CL 304 Report

On

Paper production: Resources, Reaction Scheme, Methods of Production

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Introduction

Paper has been defined as felted or matted sheets of fibre, that is often made of cellulosic material and created from a water suspension on a thin wire screen [1]. It is a versatile material that has served as a foundational element for packaging, communication, hygiene products, storage and much more. We find it being used as wrapping paper, tissue, paper, in books, for groundwood printing (newspaper, posters etc.), as well as paperboard [1].

Over the course of centuries, due to limited amount of resources paper has been made from a variety of materials such as wood, bamboo, jute, bagasse, straw, etc. Along with these materials, waste paper is also recycled and employed into paper production. The generation of paper happens after processing by pulp and paper mills. In order to produce paper, the bulky, fibrous material must break down into small, individual agglomerate fibres by following a process that is known as pulping.

With a paper making industry that is more than a century old, India has been the pioneer nation to utilise bamboo as a raw material for papermaking globally. The Indian paper industry happens to be the 15th largest in the world with a domestic market of about 16 million tonnes per annum. [4]

Raw Materials

When it comes to pulp production, the major chemical required is cellulose which can be extracted from various raw materials such as Softwoods (that include coniferous and non-coniferous woods); Grasses and Reeds (e.g. Panini, Lemon, Ulla, Siru, Munji, Sabai Grass, Bamboo, etc.); Straws that are based on rice, wheat, bagasse, barley, reeds, etc.; Cotton Linters; Hardwoods (such as Acacia, Lemon, Gum, Mysore gum, Eucalyptus, Pinus, Patula, Paper Mulberry and Rubber Plant Wood; Kenaf and Mesta [1].

Cellulosic raw materials have a lot of pre-requisites attached to them that need to be fulfilled such as: Having sufficient supply; Round the year availability to pulp mill; should not deteriorate in storage; Quality fibre with high yield; Paper conversion cost should be low; Capable of small area storage & easily transportable at low-cost; Competitive quality of paper; And must not have high priority use [1].

(lakh tons)

		Possible Production from Indigenous Raw Material					
Year	Demand	Forest	Bagasse	Straw	Waste Paper	Total	Gap Between Demand and Production
1990	24.58	12.34	1.80	2.00	2.15	18.29	6.29
1995	31.61	12.35	3.60	2.25	2.77	20.97	10.64
2000	41.12	12.35	6.00	2.50	4.75	25.60	15.52
2005	50.45	12.35	7.20	2.50	5.57	27.62	22.83
2010	62.97	12.35	8.40	2.50	8.29	31.54	31.43
2015	79.81	12.35	8.40	2.50	10.00	33.25	46.56

Source: "Kothari's Industrial Directory of India" (1994)

Table 1. Forecast of raw material requirement [1]

As is evident from the table, the production from raw materials met only 74.4% of the demand in 1990, whereas in 2015, this has been reduced to just 40.4% [1]. Meeting industry demands will require us to emphasise planned bamboo cultivation through large-scale farming, developing trees like Eucalyptus as high-yield tree crops, diversifying raw material usage by employing materials such as bagasse, betterment of waste recovery & recycling methods, and, researching into more efficient pulping methods.

Raw materials can be divided into the following two types:

Fibrous Raw Materials:

- Include paper pulp-groundwood, bleached and unbleached sulfite, and sulfate, semi-chemical pulps. The material of choice is determined by the intended applications, and mixing different pulps is frequently needed.
- 4-6 % of fibrous starting materials come from reused pulp-paper products, such as newspapers and paperboard, that are mixed with fresh pulp to make feedstock for paper mills.
- Some other materials include straw, linen, cotton, rags as well as inorganic fibres such as glass and asbestos

Non-Fibrous Raw Materials:

- A large variety of materials are needed for fillers, sizing, and coatings, making the paper industry a good customer of the chemical industry.
- Inorganic raw materials that are used include: clay, talc, titanium dioxide, zinc sulfide, calcium carbonate, calcium sulfate, barium sulfate, alum
- Organic raw materials required in the paper industry are: rosin, glue, casein, waxes, glycerol, dyestuffs

Energy Consumption

The paper industry is the 3rd highest consumer of electricity amongst high-energy consumption industries, accounting for 11% of the consumption [5]. The energy use in the paper industry is split about in half between papermaking and pulping. The consumption of energy in the industry constitutes as much as 15% of the total operating costs while the consumption of electricity per tonne of paper production in India is about 1,500-1,700 kWh [6]. Some of the factors that affect energy consumption in the Indian paper industry are low level of capacity utilisation, number & multiplicity of machinery, quality & type of paper produced, etc. When it comes to section wise divisions, Paper Machine Drives utilise 28%, Paper Finishing 19%, Ventilation System 10%, Short Circulation 23%, and, Vacuum System 20% [7].

Pulp

Pulp can be defined as the commercial form of cellulose that is derived from bamboo, bagasse, wood, etc., by mechanical or chemical methods [1].

It can be produced through various methods. Some of them are highlighted below:

- Groundwood Production- In this method, wood is debarked and shredded mechanically to form fibres that are suited for newsprint, toiletries production, and, low-cost paperbacks where strength and eased bleaching are unimportant.
- Chemical Production- Here, the cellulose from wood is made lignin-free and free of non-cellulose ingredients by action of chemical reagents. The 2 major processes under this method are sulfate (Kraft) and sulfite. This pulp can be bleached to near white/white but has only half the yield of the mechanical process (40-45%). The pulp can be used for paper of high strength and fine texture.
- Semichemical- In this method, the wood chips are mildly treated with a dilute chemical mixture of sulfate, sulfite, caustic soda, and soda ash. This leads to softened chips that are then fibrillated mechanically without excess power usage. The yield through this process is between 65-90%. The increased chemical treatment produces a better grade of fibre but reduces the yield.

With time, pulp manufacturing has grown into a separate industry and is now used by sectors other than the paper industry. Additionally, the pulp business provides refined cellulose for plastics, rayon, and explosives. The management and application of the industry's waste products have drawn a lot of interest. In addition to providing a partial answer to the industry's main issue—preventing stream pollution—the production of valuable products from lignin and waste liquors also increases revenue for the sector [2].

Kraft Process

5.1 Introduction

The Kraft process (kraft being German for strength), also known as the Sulfate process, was invented as a result of a series of basic experiments conducted by Carl F. Dahl in 1879, at Danzig, Prussia (Modern-Day Poland) [2].

It is the most dominant industrial process for converting cellulosic raw materials into wood pulp. It is an alkaline process that involves the treatment of wood chips with a hot mixture of water, sodium hydroxide (NaOH), and sodium sulfide (Na_2S), known as white liquor, that breaks the bonds that link lignin, hemicellulose, and cellulose. Since Na_2SO_4 is also added to white liquor, this process is also called the Sulfate process. The presence of sodium sulfide makes the bleaching of pulp easier and the paper produced has better strength. The process entails several steps, both mechanical and chemical, that we will discuss further.

5.2 Reaction Mechanism

The following chemical reactions take part in this process:

- Digestion- The hydrolysis and solubilisation of lignin occur here
  R-R' + NaOH → R"COONa + ROH
  R-R' + Na_2S → Mercaptans
- Recovery of chemicals from black liquor (wood digestion liquor)
  i) Smelting Furnace
  2NaR (lignin salt) + Air → Na_2CO_3 + CO_2
  Na_2SO_4 + 2C (from R) → Na_2S + $2CO_2$
  ii) Causticizing
  Na_2CO_3 (aq) + $Ca(OH)_2$ (s) → 2NaOH (aq) + $CaCO_3$ (s)
  $CaCO_3$ → CaO + CO_2
  CaO + H_2O → $Ca(OH)_2$

5.3 Process Description

Production of pulp through the Kraft Process can be largely divided into 5 major steps:

1. Digestion of wood-based materials: The wood chips flow past circumferential screen plates while cooking liquor is circulated through heat exchangers for reheating and digestion temperature control. Digestion time & temperature are adjusted for maximum lignin removal with minimum cellulose hydrolysis. Digested chips are cooled at the base by injection of black liquor, to avoid mechanical weakening of fibres.
2. Modified process for bagasse: The fibrous portion of bagasse happens to be much more difficult to break up by use of mechanical action. Therefore, the exposure to strong mechanical shredding-grinding action reduces pith to a fine powder. The preferred process for this is wet grinding in a hammer mill, with the pith being washed by water through the screens.
3. Bleaching of pulp: Earlier, chlorine bleaching used to be employed but it ended up producing dioxins & other undesirable components, therefore, Hydrogen Peroxide is now employed instead along with NaOH as an activator and Sodium Silicate as a stabiliser.
4. Finishing operations of pulp: For long-distance pulp shipping, dewatering becomes crucial. This is achieved through processes like Hydraulic Pressing (Here, the pulp is pressed at 200-300 atm to form wet lap sheets that can be further dried), Vacuum Flash Drying (Pulp is mechanically dewatered and then dried to produce a dry fluffy material that can be baled), and Extrusion (Pulp is pushed through cylindrical die to create easily handled noodles with 30-40% solids for short distances and 90% solids for longer distances).
5. Recovery of chemicals: Black liquor contains 98-99% of the digestion chemicals and hence these chemicals need to be recovered to avoid environmental problems and also to improve the process economy. The black liquor is sent through evaporative stages and a recovery boiler to increase solid content from 15-18% to 60%. Once it is ensured that it can sustain smelting, it is heated to recover the remaining chemicals. The slag formed is contacted with cold water to yield green liquor. The insoluble impurities get settled and the clear liquor is causticized by adding lime. The filtration removes $CaCO_3$ sludge while white liquor is recycled.

5.4 Process Flowsheet

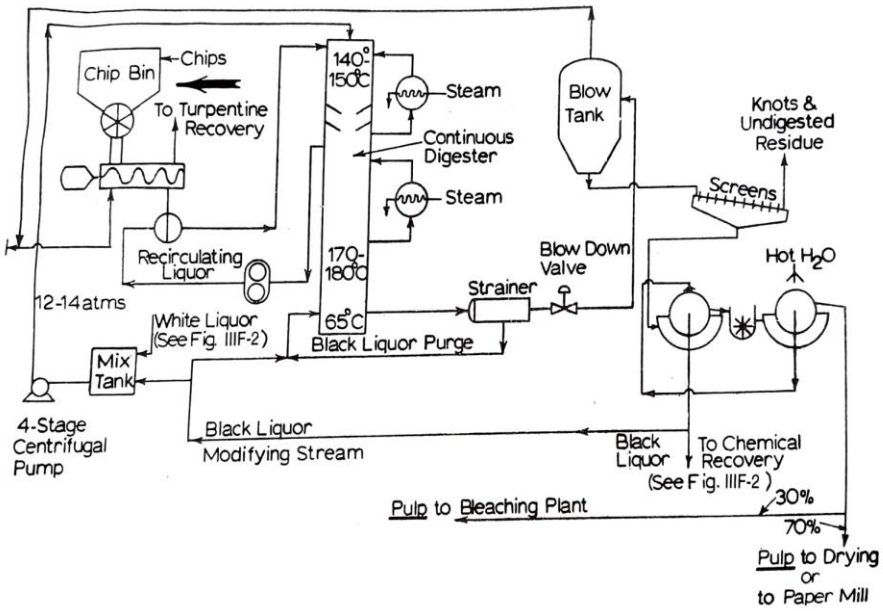

Fig. 1. Preparation of wood pulp by Kraft Process [1]

5.5 Comparison with Sulfite Process

Characteristic	Sulfate Pulp	Sulfite Pulp
Trade Name	Kraft	Sulfite/Magnifite/Neutral Sulfate
Fibrous Raw Material	All types	Bamboo, hardwoods preffered
Chemical Reagents	60% NaOH, 25% Na2S , 15% Na_2CO_3 in 10-15% aqueous solution	All use SO3 Magnifite: Mg(HSO3)2 + Free SO2 in acid Neutral sulfite: Na2SO3, Na2CO3, NaHCO3 Acid Sulfite: NaHSO3, Na2SO3
Digestor Conditions	Time: 2-5 hrs. Wood Base, 5-6 min. Bagasse Temperature: 170-180 °C Pressure: 10 atms	Time: 6-10 hrs Wood, 20-40 min. bagasse Temperature: 120-150 °C Pressure: 4-6 atms
Pulp Type	Brown Colour; ClO2 needed as end bleach; Unbleached fibres very strong	Dull white colour; easy to bleach; weaker fibres
Products Formed	Strong brown bags, brown paper, paperboard boxes, strong white paper (bleached)	White grades, book paper, sanitary tissues

Table 2. Comparison of chemical pulping processes for cellulose fibres [1]

Paper Production

6.1 Preparation of Fibre Suspension

The pulps are converted to slurries with 0.5-0.75% fibre content by mechanical disintegration through methods like beating and refining that consist of rotating drums with knife attachments or rotating discs. We add fillers to increase brightness, bulk, flexibility, opacity, softness, and weight of finished paper. An important ingredient added to reduce water/liquid penetration is sizing. Also, colouring is done through agents like organic dyestuffs as well as by water-insoluble pigments.

6.2 Formation of Paper

- Forming a Wet Web: The 99.5% water-fibre slurry is run evenly through a gravity-assisted moving wire belt at 50-500 m/min that also has a side-wise shaking motion for improved interlocking of fibres. The water collected (white water) is reused for maximum recovery and efficiency.
- Pressing the Wet Sheet: Water is reduced from 80% to 60-65% by rolling it through the press section using mild pressure. Bond or Watermark, if needed is formed on the sheets during this method.
- Drying the sheet: The sheet is passed through smoothing rolls and a series of steam-heated cylinders, where heat & moisture get transferred to a canvas belt. The sheet leaves with 5-6% moisture content and is then passed through a series of pressure/calendering rolls to produce well-finished paper.

All 3 of these steps are achieved together in an extremely complex machine known as the Fourdrinier Machine with a capacity as high as 400-500 tons per day [1].

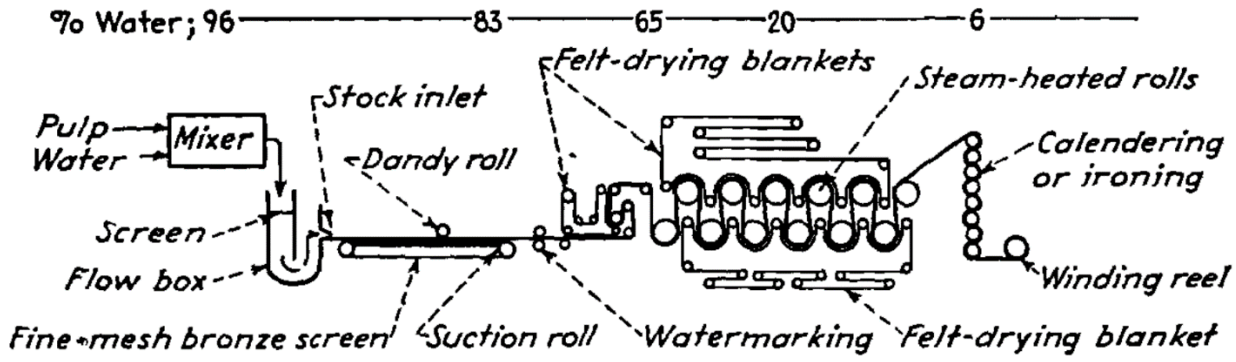

Fig. 2. Fourdrinier Machine [2]

6.3 Flowsheet

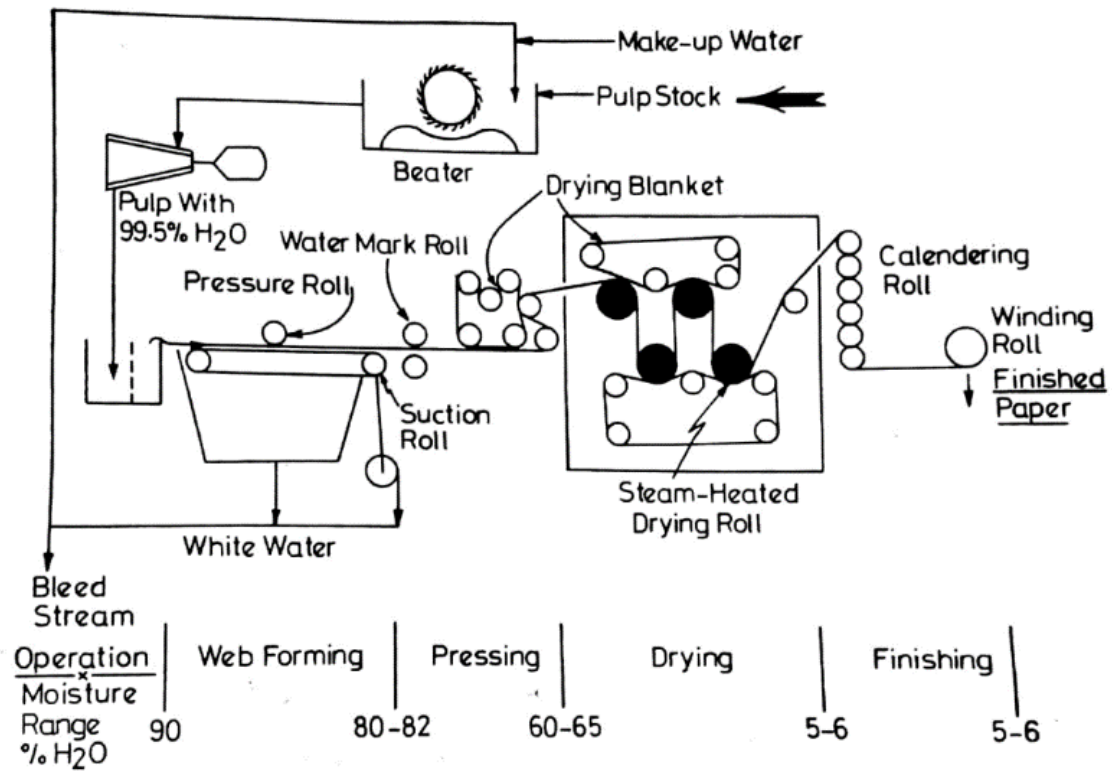

Fig. 3. Schematic drawing of a paper-making process [1]

Waste Paper and Recycling

7.1 Introduction

Globally, the use of paper and paperboard leads to more than 100 million tons (Mt) of paper waste every year. Therefore, it is essential that we utilise this waste paper by recycling it and integrating it as a raw material in existing paper and pulp production plants.

Waste paper recycling follows the following pathway [3]:

- Waste Paper: Initially the waste paper is collected and then it needs to be sorted according to its physical properties as each paper product needs to be processed separately.
- Pulping: Sorted paper is baled and sent to mills where it is shredded down and mixed with large amounts of water to form a mushy slurry called pulp.
- De-inking: This process is performed to remove dyes and inks from the paper.
- Cleaning: In this process, large contaminants such as staples, and tape are screened & removed.
- Refining: In this step, we add bleaching reagents (H_2O_2 + NaOH + Na_2SiO_3), to whiten the paper.
- Recycled Paper: Finally, we get recycled paper that can be recirculated into the consumer market.

7.2 De-inking

De-inking is a combination of various chemical & mechanical operations that removes ink from paper.

- One method is Flotation De-inking which is useful for particles larger than 10 μm. It is the most common method used in Europe for manufacturing recycled paper. The temperature range for the process is 45-55 °C. Compressed air is blown into the suspension, where the collector which has an affinity for both ink and air, attaches them together and causes them to froth & float to the surface where they are removed.
- Another method is where waste paper is sorted, dusted, shredded, and finally cooked in a digester. The digester that is used contains a mild cooking liquor (8% solution of NaOH) and cooks the pulp for around 10 hr. The digester temperature is around 200°F. The cooking process serves to break up the ink which is then washed out alongside dirt by making it go through a series of screen washers [2].

Economics of Paper Production

a) Shortage of fibrous raw materials: Due to the fast depletion of forest resources, a long-term vision is required for developing improved bamboo harvesting, utilising bagasse & eucalyptus, and effective waste reuse.
b) High Prices & Shortage of Chemicals: Improved recovery methods are required since there is a dearth of chemicals, such as Sulfur, Salt cake & Chlorine, that correspond to high prices in India.
c) Procurement of Plant and Equipment: Pulping equipment is relatively simple to procure/build, but when it comes to paper-making machinery, it is quite complex and expensive, leading to low indigenous manufacturing capability.

Conclusion

To sum up, the paper and pulp industries are vital to modern society since they produce materials needed for everyday consumption such as packing, communication, hygienic products, and many others. Paper manufacturing has a centuries-long history and has progressed from manual labour to highly automated industrial operations that employ complex machines. To meet global demand, the sector uses a wide variety of raw materials, such as wood, bamboo, bagasse, and waste paper.

The industry does, however, confront several difficulties, including the depletion of resources, energy use, and environmental effects. Therefore, recycling procedures must be used if trash is to be reduced and resources are to be preserved.

The pulping industry's main process is the Kraft process, an efficient method that reduces environmental impact and maximises raw material utilisation through chemical recovery. Through the adoption of sustainable practices, allocation of resources towards research and development, and promotion of collaboration throughout the supply chain, the industry may play a role in creating a more sustainable future for future generations.

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