typically 12-18 for softwood. The final bleaching removes all remaining lignin and decreases the Kappa number to zero^{22, 23}.

4.5.1 Oxygen Delignification:

In oxygen delignification, washed pulp is treated with a highly alkaline solution of sodium hydroxide. The high pH ionizes phenolic groups in the lignin, which are then attacked by molecular oxygen. The aromatic part of the lignin is partly destroyed and it is then depolymerised to lower molecular weight compounds. These are more soluble in water and can be removed from the fibres. It is important that the pulp has been at least partly washed beforehand because the black liquor

solids in unwashed pulp consume oxygen. After the oxygen delignification stage, the pulp has to be washed very well, as otherwise the organics carry over to the final bleaching process, consuming chemicals and there is also decreasing the environmental benefits.

The highly alkaline conditions of oxygen delignification also make carbohydrate fractions in the fibres react with oxygen to a certain extent. As these reactions break down the polymer chains of cellulose, and thus decrease the pulp strength, these reactions must be kept to a minimum. It has been found that it is the radical species of oxygen which are particularly harmful to the carbohydrates. The formation of radicals is promoted by the presence of certain metal ions. However, it has been found that magnesium salts inhibit metal ion activity, and magnesium sulphate is therefore normally added as a protector in oxygen delignification.

Oxygen is only sparingly soluble in water, and the controlling factor on the reaction rate is therefore normally the concentration of dissolved oxygen around the fibre. Originally a high pulp consistency (30-40%) was used to overcome this restriction. However, modern high intensity mixers can distribute the oxygen in very small bubbles on the fibres, and these mixers have made it possible to operate at "medium consistency" (10-12%). Medium consistency has several advantages: the equipment is simpler and the risk of fire (because of the use of oxygen) is virtually eliminated.

Oxygen delignification can significantly decrease the water pollution from the final (normally chlorine or chlorine dioxide based) bleaching. In addition, it is an effluent free process. All dissolved lignin and other organics (as well as the inorganic chemicals) are recovered in the black liquor and returned to the chemical recovery system, rather than being discharged as effluent as they are in chlorine-based bleaching. Finally, oxygen is a fairly cheap bleaching chemical, although the capital costs are high for an efficient system. On the negative side, the process has the potential to degrade the pulp strength if it is not controlled properly.

4.5.2 Final Bleaching:

The final bleaching is always carried out in several stages to improve the efficiency of the chemicals used, and to decrease the strength loss of the pulp. There are quite a number of bleaching chemicals used commercially, and many more have been tried in the laboratory.

The chemicals used are:

- Chlorine
- Chlorine dioxide
- Sodium hypochlorite
- Oxygen

- Peroxide
- Ozone

Of these chemicals, the first three contain chlorine atoms, whilst the last three use non-chlorine oxidizing compounds. Elemental chlorine (Cl_2) was for many years the work horse of the bleaching process. It is efficient in bleaching the pulp and (if properly used) does not degrade the pulp strength. However, it produces a large amount of chlorinated organic compounds in the effluent, and strenuous efforts have therefore been made to decrease its usage. For the same reason, the use of sodium hypochlorite (which also tended to affect the pulp strength) is now virtually eliminated. Modern bleach plants therefore use no *elemental* chlorine. They are what is called ECF plants: elemental chlorine free bleach plants. Chlorine dioxide, which is used instead (in addition to non-chlorine compounds), is environmentally much more benign than Cl_2 . However, while chlorine dioxide is good at preserving pulp strength, it is not as effective as elemental chlorine in delignification/bleaching. ECF plants therefore have to have a rather low incoming Kappa number, and this is normally achieved by using oxygen delignification ahead of the final bleaching.

Most ECF plants use a three step bleaching process of chlorine dioxide followed by a mixture of NaOH, O_2 and peroxide (the 'extraction' stage) and then finally chlorine dioxide again. At Kinleith, because of the efficiency of the oxygen delignification, the peroxide is no longer necessary and a sequence of chlorine dioxide then NaOH and O_2 followed by more chlorine dioxide is used. The chlorine dioxide stages normally run at a pH of 3- 4.5, and the 'extraction' stages at a pH of 10-11. The temperature is kept at 70-80 °C to achieve sufficiently fast rate of reaction.

The amount of chlorinated toxic compounds in the effluent from a correctly operated ECF plant is small (especially after secondary treatment) and the effects on the environment appear rather insignificant. However, especially in Europe, there is a perception that using "chlorine" in any form when bleaching is undesirable, and bleaching without using any form of chlorine compounds, so-called total chlorine free bleaching (TCF bleaching) has been developed. In TCF bleaching only oxygen, peroxide and ozone (in addition to caustic and certain chelating agents) are used. TCF bleached pulp can nowadays reach virtually the same brightness as ECF bleached pulp, but the strength is somewhat lower. Such plants require inevitably oxygen delignification and also, usually, cooking to a lower Kappa number. Chemical costs are also normally higher.

5. PAPER MAKING:

Paper making is the process whereby pulp fibres are mechanically and chemically treated, formed into a dilute suspension, spread over a mesh surface, the water removed by suction, and the

resulting pad of cellulose fibres pressed and dried to form paper. The mechanical treatment of the fibre normally takes place by passing it between moving steel bars which are attached to revolving metal discs - the so-called refiners. This treatment has two effects: it shortens the fibre (fibre cutting) and it fibrillates the fibre. The latter action increases the surface area, and as the fibres bond together in the paper sheet by hydrogen bonding, the increased surface area greatly increases the bonding and strength of the paper. Paper strength is dependent on the individual fibre strength and the strength of the bonds between the fibres. It is usually the latter, which is the limiting factor. Refining increases the inter fibre bonding at the expense of the individual fibre strength, but the net result will be an increase in paper strength. Pressing and calendaring (feeding through rollers) increase density and promote smoothness.

Various chemicals are added, e.g. to give water resistance, to give increased strength (see Industrial Resins article), to produce coloured paper, or to serve as inorganic filters.

Henry and Sealy Fourdrinier have given their name to the Fourdrinier paper machine, the first of which was first used in 1804. The stock is diluted to 0.5-1.0% consistency, and then flows as a flat stream onto an endless travelling wire screen. Water (containing a considerable amount of filter and fine material) is extracted through the wire screen, and this is then circulated back to dilute the oncoming stock. The wire and the web pass over suction boxes, and the web is finally removed from the wire at about 20% solids. After being pressed to some 35-40% solids, the web passes round a large number of steam heated cylinders to be dried until it finally contains some 95% solids and 5% water.

Modern developments have tended towards so-called twin-wire machines, which overcomes the difference in two-sidedness caused by water draining through the bottom side of the web only. The twin wires are nowadays usually synthetic fibre fabrics, between which the stock is introduced²⁵.

6. CONCLUSION:

With the help of the above mentioned analysis it can be concluded, that even though Paper Industry is one of the Core sector industries. The paper demand increases every day as a result of developed population and industrialization. The Kraft pulping process is very economical process in comparison to other pulping process as mentioned above. The quality of pulp from Kraft process is very strong.

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