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PULPING REVIEW

The main methods of pulping for commercial papermaking are as follows:

CHEMICAL PULPING

Chemical Pulping can be further subdivided as follows:

1 Kraft (Sulphate) Pulping
This is the dominant chemical pulping process in the world today, mainly owing to the superior pulp properties in comparison to sulphite pulping, and its application to all wood species.

2 Sulphite Pulping
This chemical pulping method has a more limited application, mainly owing to limited strength properties, the unsuitability of pine species as a raw material and the fact that environmental problems can be very expensive to solve.

MECHANICAL PULPING

This comprises of three main sub-divisions as noted:

3 Groundwood, Mechanical and Chemi-Mechanical Pulping
These pulping methods and their variants are still extensively used, and are applicable to many tree species. The predominant end product being newsprint.

CHEMICAL PULPING

1. THE KRAFT (SULPHATE) PULPING PROCESS

The sulphate or Kraft process accounting for ca. 80% of world pulp production is the most applied production method of chemical pulping processes. The importance of the sulphite process has decreased steadily over the last years. Today, only 10% of the world production are obtained by this method. The term "sulphate" is derived from the make up chemical sodium sulphate, which is added in the recovery cycle to compensate for chemical losses. In the chemical pulping process the fibres are liberated from the wood matrix as the lignin is removed by dissolving in the cooking chemical solution at a high temperature. Part of the hemicellulose is dissolved as well in the cooking. In the Kraft pulp process the active cooking chemicals (white liquor) are sodium hydroxide (NaOH) and sodium sulphide (Na2S). As a result of the large amount of sodium hydroxide used, the pH value at the start of a cook is between 13 and 14 (alkaline pulping process). It decreases continuously during the course of cooking because organic acids are liberated from lignin and carbohydrates during the pulping reaction.Today the Kraft process is the dominating chemical pulping process worlwide due to the superior pulp strength properties compared with

sulphite process, its application to all wood species, as well as to the efficient chemical recovery systems that have been developed and implemented. But the chemistry of the Kraft process carries with it an inherent potential problem of malodorous compounds. As a result of chemical reactions in the cooking stage, chromophoric groups of the residual lignin are formed thus causing the pulp to become darker in colour than the original wood.

Because of the higher pH, the Kraft pulping process induces more chromophores than sulphite pulping and unbleached Kraft pulp has a considerably lower initial brightness than unbleached sulphite pulp.

A Kraft pulp mill can be divided into four main parts: raw material handling, chemical defibration (delignification) with almost completely closed chemical and energy recovery system, bleaching with an open water system and the process external wastewater treatment system. Another more conventional division is the fibre line, recovery system and external wastewater treatment. Some auxiliary systems like reject handling, manufacturing of bleaching chemicals and auxiliary power generation are connected to the main departments.

Reception and storage of wood

Wood may be received as logs directly from the forest or as by-product chips from some other wood working industry like sawmills and plywood mills. Logs are mainly delivered with the bark on and have to be debarked before further processing. Chips are normally free of bark and can be used after screening and possibly washing. The wood is transported to the mills by ship, truck or rail but also to a limited extent by floating logs to the mill site. Where the latter is used, there will be some leaching of resin acids and nutrients while the wood is in contact with water.

Mechanical pulping techniques may use either logs or chips but chemical pulping techniques will always use chips. The objective in chipping is to form uniform sized chips, which will result in a better pulp product. Some chemical pulp mills store wood chips in piles for up to 40days during which time there is some degradation of extractives within the wood by oxidative and enzymatic mechanisms. The pile of wood chips can become quite warm during this maturation period. Storage for greater than 40 days would be expected to reduce the subsequent fibre yield. Mechanical pulping on the other hand requires fresh wood and in all cases it is desirable to maintain the moisture content of the wood.

Debarking

The most common method for debarking is drum debarking. Bark is removed as the logs rub against each other when made to tumble by the rotating action of the debarking drum. Loose bark and wood sticks fall from the drum through special chutes. Debarked logs are showered with water before being delivered to the pulp mill.

The wet debarking process uses large volumes of water. In recent years "dry" debarking has been installed in many mills. Dry debarking gives bark with lower
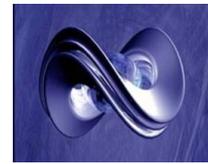
water content, which will result in a better energy balance for the mill if the bark is burnt.

In Nordic Countries frozen logs and snow are thawed before debarking. This can be done in the debarking drum with hot water or steam or on special de-icing conveyors before the debarking drum.

Bark from the debarking unit is typically fed into a bark shredder and, if wet, pressed for burning. Some alternative uses for the bark exist and in some cases it is sold off site but the sheer volume involved in large installations favours on site disposal and energy recovery.

Wood Chipping and Screening

For chemical pulping processes the logs are reduced to chips in a chipper. A uniform chip-size distribution is necessary for the efficiency of the processes and for the quality of the pulp. The more uniform the chips are after the chipper, the lower the raw material consumption. After the chipper station the chips are screened in order to remove oversized chips and sawdust. However, sawdust can also be cooked together with chips or separately in a sawdust cooker, or it can be burnt or used for other purposes. Oversized chips may go for re-processing in a crusher or re-chipper.

Chips are screened for thickness, as this is a critical parameter both in chemical and mechanical pulping. Often the overall optimum is reached by sacrificing some raw material to secure stable processing conditions, which, in turn, promote better pulp quality and less pollution. The material removed in the screening operation can be sold for other purposes or burnt in a solid fuel boiler with heat recovery.

Cooking and delignification

In the Kraft process the fibres are liberated in the cooking plant by dissolving the lignin and part of the hemi cellulose in the cooking chemical solution (white liquor), which contains sodium hydroxide and sodium sulphide as active chemicals. When the final product is unbleached pulp, the cooking is the only delignification stage.

The cooking process can be performed either in batch digesters or in a continuous digester.

When using batch processes, in the cooking stage the wood chips and the liquors are charged into a batch digester where the cook is carried out in elevated temperature and pressure. When the desired residual lignin content (measured as Kappa number) is reached, the contents are discharged to a blow tank and the cooking cycle is repeated. The amount of lignin that remains in the pulp can be determined approximately by multiplying the kappa number by the factor 0.165 [Uhlmann, 1991] i.e. a kappa number of 30 relates to about 4.95% residual lignin.
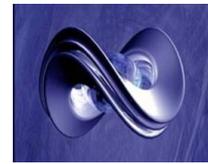
The cooking can also be carried out in a continuous digester where the wood/chemical charge and retention time as well as the temperature in the cooking zone defines the resulting lignin content. The chips are pre-heated by steam before entering the continuous digester in order to remove air, which interferes with the impregnation. After entering the digester, the chips are impregnated with cooking liquor and the temperature raised to 155 -175°C. The cooking time at the maximum temperature is in the range of 1-2h. In conventional cooking the delignification of softwood (spruce or pine) can be brought down to a Kappa number of 30 - 35 whilst maintaining acceptable pulp strength properties. For hardwood (aspen, birch and eucalyptus) the Kappa number can be brought down to 14 – 22.

As a result of the poor bleachability of Kraft pulps and the pollution caused by pulp bleaching, several cooking modification methods have been developed with the aim of removing more lignin from the wood during cooking without reducing the yield. The Kappa number from the cooking of softwood can be reduced to a level of 15 - 25 through extended delignification [Finnish BAT report, 1996], while the yield and strength properties are still maintained. This means that 25 - 50% less lignin is left in the pulp compared with pulp that has a kappa of 32.The requirements for any subsequent bleaching chemicals are, therefore, reduced and the effluent discharges from the bleaching plant are decreased. Comparable Kappa reductions can be achieved in the cooking of hardwood.

Washing and screening

The pulp coming from the digester contains both fibres and spent cooking liquor (black liquor). About half of the wood is dissolved in the cooking. Consequently the black liquor contains inorganic chemicals and a large amount of organic substances. The black liquor is removed from the pulp in the subsequent washing and led to the chemical recovery system, where cooking chemicals and energy are recovered.

The dissolved organic substances together with the spent cooking chemicals are washed away from the cellulose fibres in the brown stock washing stages. Modern systems normally recover at least 99% of the chemicals applied in the digester. Washing the pulp coming from a conventional batch digester plant is normally carried out with drum washers, while a continuous digester plant utilises the Hi-heat wash zone in the digester with additional drum washers or diffuser washers. In today's batch as well as continuous cooking fibre lines, washing starts already in the digester by displacing hot black liquor with cold wash liquor. Subsequent washing is carried out in various types of washing equipment, e.g. vacuum drum washers, wash presses, diffusers or wire type washers.

Efficient washing reduces the carry-over of black liquor with the pulp resulting in a decreased consumption of chemicals in bleaching and reduced discharges from the bleaching plant.

Efficient washing reduces chemical consumption also in oxygen delignification. The outcome of the washing is highly dependent on the efficiency of the equipment used, the outlet consistency of the pulp and the amount of wash
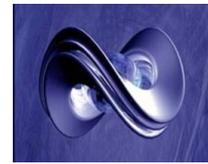
water applied. However, if washing is improved by increasing the amount of wash water, the demand for steam will increase in the subsequent stage to evaporate and concentrate the black liquor.

Wash presses and diffuser washers are especially effective in the removal of dissolved organic substances, and this is one reason why wash presses have become more common, especially as the last washing stage before bleaching. Washing with the longest delay can be achieved in a diffuser type of equipment. Adding carbon dioxide to the wash water will improve the washing effect.

Before further processing, the pulp is screened with pressure screens and centricleaners. The objective of screening is to separate knots and fibre bundles from the main pulp stream with a series of vibrating equipment, filtration through pressure screens and centrifugal separation of fibres and other particles with different specific weights. Rejects from screening constitute a further waste stream to be dealt with.

Oxygen delignification

After cooking, delignification can be continued by oxygen in one-stage or in two stages with or without intermediate washing. Oxygen delignification can be combined with conventional and extended cooking.

Oxygen delignification takes place in alkaline conditions. In order to maintain the sodium balance of the mill, the oxygen stage normally uses the oxidized white liquor, where sodium hydroxide is the main alkaline chemical and sodium sulphide has been oxidized to thiosulphate.

Due to relatively low solubility of oxygen to the alkaline liquor, the delignification reactor is pressurised and the temperature is elevated to about 100 ºC. In oxygen delignification magnesium salt ($MgSO_4$) is added in order to preserve the strength of the pulp. The oxygen is mainly purchased but also some on-site plants are in operation. Because of better selectivity and lower investment costs the Medium Consistency (MC, 10-15%) system has dominated mill installations for the past ten years but high consistency installations (HC, 25-30%) are in use as well. Recently the industry has opted to install two-stage oxygen delignification systems to increase the selectivity of the treatment. Oxygen delignification is usually an intermediate stage in the pulp washing. The wash water is added onto the last washing stage after oxygen delignification and led counter-current to the pulp flow. Washing after oxygen delignification is usually done with one or two wash presses alone or in combination with some other type of washer. The organic material that is dissolved during oxygen delignification can be recovered and led to the chemical recovery system without major changes in the process. The recovery reduces the amount of organic material ending up in the wastewater and the amount of chemicals needed.

The degree of further delignification is 40-50% in a one-stage system and can be up to 70% in a two-stage system [Finnish BAT report, 96]. The Kappa number after conventional cooking and oxygen delignification is typically 18-22 for softwood and 13-15 for hardwood without extended delignification (CEPI, 1996). Depending on the wood species, oxygen delignificationwith extended
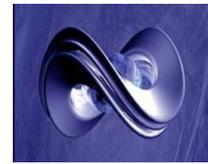
cooking can achieve a reduction in Kappa number to around 8 - 12. The overall pulp yield might decrease by 1.5 - 2.5% and there is still lignin left that has to be removed by other means when high brightness pulp is demanded.

The reduction of the Kappa of unbleached pulp (brown stock), whether it is achieved through extended digester delignification, oxygen delignification or some other method, will reduce the load of bleaching-plant pollutants that enter the external effluent treatment system. This is
because dissolved substances are piped to the recovery system and then burned in the recovery boiler.
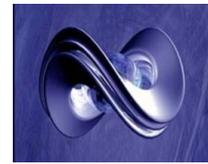

Bleaching

The purpose of bleaching chemical pulp is to obtain certain pulp quality criteria with respect to brightness, brightness stability, cleanness and strength. The brightness of unbleached Kraft pulp is rather low, below 30% ISO whereas fully bleached pulp has a brightness of 88% ISO or higher. Cooking and oxygen delignification cannot remove all the lignin and to achieve this brightness it is necessary to remove or oxidize the remaining lignin and impurities in the pulp.

The Kappa number after bleaching is reduced below 1 unit [CEPI, 1996]).
Whereas delignification can be carried out within closed water systems bleach plants tend to discharge effluent to external treatment. These effluents from the bleach plant cannot easily be recirculated into the chemicals recovery mainly due to the fact, that these bleach plant effluents would increase built-up of chlorides and other unwanted inorganic elements to the chemical recovery system which can cause corrosion, scaling and other problems. Nevertheless, there are running projects on how to close up the bleach plant and some plants are operated with semi-closed water systems.

The bleaching of Kraft pulp is carried out in several stages, usually four to five. The most commonly used chemicals are chlorine dioxide, oxygen, ozone and peroxide. Lately, peracetic acid has become commercially available as a bleaching chemical. Chlorine and hypochlorite have largely been phased out as primary bleaching chemicals over recent years (e.g. PARCOM) Decision on the Phasing-Out of the Use of Molecular Chlorine (Cl_2) in the Bleaching of Kraft and Sulphite Pulp). Small amounts of chlorine are formed as a by-product in most of the chlorine dioxide generation systems used, and a part of this chlorine will be present when
chlorine dioxide is used in bleaching. Chlorine dioxide and ozone have to be produced on site. Peroxide, oxygen and alkali can be delivered to the mills.

Ozone is a very reactive bleaching agent whilst chlorine dioxide, oxygen and hydrogen peroxide are less reactive. Because of the different reaction mechanisms different types of bleaching chemicals are utilised in a bleaching sequence. Acid and alkaline stages are used to complement each other.

Peroxide bleaching is relatively slow and requires long reaction times and therefore large reactor volumes or increased pulp consistency. Increased pressure makes higher reaction temperatures possible, resulting in a reduced

reaction time or improved bleaching outcome. It is necessary to remove metal ions to avoid degradation of the hydrogen peroxide by using metal chelating agents (i.e. EDTA or DTPA) or acid washing. An advantage with peroxide compared with the other oxygen bleaching chemicals is that peroxide bleaching at optimal conditions brightens the residual lignin.

Enzyme treatment before bleaching has been in use at some plants since 1991. It can be combined with different bleaching sequences to enhance the effectiveness of the chemicals used but typically results in a small loss of yield.

2. THE SULPHITE PULPING PROCESS

The production of sulphite pulps is much smaller than the production of Kraft pulps and sulphite pulps are more used in special purposes in papermaking rather than being an alternative market pulp grade for Kraft pulps. Very little unbleached sulphite pulp is made and the yield is a little higher which can be attributed to the lower pH in the cooking.

The main reasons of more limited applicability of sulphite pulps are as follows:
- it is not possible to use pine as raw material in the acid cooking process which limits the raw material base of sulphite pulping
- the strength properties of the pulps as measured by the papermaker are generally not as good as those of Kraft pulp, although for some speciality pulps these properties may be equally good or even better
- environmental problems have in many cases been more expensive to solve and this has decreased the cost-competitivity compared to the Kraft pulping (e.g. pH-regulation of evaporation condensates, minimisation of sulphur emissions and removal of organic compounds).

The sulphite process is characterised by its high flexibility compared to the Kraft process, which is a very uniform method, which can be carried out only with highly alkaline cooking liquor. In principle, the entire pH range can be used for sulphite pulping by changing the dosage and composition of the chemicals. Thus, the use of sulphite pulping permits the production of many different types and qualities of pulps for a broad range of applications. The sulphite process can be distinguished according to the pH adjusted into different types of pulping the main of which realised in Europe are compiled below.

Process	pH	Applications
Acid (bi) sulphite	1-2	Dissolving pulp, tissue,
Bisulphite (Magnephite)	3-5	Printing paper, tissue
Neutral Sulphite (NSSC)	5-7	Corrugated medium, Semi-chemical pulp
Alkaline Sulphite	9-13	Kraft type pulp

The sulphite cooking process is based on the use of aqueous sulphur dioxide (SO2) and a base -calcium, sodium, magnesium or ammonium. The specific base used will impact upon the options available within the process in respect of chemical and energy recovery system and water use. Today, the use of the
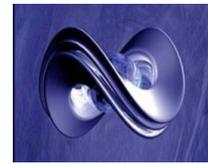
relatively cheap calcium base is outdated because the cooking chemicals cannot be recovered. In Europe there is still one mill (FR) using ammonium as a base. The dominating sulphite pulping process in Europe is the magnesium sulphite pulping process with some mills using sodium as base. Both magnesium and sodium bases allow chemical recovery. The ligno-sulphonates generated in the cooking liquor can be used as a raw material for producing different chemical products. Because of its importance in terms of capacity and numbers of mills running in Europe in the following the focus is on magnesium sulphite pulping.

2.1 Applied processes and techniques

Sulphite pulping consists of three main entities: the fibre line, recovery of chemicals and energy (excluding calcium sulphite pulping where recovery is not possible but where the spent cooking liquor can be evaporated and the components used for other purposes) and external wastewater treatment. As in Kraft pulping some auxiliary systems like reject handling, manufacturing of bleaching chemicals and auxiliary power generation are connected to the main departments.

In many respects the Kraft and sulphite processes have similarities not least regarding the possibilities of taking different internal and external measures to reduce emissions to environment.

Due to this number of similarities only some process steps of sulphite pulping technology are discussed in detail. For process steps of which the principals are same or which are even identical to Kraft pulping it is referred to the corresponding paragraphs. This is true for:

- Wood handling
- Washing and screening
- Bleached stock screening
- Drying

The major differences between the two chemical pulping processes from an environmental point-of- view are to be found in the chemistry of the cooking process, the chemical recovery system and less bleaching sequences required because of better initial brightness of sulphite pulp.

Furthermore, the sulphite process does enjoy less of an inherent odour problem compared to the Kraft process, which tends to be surrounded by unpleasant odours in the neighbourhood of the mill. These differences result in different emission ranges and some differences concerning the abatement techniques applied.

A sulphite pulp mill includes usually the production unit's wood room, digester house, wash room, screening room and bleach plant. Raw-water treatment, bleaching chemicals preparation, drying machine (optional), recovery system and a boiler house.
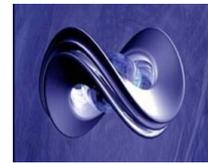
2.1.1 Wood handling

The wood raw material consists usually of roundwood and sawmill chips. Debarking is needed when wood is delivered to the mill as unbarked roundwood. A certain amount of wood can be delivered as woodchips from sawmills. In debarking of pulpwood debarking takes place in drums where the contact between rolling logs and water debarks them. After debarking wood chips are produced from roundwood logs and they are screened and stored in big chip piles prior to feeding in the next process stage. Sawmill and other off-site chips require only screening and storage in the wood handling.
Bark and screening rejects from chipping and chip screening are excess solid wastes generated in this process stage. Most of them are usually collected, dewatered and incinerated for energy recovery in a special bark and wood waste boiler.

### 2.1.2 Cooking and delignification of unbleached pulp

In the manufacturing of conventional unbleached pulp the lignin is extracted from the wood using a concentrated cooking liquor with magnesium sulphite and magnesium bisulphite as active constituents. In the cooking stage the wood chips and the liquors are charged into a batch digester where the cook is carried out in elevated temperature and pressure. When a desired residual lignin content (measured as kappa number) is reached, the contents are discharged to a blow tank and the cooking cycle is repeated. Batch digester plant consists of a series of batch pressure vessels, which are operated according to a certain cooking program.

Cooking can also be carried out in a continuous digester, but this has been practiced with sulphite pulping much less than with Kraft pulping. In the magnephite process the delignification of softwood (spruce) can be brought down to a kappa number of 21-23 in order to maintain acceptable pulp strength properties. In acid sulphite cooking common kappa numbers are between 14-22 for softwood and 10-20 for hardwood. The kappa number and can be further decreased before bleaching by an oxygen stage. Two stage sulphite cooking can bring the kappa number down to less than 10. Cooking can be extended further to produce a speciality pulp for dissolving uses but at the expense of yield.

From the digesters, the pulp is blown to blow tanks. From these tanks, the pulp is then pumped to the washroom.

2.1.3   Screening and washing of unbleached pulp

After the cooking the pulp is washed in drum washers or screw presses and screened with pressure screens and centricleaners. The objective of screening is to separate knots and fibre bundles from the main pulp stream with a series of vibrating equipment, filtration through pressure screens and centrifugal separation of fibres and other particles with different specific weights. The cooking liquor with its content of dissolved wood substance is separated from the pulp, and so-called spent liquor or weak liquor is obtained. Coarse reject and other reject from the screening are normally dewatered and burned in the boiler house. After screening, the pulp is bleached.
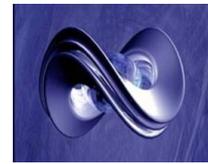
2.1.4 Oxygen delignification/bleaching

The distinction made here between delignification and bleaching is that effluents from a bleaching stage cannot be recirculated into the chemicals recovery system, whereas from delignification this is possible. Consequently oxygen can be used as a delignification and bleaching chemical in the same mill.

Oxygen delignification for sulphite pulping is more rare than in Kraft pulping where it is widely and increasingly used. However, there are a number of sulphite mills in Europe using this technique for further delignification thereby reducing the kappa number by about 10 units. This is mainly due to the fact that also without oxygen delignification only a short bleaching sequence is necessary to achieve full brightness of pulps. Furthermore for oxygen delignification a pressurised process is necessary and a base is needed to increase pH up to alkaline conditions. The chemical base used has to be compatible with the cooking chemicals i.e. for magnesium bisulphite MgO has to be used. Only in that case the organic material that is dissolved during oxygen delignification can be recovered and led to the chemical recovery system without major changes in the process. One mill in Germany has applied this technique thereby loosing some points of brightness.

It has however been shown to be possible to concentrate the effluent with ultra-filtration and burn the concentrate in the bark boiler. Measured as COD the reduction is about 50% of the discharges of organic substances from the oxygen stage.

2.1.5 Bleaching, screening and drying

Bleaching at sulphite pulp mills within Europe is carried out without the use of molecular Chlorine and in many sulphite pulp mills chlorine dioxide is no longer used neither as bleaching chemical i.e. pulp manufactured is thus TCF-pulp (Totally Chlorine Free). Usually oxygen, sodium hydroxide and hydrogen peroxide are used as bleaching chemicals. EDTA is added as complex former (0.5 – 2 kg/t). The bleaching chemicals used are usually bought from external producers.

The bleaching of pulp increases primarily the brightness of pulp and secondarily it also removes non-fibrous particles and extractives from the pulp. Like in Kraft pulping bleaching of sulphite pulp is based on lignin removing methods and it can be considered as continued and selective lignin removal stage.

The lignin removal by bleaching is carried out in a sequence of one or two bleaching stages where oxygen and peroxide is added. In a two stage bleaching sequence in the first place the pulp is heated up to 60-8□C and sodium hydroxide, oxygen and/or peroxide is added. The first bleaching stage reduces the residual lignin by 45-55%. The bleached pulp is then pumped to washing filters and sometimes lead to a twin wire press in order to reduce the carry-over of undesirable substances from the first bleaching stage and to further de-water the pulp. In several European sulphite mills (Ahlfeld, Ehingen, Stockstadt, DE; Gratkorn, AU) the second peroxide bleaching stage (EP) is carried out as high
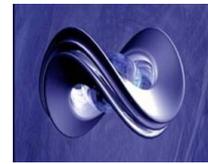
consistency bleaching (symbolic shorthand: EP (HC) = 35 – 40% DS). Advantages of HC bleaching are energy (steam) savings by high pulp density, lower COD emissions by soft bleaching conditions, low pulp losses in the bleaching stage and less consumption of bleaching chemicals. After the second bleaching stage the pulp is diluted with water and another washing takes place. In the sulphite process, the specific process heat and power demand for TCF bleaching are lower than those needed for ECF bleaching.

After bleaching there is generally a final screening of pulp and the reject is burned in the boiler house. The pulp to be sold externally (if the pulp is not used for manufacturing of paper at the same mill site) is dried and the remaining pulp is pumped to the paper mill for the manufacture of different paper grades (fine paper, tissue etc.) paper. Sulphite pulp mills are mainly integrated mills manufacturing paper at the same site.

### 2.1.6 Chemicals and Energy Recovery System

The cooking chemical recovery includes evaporation of the spent liquor to concentrated liquor, combustion of the concentrated liquor and preparation of new cooking acid from recovered chemicals. The degree of liquor recovery is at least 97%.

The recovery of chemicals of the unit processes for unbleached pulp consists typically of the following major principles:

- Counter current washing and evaporation of weak cooking liquor

- Incineration of the concentrated liquors (bio-fuel) in a recovery boiler where substantial amount of energy can be produced for steam and power generation of the pulp mill.

- During the combustion, solid magnesium oxide (ash) and gaseous sulphur dioxide are formed. The magnesium oxide is separated from the flue gases in electro filters and converted to magnesium hydroxide by dissolving in water.

- This slurry is used to absorb the sulphur dioxide and trioxide from the flue gases from the recovery boiler and the collected gases from digesters, washers and evaporators by use of multi-stage venturi scrubbers.

The liquid from the flue gas purification is clarified (sedimentation or filtration) and reinforced with sulphur dioxide from either combustion of elemental sulphur in a sulphur burner or addition of liquid sulphur dioxide. The freshly formed cooking acid (magnesium bisulphite) is pumped into the digester house after separation of soot particles and other undissolved impurities.

Magnesium based mills have difficulty in recycling water from associated stages where sodium hydroxide is used to control the pH. A key issue for sulphite mills is the separation of effluents containing different chemical bases. For instance, sodium hydroxide may be needed to achieve the required pH conditions in some brightening stages and measures. In that case it is not possible to lead the
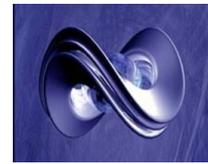
bleach plant effluents back to the recovery island because sodium has to be prevented from contaminating a magnesium based cooking process.

Besides the recovery of cooking chemicals the recovery boiler(s) produce steam. Often sulphite pulp mills operate auxiliary boilers burning bark, oil or other fuels. In these boilers, knots, rejects and sludge from the effluent purification may also be burned. The steam from the boilers is lead to counter-pressure turbines where electrical power is produced.

2.1.7 Magnephite process

The magnephite process is using a higher pH range, pH 3 – 5, than the acid sulphite process that is operated at a pH value of 1 – 2. This results in softer cooking conditions with increased pulp strength properties and slightly higher yield compared to the acid sulphite process. In Europe, for both processes the predominant base that is used is magnesium. There are two major technical differences to consider. In the magnephite process in the white liquor preparation a pH value of 4 can be achieved without SO_2-reinforcement measures. The operation of a pressure storage tank for sulphur dioxide is therefore not necessary. The SO_2 in the white liquor occurs in the bisulphite form. Then the other steps of pulp production are similar to the acid sulphite process. The kappa numbers of unbleached pulp after magnephite cooking are higher than after acid cooking. With the magnephite process kappa numbers from 21 to 26 for paper pulp are achievable. Against that kappa numbers of 12 to 16 can be reached with the acid sulphite process (e.g. Hallein and Neusiedler, AU; Ahlfeld, Stockstadt and Ehingen, DE). As a consequence, the pulp bleachability of magnephite pulp is not as good as with acid sulphite pulp.

Longer bleaching sequences are therefore necessary in order to achieve high brightness. This causes slightly higher loads of COD and BOD in the effluents from the bleaching stages. The magnephite process is operated in four paper pulp mills in Europe (Nymölla and Utansjo, SE; until 1999 Hundsfos, NO; Gratkorn, AU).

3.1.8 Neutral Sulphite Semi-Chemical Pulp

The most common type of semi-chemical pulp is the Neutral-Sulphite Semi Chemical (NSSC) pulp. The process is a combination of chemical and mechanical pulping and has a high yield.

The pulp is mainly used to produce fluting, the inner part of corrugated board. The yield is about 80% for fluting. Wood can be used without prior debarking. In the process wood chips are partially digested to weaken the bonds between fibres. The chips are then mechanically treated in a refiner. Some of the stand-alone plants have no chemical recovery. Very few mills in Europe use cross recovery.
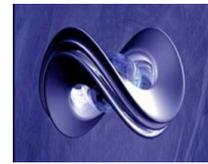
2.1.9 Dissolving Sulphite Pulp

In Europe, there are very few companies manufacturing dissolving sulphite pulp. In principle, the process is very similar to the manufacturing of sulphite pulp used for paper manufacturing. The same chemicals are used as in the common magnesium-bisulfite process. Therefore, the chemicals and energy recovery system is very similar. The major differences can be found in cooking and bleaching. The aim of cooking in dissolving sulphite pulp manufacturing is to achieve a low viscosity i.e. a low length of the molecule chain of the cellulose. This is adjusted in the cooking plant. The similarities and differences are discussed in the following by use of an example.

In one of the European dissolving sulphite pulp mills (Austria, manufacturing of viscose fibres) the delignification of hardwood (beech) is brought down to a kappa number of 4 – 7 before bleaching. There are no effluents before the pulp enters the bleach plant. The bleaching sequence of the plant is carried out in three stages: OPE – Z – P (TCF bleaching).

In the first bleaching stage consisting of oxygen and peroxide delignification and alkaline extraction the kappa number is decreased to 2 and an alpha-cellulose content of 91% is achieved.

Around 50 kg NaOH/t of pulp (oven dry) is used. The releases of this bleaching stage (COD load ca. 85 kg/t) are treated in an evaporation plant. The concentrates are incinerated in a so-called soda boiler. This eliminates the bulk of the pollution load from the bleach plant.

The second bleaching stage is using ozone as bleaching agent. The last bleaching stage is using peroxide, which brings the kappa down to 0,5 (>90% ISO, alpha-cellulose content > 91%). The COD load from the second and third bleaching stage is 15 kg COD/t before treatment and is purified in a biological wastewater treatment (reduction rate > 90%).

Besides the bleach plant, the major source of water pollution is the condensates from the evaporation plant. The pulp mill of our example is extracting acetic acid and furfural as valuable products from the evaporator condensates thus reducing the COD load of the condensates by 75%. The remaining pollution load is 30 kg COD/t that is treated in the biological wastewater treatment (reduction rate > 90%) together with the other partial wastewater streams.

The initial pollution load of the wastewater from dissolving sulphite pulp mills depends on the amount of so-called □□-cellulose to be achieved and on the applied internal measures for reduction of emissions. Higher alpha-cellulose content corresponds to higher product qualities.

Higher alpha-cellulose content of the pulp means a higher dosage of NaOH. This results in lower yields and higher pollution loads in water. For instance, the use of 90-100 kg NaOH/t of pulp to produce pulp with alpha-cellulose content of 92.5% would double the organic load in the effluents as mentioned above (and reduce the yield by 5%). The manufacturing of dissolving sulphite pulp is a combination of delignification and finishing.

3. MECHANICAL PULPING AND CHEMI-MECHANICAL PULPING

In mechanical pulping the wood fibres are separated from each other by mechanical energy applied to the wood matrix causing the bonds between the fibres to break gradually and fibre bundles, single fibres and fibre fragments to be released. It is the mixture of fibres and fibre fragments that gives mechanical pulp its favourable printing properties. In mechanical pulping the objective is to maintain the main part of the lignin in order to achieve high yield with acceptable strength properties and brightness. Mechanical pulps have a low resistance to ageing which results in a tendency to discolour.

The main processes and techniques are Stone Ground wood Pulping (SGW), Pressure Ground wood Pulping (PGW), Thermo-Mechanical Pulping (TMP) or Chemi-Thermo-Mechanical Pulping (CTMP). The main raw materials, yields on wood and end-uses of pulps are summarised below.

Ground wood pulp;
Raw Material: Spruce and fir (softwood) **Yield:** 95-97 % **End Uses:** Printing & writing papers and newsprint.

TMP;
Raw Material: Spruce and fir (softwood) **Yield:** 93-95 % **End Uses:** Printing & writing papers and newsprint.

CTMP;
Raw Material: Dominantly Spruce but also Aspen and Beech **Yield:** 90-94 %
End Uses: Printing & writing papers, tissue and packaging boards.
Raw Material: Other Hardwoods and non-wood species such as Bagasse and Arundo Donax **Yield:** 77-78 %

There are two main processes used for the manufacturing of mechanical pulping. In the stone ground wood process (SGW) or in the pressurised ground wood process (PGW) logs are pressed against a rotating grinder stone with simultaneous addition of water. Refiner Mechanical Pulps (RMP, Thermo-Mechanical Pulps = TMP) are produced by defiberizing wood chips between disc refiners. The elements causing the mechanical action - grit on a pulp stone in the grinder and bar edges on a steel disc in the refiner - will give the resulting pulps a typical blend of fibres and fibre fragments. Ground wood pulp has a higher proportion of fine material and damaged fibres giving the pulp good optical and paper-surface properties. The more gentle treatment in the refiners produces a higher yield of intact long fibres, which gives the pulp higher strength, which is valuable in, furnishes for products with a high requirement on runnability.

The characteristics of the pulp can be affected by increasing the processing temperature and, in the case of refining, by the chemical treatment of the chips. Both steps will increase the energy consumption as well as the pollutant level because of a lower pulping yield. The chemi-thermo-mechanical- pulping process (CTMP), in which the wood is pre-softened with chemicals, is generally considered to be a mechanical pulping technique since the chemicals principally
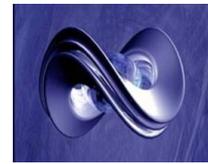
soften the lignin prior to the mechanical stage rather than fully dissolve it out as in true chemical pulping processes.

Most mechanical pulping is integrated with paper manufacture. Mechanical pulp is typically included in a paper furnish to increase the opacity of the paper product.

3.1 Applied Processes and Techniques

3.1.1 Ground wood Pulping

Ground wood pulping consists of a fibre line, reject handling and auxiliary systems. The latter are: storage of chemicals and auxiliary steam and power generation. Ground wood pulp mills are in practice always integrated with a paper mill and therefore the pulp is normally not dried with a drying machine.

3.1.1.1 Wood Handling

The logs required for the ground wood process are obtained by thinning out forests and are usually 10-20 cm in diameter. If the wood for mechanical pulping is stored, drying should be prevented, e.g. through storage in water or sprinkling of log piles. This may require water collection systems in the wood yard in order to avoid discharge of organic substances collectively characterised as COD and toxicity. The bark has to be removed before the logs are processed. The debarking of pulpwood usually takes place in drums where the contact between rolling logs and water debarks them. Water is also used in debarking for the de-icing and washing of wood in the debarking drum.

3.1.1.2 Grinding

The initial defibration takes place in grinders by forcing logs against special rotating grinding stones with the wood fibres parallel to the axis of a stone, producing a pulp at around 2% consistency. The grinder stones used are as a rule of the ceramic-bound type and have to be resharpened periodically.

Most of the energy put into the grinding process is transformed into heat. Wood is warmed and by presence of enough water lignin bonds are softened and fibres are released from the grinding surface. Grinding stones are cooled with shower water that is used also for disintegration of fibres and transportation to the next process stages. Therefore, for this process the availability of water is of basic importance (heat dissipation and friction reduction of the fibres).

The specific energy requirement (kWh/t) for ground wood production is an important process parameter e.g. an increase in the specific energy requirement is always linked with better strength properties, but also with a lower drainage capacity (freeness).

The superior strength properties of refiner mechanical pulps, especially for TMP, forced further development of the conventional grinding process for competitive reasons. The Pressure Grinding Process (PGW) was developed where the grinding process takes place at overpressure (up to around 3 bar). That allows
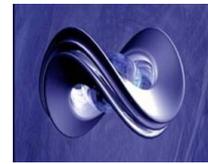
the process to be operated with white water temperatures of 95ºC and grinder pit temperatures of 125ºC. The more intensive softening of lignin associated with these temperatures results in improved ground wood qualities (higher strength) but the technical and financial requirements are considerably higher. Subsequently low-pressure steam is generated when the pulp is de-pressurised. The recovered low-pressure steam is mainly used for the production of warm process water. Another, relatively inexpensive method to improve the quality of ground wood is the thermo grinding process (TGW). In this process the heat losses, which result from evaporation in the grinding zone, are reduced and the process temperature is optimised without using over-pressure but stability controllers.

3.1.1.3 Screening and Cleaning

All mechanical pulps contain undesired components such as large, insufficiently pulped fragments (e.g. coarse rejects) and the shives that consist of many fibre bundles. The shives have to be removed because they reduce the strength and the printing quality of the paper.

A screening installation consists of various stages in order to reduce the strain on subsequent installations and to save most of the acceptable components contained in the rejects. The screening out of the coarse rejects is easy to perform, but the removal of the shives requires a more elaborated technique. The shive content of unscreened mechanical pulp may be as high as 5% depending on the process used. The purpose of screening is to remove the shives to a large extent and, at the same time, to keep the simultaneous screening out of valuable long fibres as low as possible.

The coarse rejects are removed from the main pulp stream by vibrating flat screens equipped with perforated plates. Hammer mills or pulpers are used for the reduction of the coarse rejects. The retained coarse shives are usually added to the rejects of the fine screening system for further processing by means of filtration through pressure screens, which retain shives above a certain size depending on the type of paper required.

The screening process is carried out at high dilutions (below 1 % dry content). The fine screening is followed by a centrifugal separation of fibres and other particles with different specific weights (centricleaners). Separated rejects of the last stage are thickened and treated with special reject handling equipment like reject refiners and are then recycled to the screening process (secondary screens and centricleaners). Accepted pulp from reject handling stages can be recirculated back to the main fibre line. Final rejects are discharged from the process as solid wastes. Depending on the reject-handling concept the dry solids content of these wastes may vary between 5-30 % [CEPI, 1997b]. The screening reject rate may be as high as 30% of the inflow and in case of ground wood the energy requirement for screening, thickening and refining the screen rejects are significant (accounting for about 25% of the total energy).

The screened and cleaned mechanical pulp is thickened by use of disc filters or thickening drums and then stored in tanks and storage towers.
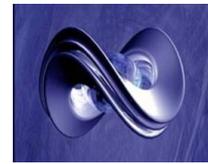
3.1.2 Refiner Mechanical Pulps

The objective of the refiner process is the same as that of ground wood manufacturing, i.e. the softening of lignin bonds and fibrillation of the wood fibres.

In refiner mechanical pulping, chips are ground between steel discs with bar patterns in a refiner. Depending on the quality, the refining can be repeated in a second-stage and sometimes even a third-stage refiner. The forces from the impact of the bars cause the chips to break down into fibre bundles, individual fibres and fibre fragments. With the progressing treatment the impact also modifies the walls of the individual fibres. Most of the applied energy (friction work) transforms into heat, which flashes part of the moisture in the chips. To prevent the wood from burning in the refining zone, cooling (dilution) water has to be added. The refiners normally operate at a high discharge consistency (25-50%). The large quantity of steam released in the refining process is normally captured in a heat recovery system for further use.

In the original refiner pulping process (RMP), which is hardly used today, chips were refined at atmospheric pressure. Because of the low temperature the process produced a high amount of damaged fibres but the optical properties of the RMP pulp were relatively good. To improve the pulp quality, process modifications aiming at increased softness of the wood in the refining zone have been applied. These included the preheating of chips (TRMP and TNP) or pressurisation of the refiner (PRMP). These processes produce pulps of slightly higher strength and reduced shive level at almost unchanged optical properties.

A more dramatic strength improvement and shive reduction is gained in the TMP process, where the chips are heated under pressurised conditions and the refining is also pressurised.

Mild chemical pre-treatment of the chips also enhances the softening of the wood and improves the properties of pulp produced by refining at atmospheric pressure (CRMP) or pressurized refining (CTMP).

With stronger chemical treatment and refining at atmospheric pressure, pulps with high-strength properties can be produced from both softwood and hardwood. These mechanical pulps (CMP) are comparable to semi-chemical pulps.

3.1.2.1 Thermo mechanical Pulping (TMP)

Thermo mechanical pulping consists of a fibre line and auxiliary systems. The latter are e.g. reject handling, storage of some chemicals and auxiliary power generation.

In the following only the TMP process itself i.e. the main unit processes that have to be distinguished from ground wood pulping from an environmental point-of-view are described in more detail.
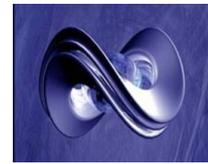
In the thermo-mechanical pulping (TMP) process washed and screened wood chips are subjected to thermal pretreatment, and the disintegration and defibration process is carried out in a series of disc refiners at pressure.

A certain amount of wood can be delivered as woodchips from sawmills. Sawmill and other off-site chips require only screening and storage in the wood handling. If barked roundwood is used wood is first debarked and chipped. Chips for mechanical pulping must not contain stones, sand, scrap metal or other hard contraries that may cause wear or damage to the refiner plates. In most chip refining processes the chips are therefore washed to remove contraries before refining. This results in a reject from the chip washer as water effluent.

After chipping and washing, the raw material is preheated with steam and then refined either in a single stage at an elevated temperature and pressure or in a two-stage refining system in which the first stage is followed by a second refining stage under pressure or at atmospheric pressure.

The pulping of screen rejects is often carried out in the second stage refiner. Part of the organic substances of the wood is dissolved in water and discharged from the process either from the mechanical pulp plant or from the paper machine side.

A large share of the comparatively high amount of electric energy required in refiner mechanical pulping is converted into heat as steam that is evaporated from wood moisture and dilution water in the refiners. Because of the pressurised conditions (excess pressures of up to 5 bar), in many mills, a significant amount of the steam generated may be recovered, cleaned through heat-exchanger to produce clean process steam, e. g. for the use in paper drying. A part of the energy of the released steam may also be recovered as hot water. After refining, the pulp is discharged and diluted, screened and cleaned. After screening follows dewatering and storage in a pulp tower at high consistency. The application of more mechanical energy instead of chemical dissolution results in more pronounced fibre fragmentation and formation of fine material. The significance of water in the mechanical pulping processes implies that fresh wood is to be preferred as raw material. If the wood for mechanical pulping is stored, drying should be prevented, e.g. through storage in water or sprinkling of log piles. This may require water collection systems in the wood yard in order to avoid discharge of organic substances collectively characterised as COD and toxicity. The use of chips makes refiner-based pulping somewhat more versatile with regard to the supply of the raw material.

Since the wood loss during the TMP manufacturing is very low and most of the wood material is converted into pulp, the heat value of the wastewater in a TMP mill is too low to be recovered in the same way as in a chemical pulp mill (black liquor). This implies that external effluent treatment of the wastewater is normally necessary in a TMP mill.

TMP is nearly almost always produced in connection to a paper mill due to the possibility of reusing the heat from refiners for production of steam and better energy efficiency. Therefore, TMP is not normally dried with a drying machine.
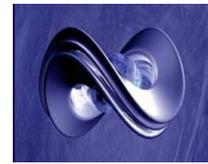
3.1.2.2 Chemi-mechanical Pulping

The addition of chemicals in the refiner process has become important because wood chips can be impregnated very easily. The mild chemical pre-treatment of the chips enhances the softening of the wood and improves the properties of pulp produced by refining at atmospheric pressure (CRMP) or pressurised refining (CTMP). The latter combines the TMP process with a sulfonation of the wood chips. In most cases chemical pre-treatment increases release of pollutants as a consequence of the yield loss caused by the chemical treatment. Different kinds of treatment are used for different wood species and the properties of the CTMP can be varied to a great extent by changing the amount and the nature of the chemicals. The chemi-mechanical pulping methods produce clean pulps of sufficient strength and acceptable optical properties and can be used as the main fibrous component in printing paper, packaging board and hygienic paper furnishes.

Chemi-mechanical pulping consists of a fibre line and auxiliary systems. The latter are e.g. reject handling, storage of some chemicals and auxiliary power generation.

The CTMP process combines the TMP process with a chemical impregnation of the wood chips. In the following only the CTMP pulping process itself is described i.e. only the main unit processes that have to be distinguished from TMP pulping.

After debarking, chipping, chip washing and screening the wood chips are first impregnated in an impregnation tower where the chips are immersed in an alkaline chemical solution. Sodium sulphite (Na_2SO_3) is mostly used for softwoods, and lately alkaline peroxide has been predominantly used for hardwoods. After chemical impregnation the chips are pre-warmed and their temperature increases further in the 1or2 stages of refining (rotating refining plates) resulting in softening of lignin bonds and fibres are released. The manufactured CTMP is mixed with recycled process water, which is used also for disintegration of fibres and transportation to the next process stages.

A further development of the CTMP process is the CMP process. With stronger chemical treatment and refining at atmospheric pressure pulps with high strength properties can be produced from both softwood and hardwood. After chemical impregnation the chips are cooked in a temperature ranging from 70-170 ºC. The cooking time depends from the process and can vary between 15 minutes to a couple of hours. Different kinds of treatment are used for different wood species. Optical properties are drastically reduced and the yield can fall below 90%.

Both the increase in the refining temperature and the use of chemicals (alkaline treatment) increase the generation of pollutants as a consequence of the yield loss in refiner mechanical pulping. In most cases chemical pre-treatment increases the energy consumption. Optical properties are drastically reduced and CMP can only form a minor part of the furnish for printing papers.

CTMP is often produced in connection to a paper or board mill due to the possibility of reusing the heat from refiners for production of steam and better
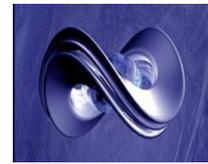
energy efficiency. However, CTMP is sometimes manufactured as market pulp and dried with a flash dryer up to 90 % dry solids content.

3.1.2.3 Alkaline Peroxide Mechanical Pulping

There is a more recent technology, which combines pulping and bleaching in the one process, Alkaline Peroxide Mechanical Pulping.

Alkaline Peroxide Mechanical pulping: this process involves the impregnation of the chips with an alkaline peroxide bleach liquor in one or more steps prior to atmospheric refining, hence combining pulping and bleaching in a single operation. This process is of particular interest for the production of high brightness hardwood kraft pulp substitutes. The potential for reduction in refining energy is another specific feature of this technology because moderate to large quantity of bleach chemicals is added to the process.

3.1.3 Bleaching of Mechanical Pulps

With the increased demand for high-brightness paper and board, the bleaching of mechanical Pulp has become more common. The bleaching of mechanical pulp is in principle totally different than that of chemical pulps because it is based on lignin-saving methods instead of lignin-removing ones. The bleaching of mechanical pulps aims at changing chromophoric groups of lignin polymers into a colourless form. Thus, the bleaching of pulp increases primarily the brightness of pulp with minimum losses of dry solids and overall yield from wood. The effect is not permanent and the paper yellows to an extent with time. As it does not result in permanent brightness gain bleached mechanical pulp is more suitable for newsprint and magazine paper than for books or archive papers. The lignin-saving bleaching is carried out in 1-2 stages depending on the final brightness requirements of the pulp. The bleaching stages are distinguished according to the bleaching agent applied

Reductive bleaching uses sodium dithionite (Na$_2$S$_2$0$_3$)

In dithionite bleaching (symbolic shorthand: S) organic material is not dissolved from the pulp.

Typically using 8 to 12 kg dithionite per tonne of pulp this technique results in a minimal yield loss and brightness can be increased by up to 12 units from an initial brightness level of 58-70 ISO to about 70 - 76% ISO [Finnish BAT Report, 1997]. A suitable pH value is 5.6 to 6.5 and a temperature up to 70ºC accelerates the bleaching process. Residual dithionite in the pulp can cause corrosion with metallic components downstream in the process. In most mills a metal chelating agent (e.g. EDTA, DTPA) is used to prevent degradation of the dithionite. The consistency in conventional hydrosulphite bleaching is 3-5%. Medium consistency (MC) pumping has made it possible to bleach at 10-12% consistency with increased efficiency.

Oxidative bleaching using peroxide (H_2O_2)

The yield drop in peroxide bleaching (symbolic shorthand: P) is approximately 2%, mainly due to the alkalinity during the bleaching that results in an increasing dissolving of organic substances out of the wood (and in an increase of pollution load).

Peroxide bleaching influences the pulp properties - in addition to increased brightness, the strength of the pulp improves, the content of extractives is reduced and the water uptake capacity improves. When applying the maximum economical amount of peroxide an increase in brightness of up to 20 units to 78 - 84% ISO can be achieved [Finnish BAT Report, 1997]. The bleaching process results in lower brightness in the presence of heavy metal ions. Therefore, chelating agents (e.g. EDTA, DTPA) are added before bleaching to form complexes with heavy metals (Fe, Mn, Cu, Cr), which prevents the pulp from discolouring and the peroxide from decomposing. EDTA and DTPA contain nitrogen, which will show up in the wastewater. Introduction of a washing stage between pulping and bleaching is effective in reducing the problematic metals and can thus reduce the amount of chelating agent needed and improve the effectiveness of the applied peroxide. The bleached pulp is finally acidified with sulphuric acid or sulphur dioxide to a pH of 5 - 6. Modern peroxide bleaching is conducted at a consistency level of 25 - 35%.

The two bleaching processes are also used in combination. A higher final brightness can be reached with peroxide bleaching than with dithionite bleaching but with reduced opacity. The achievable pulp brightness is dependent on the initial pulp brightness that in turn is feedstock and process related. In particular it is not only the wood species but also the degree of decay of the pulpwood, which is important.

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