2 – Pulp and Paper Industry

1. The Pulp and Paper Industrial History

In the 1800s, there was a shift away from using cotton rags to make paper. Instead, industrialisation helped wood become the most important source of fibre. The switch from a scarce fibre supply to a plentiful one opened up a vast, renewable, low cost source of fibre raw material, making large-scale paper production possible. Since that time, first mechanical and then chemical methods have been developed to produce pulp from wood.

The pulp and paper industry converts wood or recycled fibre into pulp and primary forms of paper. *Pulp mills* separate the fibres of wood or from other materials, such as rags, linters, wastepaper, and straw in order to create pulp. *Paper mills* primarily are engaged in manufacturing paper from wood pulp and other fibre pulp, and may also manufacture converted paper products. Other companies in the paper and allied products industry use the products of the pulp and paper industry to manufacture specialised products including paper board boxes, writing paper, and sanitary paper.

The Sources

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Profile of the Pulp and Paper Industry. EPA Office of Compliance Sector Notebook Project, 1995.

See also *Case Study 5* on Pulp and Paper Production.

The manufacture of wood pulp is the single most important method for chemically converting wood into useful products, and as such is a highly important component of the global manufacturing industry in both economic and environmental terms. In certain regions, pulp and paper manufacture is a dominant industry and is responsible for a large portion of regional economic activity.

At the same time, pulp and paper manufacture can have potentially serious impacts on environmental quality and hence the health of both human and wider ecosystems.

Environmental Concerns

The presence of resin acids and other unidentified constituents continue to present toxicity problems for all kraft mills, regardless of bleaching chemicals. Ecosystems close to pulp mills which meet relatively tough existing environmental regulations continue to experience significantly reduced diversity in the plants and animals able to live near them. These facts emphasise the need to pursue closed loop strategies.

Additionally, the effects of mill process changes on workers and local communities have rarely been factored into the mainstream debate on best routes forward. Exposure to bleaching chemicals, process gasses, emissions from water treatment ponds, and bacteria and fungi on wood chips and sludge all directly impact the health and safety of the people working in the mill and the people who live near by. Decisions on how to make an ecologically responsible pulp mill must take these issues into account.

For mass-balance, environmental impact evaluation and cleaner production measures identification, the production process (in a life-cycle perspective) can be divided into 7 subprocesses:

1. Raw materials processes.
2. Wood-yard.
3. Fibre line.
4. Chemical recovery.
5. Bleaching.
6. Paper production.
7. Products and recycling.

2. Main Process Technologies

Pulp Production

The objective of the paper production technology is to separate cellulose fibres from the wood structure. The free fibres in the pulp are then the main raw material for paper production. Pulping processes can be of different types that determine what chemicals and amounts of water and energy used in the processes and, consequently, the environmental impacts of production.

Possible types of pulp production are Kraft (68%), mechanical (22%), semi-chemical (4%), sulphite (4%) and dissolving (2%).

Mechanical pulping is a process that uses mechanical force to separate fibres from the wood structure. *Ground wood pulping* was the first type of mechanical pulping process developed in Germany in the 1840s. In this process, wood is mechanically ground against large sandstone cylinders. The pulp is then screened to remove large pieces such as knots, etc. Next, the pulp is washed and bleached for use in paper making. One of the main things to note here is that this kind of pulp still contains lignin (essentially the glue that holds the cellulose fibres together), which means that its strength and brightness are low compared to pulp made from other processes. On the other hand the pulp yield is about 90% (defined as the amount of wood fibres produced per amount of wood raw material used).

Refiner mechanical pulping was introduced in the 1960s. In this process, wood chips pass between disks rotating in reverse directions to separate the fibres. The most common refiner pulping methods are Thermo-mechanical pulping (TMP) and Chemo-thermo-mechanical pulping (CTMP). In these processes, the wood is chopped into chips and then preheated with steam to about 120°C before mechanical force is applied in a disc refiner. In the CTMP process the wood chips are impregnated with sodium sulphite (Na_2SO_3). CTMP produces a pulp that is stronger and somewhat more light-coloured than TMP pulp. Thermo-mechanical pulp is mainly used in the production of newsprint as it is relatively cheap to produce and delivers adequate strength for this end-use. CTMP gives a pulp that has many usage areas, e.g. printing and writing paper and tissue paper.

Chemical pulping, as its name suggests, uses chemical rather than mechanical means of separating the cellulose fibres from each other by removing the lignin, leaving behind the fibre used in paper making. Here, the wood chips are "cooked" in a chemical solution, which dissolves lignin and other impurities.

Since chemical pulping removes lignin and other impurities, it produces a strong, bright pulp that is suited for the production of grades that require these properties, such as fine writing paper.

The first type of chemical pulping developed was *soda pulping*. This process used caustic soda as the chemical solution and was developed in England in the 1850s.

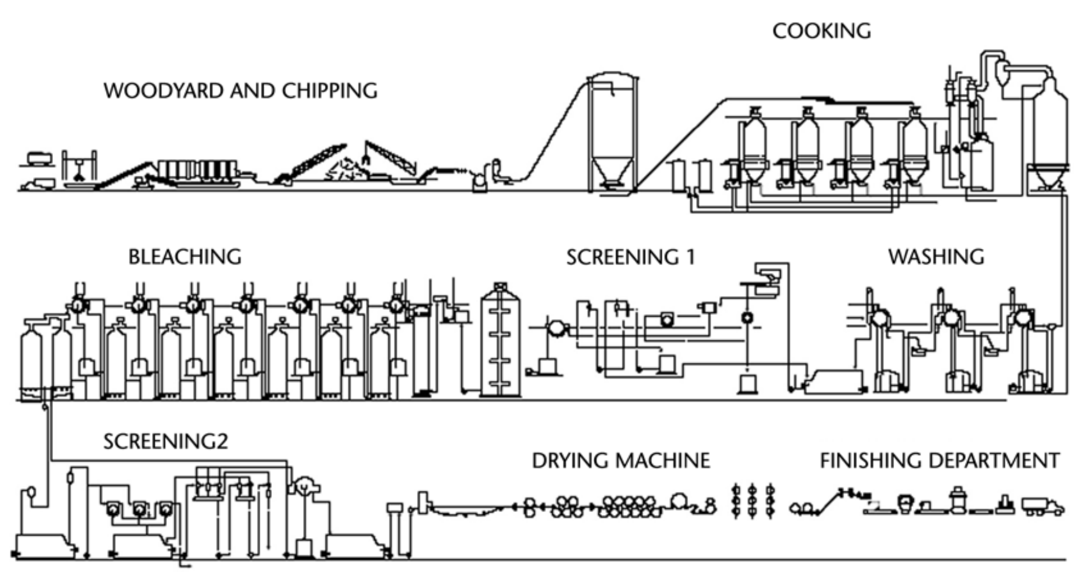

Figure 2.1 *Simplified flow diagram of an integrated pulp and paper mill (chemical pulping, bleaching and paper production) [EPA, 1995].*

A few years later in 1867, *sulphite pulping* was introduced. This process uses calcium, sodium, magnesium or ammonia salts of sulphurous acid as the chemical solution for dissolving lignin.

Sulphate or Kraft Pulping

Sulphate or Kraft pulping was invented in Germany in 1884 and remains the dominating technology today. It produces pulp with much higher strength compared to sulphite pulping. Note that "kraft" means strong in several European languages, including German and Swedish and both Germany and Sweden have long paper industry traditions. Kraft pulping can also use a wider variety of wood species than the sulphite pulping process as it is more effective at removing impurities like resins.

In the kraft pulping process, wood chips are "cooked" in a digester in a solution of sodium hydroxide and sodium sulphide called white liquor. In Kraft pulping the pulp yield is less than 50%.

A bonus of Kraft pulping is that the chemicals can be recycled and re-used in the mill. Another is that kraft fibre is exceptionally strong.

The fact that kraft pulping is the dominant pulping process in the world is the reason why we concentrate on this type of pulping when describing sub-processes within the industry.

Sulphate pulping starts in the *wood yard*: bark and dirt is removed from the wood logs (dry or wet *debarking*), reduced to chip fragments in chippers (*chipping*) and screened for separating fines and oversize chips (*screening*). During *digestion* chips are cooked in a chemical solution called *white liquor*. Batch digesters were developed first and this concept was further developed to create a continuous digester process. Both batch and continuous digesters are used in modern mills today.

In the batch process, the chips are cooked in the white liquor in a digester for several hours under pressure and at high temperature. Following the cooking stage, the chips are then blown into a blow pit which helps to break apart the fibre bundles.

In the continuous process, the chips are first steamed before being continuously fed into the top of the digester. The chips are impregnated with white liquor and cooked as they move downwards through each stage of the digester. The brown stock *washing* is done in several countercurrent stages in the lower half of the digester. The filtrate from this washing is called *black liquor* which is sent to the chemical recovery system. Then knots, bark, shives and other contaminants are removed from the pulp by *screening*. Before the pulp is sent to the bleaching stage (where required), an *oxygen delignification* stage usually is included as the final stage of the cooking section of the process. This process involves treating the pulp with oxygen to further oxidise and dissolve the remaining lignin in the pulp. It is designed to lower the "*kappa number*" of the pulp, which is a measure of its remaining lignin concentration. After the digester a typical coniferous pulp has a kappa number of between 20 and 30, which has a rather dark brown colour. The oxygen delignification stage reduces the kappa number to 10-12. During further *oxygen delignification* approximately half of the remaining lignin can be removed.

Bleaching

Bleaching is needed to remove colour associated with remaining residual lignin. Bleached kraft pulp is mainly used for printing and writing grades, while unbleached kraft pulp is used in the production of packaging grades. The three general approaches to bleaching are:

1. Elemental Chlorine Bleaching.
2. Elemental Chlorine Free Bleaching (ECF).
3. Totally Chlorine Free (TCF) bleaching.

The bleaching chemicals are *injected* into the pulp and the mixture is *washed* with water. This process is repeated several times and generates large volumes of liquid waste. Additionally, vents from the bleaching tanks emit hazardous air pollutants including chloroform, methanol, formaldehyde, and methyl-ethyl-ketone.

Depending on the bleaching chemicals used, the wastewater streams from the bleaching process may contain chlorine compounds and organics. The mixture of chemicals may result in the formation of a number of toxic chemicals (such as dioxins, furans and chlorinated organics). Although this effluent is generally released to a wastewater treatment plant, the chemicals named above simply "pass through" the plant (i.e. the treatment plant does not significantly reduce the concentrations of these pollutants) and accumulate in the rivers, lakes and oceans to which the treatment plant discharges.

Commonly used bleaching chemicals are elemental chlorine (C), sodium hypochlorite (H), chlorine dioxide (D), oxygen (O), ozone (Z) and hydrogen peroxide (P). In ozone and hydrogen peroxide bleaching it is necessary to stabilise the bleaching chemicals by removing metals from the pulp with a complexing agent (Q) such EDTA or DTPA. The E extraction stage uses sodium hydroxide to extract water insoluble chlorinated lignin and other coloured compounds from the pulp.

The bleaching process generally consists of a series of stages utilising alternating acidic and alkaline bleaching agents. Figure 2.2 shows some examples of typical bleaching sequences.

The Process Flowsheet

The process flowsheet of the kraft process is designed to recover the cooking chemicals and heat. In the recovery line, spent cooking liquor and the pulp wash water are combined to form a weak black liquor which is concentrated through *evaporation* from 16% to 60-80% solids in a multiple-effect evaporator system. The strong black liquor is then incinerated in a *recovery boiler*. Combustion of the organics dissolved in the black liquor provides heat for generating process steam. The carbon dioxide formed in the combustion reacts with part of the sodium in the black liquor to sodium carbonate (Na_2CO_3) and the sulphur content is converted to sodium sulphate (Na_2SO_4). The sulphate is converted to sodium sulphide (Na_2S) by reduction with carbon present in the melted slag at the bottom of the furnace.

The smelt is dissolved in water to form *green liquor*, which is transferred to a causticizing tank where quicklime (calcium oxide) is added to precipitate the carbonate content in the green liquor as calcium carbonate and instead produce the sodium hydroxide needed to convert the solution back to white liquor for return to the digester system. The precipitate from the causticizing tank is calcined in a lime kiln to regenerate quicklime.

Production of paper starts with *stock preparation* where various grades of pulp are mixed in a *mixing chest* to obtain the desired properties, *refined* to increase the strength of the paper, *screened* and *cleaned*. After that, different dyes, defoamers, fillers and retention agents are added (*filling*) and the consistency is adjusted with the addition of water ("white water") before the pulp suspension enters the head box of the paper machine.

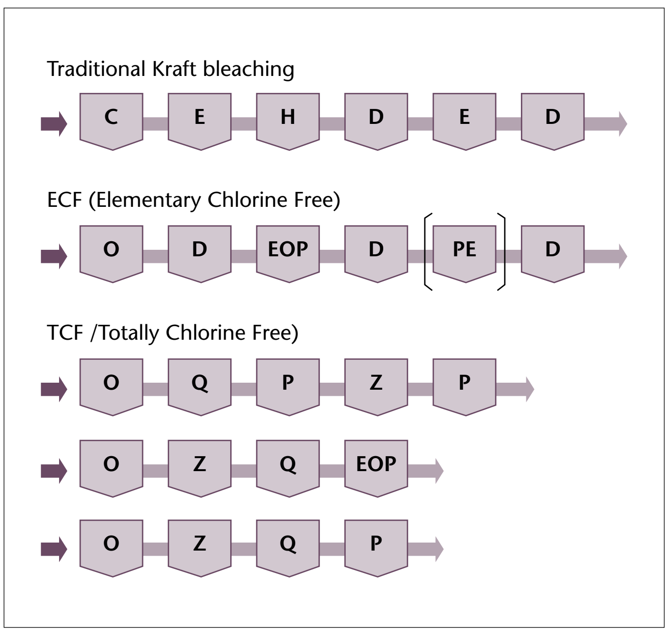

Figure 2.2 *Examples of bleaching sequences [adapted from Miljö-info från Skogsindustrierna, 1995].*

In the paper machine the fibre suspension is introduced to the wire net, where water is drained assisted with rolls, foils, and vacuum boxes (*dewatering*). It is further dewatered by *pressing* (up to a solid content of around 50%), and *drying* (to about 95% solids content).

Examples of *finishing operations* are sizing, coating, dyeing, and calendering. It includes not only the processes that take place at the factory itself, but also those of raw materials and products, such as transportation and final disposal. This life-cycle approach can be useful to define cleaner production measures as they can probably involve product modification or raw materials substitution.

3. The Most Important Cleaner Production Measures

The following CP measures are the most important in pulp and paper industry:

- *Chlorine-free production* – decreasing wastewater and air emissions toxicity. Almost without exception, the literature indicates that oxygen based bleaching sequences have also a superior efficiency over chlorine dioxide based sequences in this area. Even when combined with potential increased energy consumption in some oxygen based configurations, these mill designs are the most energy efficient available. Oxygen based kraft pulp show no appreciable shortcomings in quality relative to chlorine dioxide bleached products whereas oxygen based bleaching chemicals present the least immediate and long term hazards for workers and the general public.
- *Co-production* – recovering by-products from main production residue (decreasing solid wastes and wastewater amount and decreasing recourse consumption by creating a type of industrial symbiosis).
- *Closed loop operations* – decreasing discharges and saving water and resource consumption.
- *Chemicals recovery* – decreasing recourse consumption, wastewater amount and accident risks connected with chemicals transportation.
- Increasing the amount of *product recycling after use* (decreasing recourse and energy consumption and solid wastes to landfill).
- *Effective waste management* – segregating waste streams, waste separation prior to disposal for further recycling;

increasing recycled wastes within a company (chips, pulp, paper); producing energy from wastes; training employees in hazardous waste regulations.

- *Reduction of water consumption* – monitoring and analysing water consumption; reducing or elimination freshwater use where possible (wood-yard, brown stock washing, screening, causticizing system); replacing pump seals with mechanical seals; choosing less water-demanding process types (e.g. dry debarking).
- *Energy conservation* – choosing less energy-demanding process types (e.g. dry debarking); generating company's own power (e.g. from wastes or steam); improving the efficiency of high energy consumption equipment; steam meters provision; using "clean" fuels.
- *Effective wastewater treatment* – avoiding excessive treatment chemicals; conducting chemical analyses; comparing analytical results with compliance levels on a daily basis; recycling a part of the treated effluent back into the process.
- *Equipment maintenance* – effective belts for drainage, filtration, pressing etc.; design for decreasing discharges.
- *Effective air pollution prevention* – removing hazardous substances from the air by effective gas collection and gas treatment systems.
- *Increasing processes efficiency* – choosing more effective process types (e.g. kraft pulping instead of soda pulping).
- *Safe product and raw material handling and storage* – training employees to keep accurate records of chemicals used; keeping minimum supply of chemicals needed; labelling areas with keeping hazardous substances.
- *Reducing employees' hazards* – eye protection and noise reduction measures; spill collection systems; training employees on safety handling spills and spill reporting.

Thus, an *ideal paper mill* from cleaner production point of view is a chlorine-free and zero-discharge one, with minimised quantity and toxicity of air pollution and solid wastes. It is seen that closed loops represent the most effective approach to save both energy and resource consumption and at the same way to decrease all kind of wastes production. Such an approach is developed in the form of paper recycling, different types of substances reuse during production processes, co-production and chemicals recovery; nonetheless, it still provides opportunities to improve the processes. *Future research* can develop more sustainable reuse options for kraft pulping solid wastes, as well as pulping methods that result in purified by-products that can serve as feedstock for other manufacturing processes.

4. The Raw Materials

Wood

Raw materials for the pulp and paper production processes start with the forestry or chemical industry, which is followed by transport to the place of use and storage.

Important cleaner production measures include:

- Maintaining *moisture content* of the raw materials constant all year around.
- Keeping *chemical inventory to a minimum* (only as much as needed for current production) and buying small containers of infrequently used materials.
- *Labelling* storage area for hazardous substances.
- Providing *spill containment and collection systems* during storage.
- *Genetically modifying* forest trees.

Pulp and paper industries exploit biological raw materials, which are synthesised, modified and degraded in nature by microbes using a vast array of specific enzymes. Even though the pulp and paper industries have traditionally relied on mechanical and chemical processes, the potential for biotechnology is significant. Today, there is an increasing interest in biotechnology in order to develop environmentally compatible processes, to lower the energy consumption in mechanical pulping procedures and to develop new tools for improving the quality and the performance of the products.

Lignin is the main wood component that must be effectively removed from the pulp in order to guarantee high brightness of the subsequent paper products. The biochemistry and molecular biology of lignin biosynthesis are currently well understood, so it has been possible to use genetic engineering to modify lignin content and/or composition in poplars.

For example, suppression of the final enzyme in the biosynthesis of lignin monomers results in lignin with altered structure. Suppression of an enzyme involved in syringyl (S) lignin synthesis, results in dramatic reduction in S lignin content.

Kraft pulping of the transgenic tree trunks showed that these genetic modifications had improved characteristics, allowing easier delignification, using smaller amount of chemicals, while yielding more high-quality pulp.

Owing to the genetic modification savings in energy and pollutant chemicals were also achieved, thus leading to an environmentally more sustainable process.

The Wood-yard

Raw materials for the pulp and paper production processes start with the forestry or chemical industry, which is followed by transport to the place of use and storage.

Important cleaner production measures include:

- Maintaining *moisture content* of the raw materials constant all year around.
- Keeping *chemical inventory to a minimum* (only as much as needed for current production) and buying small containers of infrequently used materials.
- *Labelling* storage area for hazardous substances.
- Providing *spill containment and collection systems* during storage.

Wood-yard process includes debarking, slashing, chipping of wood logs and then screening of wood chips/secondary fibres (some pulp mills purchase chips and skip this step). The process is designed to supply a homogenous pulping feedstock.

The bark is usually either stripped mechanically or hydraulically with high powered water jets in order to prevent contamination of pulping operations. Hydraulic debarking methods may require a drying step before burning the bark. Usually, hydraulically removed bark is collected in a water flume, dewatered, and pressed before burning. Treatment of wastewater from this process is difficult and costly, whereas in dry debarking methods the removed bark can be channelled directly into a furnace.

Wet debarking produces 3-20 m³ wastewater/t processed material containing 15-50 kg suspended solids/t and 5-10 kg BOD_5/t and consumes about 20 kWh energy/t. Dry debarking will give 0-5 m³ wastewater/t processed material containing 0-10 kg suspended solids/t and 0-3 kg BOD_5/t and consumes about 20 kWh energy/t.

Important cleaner production measures include:

- Pulp *mills integrated with lumbering facilities*: acceptable lumber wood is removed during debarking; residual or waste wood from lumber processing is returned to the chipping process; in-house lumbering rejects can be a significant source of wood furnish.
- *Avoiding hydraulic debarking* – saving energy and water consumption, reducing wastewater amount.
- *Reusing leachate water*.
- *Co-production from bark*: mulch, ground cover, charcoal.
- *Burning bark* from debarking and small chips from chipping for energy production (depends on the moisture content).

Chemicals Recovery

Chemical recovery serves several important functions in a modern pulp mill: it removes water from the weak black liquor in evaporators and concentrators to enable incineration of the black liquor; it selectively removes organic contaminants from the water to allow for reuse in the pulp mill; it incinerates the concentrated black liquor in the recovery boiler; it recovers heat from the incineration process for steam generation and it dissolves the produced chemicals in water for future processing for pulping liquor generation.

Kraft pulping is a closed loop process in which the chemicals used to make pulp are recycled and reused in a digester. The recovery boiler is crucial to the process. It serves three critical functions in this process. Firstly it makes use of chemical energy in the organic portion of the liquor, to generate steam for the mill, secondly, it plays a major part in the sulphate process as a chemical reactor, and thirdly it destroys the dissolved organic matter and thus eliminates an environmental discharge. The black liquor recovery boiler functions as both a steam boiler and chemical reactor. It generates steam from the energy liberated during combustion of the organic constituents of black liquor, while chemicals from pulp digesting, such as sulphur and sodium, are recovered as smelt.

Important cleaner production measures include:

- Use of *new technologies* (Combined Heat and Power generation (CHP), heat transfer, heat exchange).
- Improvements of the *technical parameters of the recovery boiler* or furnace (geometrical shape etc.).
- *Use of light gas strippers and gas separation systems* which will remove hazardous and foul smelling pollution from the air and increase work place safety.
- *Deaerator tanks ahead of the boilers* to help reduce the intake of freshwater.
- Air emissions control devices.
- Providing *spill containment and collection systems*.

Use of Recycled Paper

After the production stage the product is transported to the place of distribution and use; after use it becomes either solid waste (and disposed to landfill or burnt) or can be considered as secondary resource for production.

Important cleaner production measures include:

- *Increasing recycling rates.* Recycling reduces energy consumption, decreases combustion and landfill emissions, and decreases the amount of carbon dioxide in the atmosphere. When paper products are reduced or recycled, trees that would otherwise be harvested are left standing. These living trees absorb carbon dioxide, a greenhouse gas. This process also saves money since recycling fibre is cheaper than harvesting and processing virgin fibre.
- Possibility for *easy packaging recycling*.
- Using *"green" fuel for transportation*.

Almost any kind of paper (newspaper, cardboard, packaging, postal mail, wrapping paper, catalogues) can be recycled. The use of recovered paper for new paper production substitutes the wood fibre and extends the life cycle. This is described as “the urban forest” as opposed to “the natural forest”. The wood fibre, depending on quality can be reused four to six times in process of forming new paper. The recycling of paper is a perfect example of the paper industry’s sustainable use of resources.

The Recycling Process

In Europe an average of 56% of used paper is recovered. The recycling process includes following stages:

Sorting: not all paper can be recovered. There are paper products that cannot be either collected or recycled. The portion of such paper products, which consist, for example, of cigarette papers, wallpaper, tissue papers and archives, is estimated to be about 19% of the total paper consumption. Sorting is the first stage of conversion of waste paper into the new one. Waste paper is divided into categories (newsprint, computer paper, magazines). The part that is suitable is shipped to further processing.

Dissolving: in this stage of paper recovery stickies and dioxins are eliminated. Paper is soaked and broken in giant washers and treated with chemicals. Stickers – sticky contaminants such as tapes or plastics covers – reduce paper quality and cause paper machines downtime. To eliminate sticky contaminants paper fibres should be grounded to particles size of <0,5 mm. Then the paper is extracted with CO_2 in 60°C and 34.5 MPa. Extraction efficiency for stickers removal is 55-75%. Another problem is presence of small quantities of dioxins and other chlorinated organic compounds. Kraft pulp may contain small but detectable levels of dioxins and related compounds, especially if their bleaching process used elemental chlorine. To eliminate dioxins recycled paper also is grounded to particles size of <0,5 mm. CO_2 solvent extraction conditions are 71°C and 34,5 MPa. Dioxin extraction efficiency is up to 95%.

De-inking: it is one of the key operations performed in recycling paper. The heat used in laser printing makes ink hard to remove because it deposits ink on the fibres. Traditional deinking processes rely on chemical and mechanical actions to remove ink from fibres and include several dispersion, flotation and washing steps. They thus reduce fibre strength, which must be compensated for with the addition of fortifying chemicals. A new technology, based on the electric field has been developed. The reactor comprises an anode and a cathode. Applying the direct current field to a reactor full of fibre slurry attracts the ink particles away from the fibres and causes the ink to coagulate. The massed particles float to the surface of the slurry with some help from gas bubbles generated by the electric field. The coagulated ink is then skimmed off the top of the slurry using rotation scoops, continuous conveyors. The current also helps remove dust particles from the fibre and creates oxygen in the reactor, both actions improve fibre brightness and whiteness.

Mixing: finally, the wet, shredded waste paper is blended with another material (wood pulp, chemicals) according to the type of end product is desired. Paper cannot be recycled indefinitely. Each time it is recycled, its quality degrades slightly because the fibres become more and more broken. At some point recycled paper has to be mixed in with virgin material, and eventually after repeated uses, it ends up in a landfill or and incinerator.

The paper making process itself is pretty much the same whether one uses virgin materials, recycled materials, or a mixture of the two.

Internet Resources

EIA Renewables

http://www.eia.doe.gov/cneaf/solar.renewables/at_a_glance/wood/woodenfa-03a.htm

EUROPA – Forest-based industries

http://europa.eu.int/comm/enterprise/forest_based/pulp_en.html

Reach for Unbleached Foundation – Human Health

http://www.rfu.org/cacw/pollutionhealth.htm

Paperonline

http://www.paperonline.org/

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Vu Tuong Anh CLEANER PRODUCTION AUDIT IN THE PULP AND PAPER INDUSTRY: A CASE STUDY IN VIETNAM – Thesis submitted in partial fulfilment of the requirement for the degree of Master of Science

http://www.faculty.ait.ac.th/visu/Data/AIT-Thesis/Master%20Thesis%20final/Tuong%20pdf%2096.pdf

Gouvernement du Canada

http://www.biostrategy.gc.ca/english/view.asp?x=540&mid=50

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http://www.epa.gov/compliance/resources/publications/assistance/sectors/notebooks/pulppasn.pdf

Reach for Unbleached Foundation – Sludge from Pulp and Paper Mills

http://www.rfu.org/cacw/pollutionSludge1.htm

The Irish Scientist

http://www.irishscientist.ie/2002/contents.asp?contentxml=02p153b.xml&contentxsl=is02pages.xsl

Damage Caused by the Paper Industry

http://www.cwac.net/paper_industry/

Inland Paper board and Packaging, Rome Liner board Mill Energy Assessment

http://www1.eere.energy.gov/industry/bestpractices/pdfs/inlandpaper.pdf

De-inking Recycled Paper: A brighter future thanks to Georgia Tech de-inking research

http://gtresearchnews.gatech.edu/reshor/deink.html