New developments in pulping technology

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Abstract

Over the years, different driving forces have accelerated the development of the chemical pulping process. Besides the environmental aspects, however, investment and production costs have always been the main drivers in research and development. For pulp producers, the new task is to integrate the entire pulp mill more closely into the energy generation process as well as into other areas of the mill. Opportunities for the production of completely new products are also undergoing intensive research and development.

Different parameters determine which factors are important for pulp mills: geographical location (in the Northern Hemisphere, softwood is a dominant raw material, while hardwood and eucalyptus dominate in the Southern Hemisphere), logistics, general infrastructure, and water availability.

The most recent research and development topics were how to increase pulping yield, reduce mill effluent, and improve power and energy efficiency. Good results have been obtained for polysulfide cooking in mill-scale operations.

Pre-hydrolysis kraft pulping has proved its ability to be a real alternative to the previous, sulfite-based method for production of dissolving pulp. Several kraft pulp cooking systems have been converted to the pre-hydrolysis method, which also involved changes in the rest of the fiberline.

Bleaching effluent flow is reduced conventionally by recirculating bleaching filtrates within the bleaching process. One method that is not yet common is to recycle part of the bleaching filtrate to brown stock washing. This leads to an increased chlorine input in the chemical cycle and requires measures to remove chlorine and balance the chemical input.

Encouraging results have been obtained in the reduction of mill effluent by re-using biologically purified waste water in bleach plant washing. Positive experience has been gathered in mill-scale operations over a period of one year.

Keywords: kraft pulping, cooking, bleaching

Introduction

The first eucalyptus pulp mills were built decades ago. From the 1950s onwards, eucalyptus wood began to play a certain role in pulp production. The 1980s saw a sharp increase in the use of eucalyptus as raw material for pulp production. The industry then learned about the use of short-fiber pulp and its advantages in paper manufacturing, resulting in a dramatic increase in demand for this type of pulp. Since the 1990s, there has been a huge jump in eucalyptus pulp production. Besides the rise in pulp production, research and development activities have been established in the wood plantation and pulping sectors.

Today, eucalyptus pulp is the most desirable raw material for fine paper. This is due to its good fiber properties and, above all, to its uniform quality. Approximately 30 million tons of eucalyptus pulp are produced annually today, some 60% thereof in Brazil. This quantity is increasing rapidly in the Southern Hemisphere. In this region, the fast-growing wood plantations produce favorable pulp raw material of uniform quality and in locations close to the pulp production plants. The growth cycle of these fast-growing wood plantations is between six and eight years, so the wood supply areas need not be large. Besides wood availability, the main drivers of developments are investment and production costs, energy generation, and environmental sustainability. Hence, one clear trend in meeting these targets has been to dimension the mills' production capacities as high as possible in single-line/single-unit implementations. At the moment, the maximum size is already over 1.5 million t/a, and the trend seems to be growing.

The genetic development of eucalyptus wood has resulted in enormous improvements in wood growth and suitability for pulping, not to mention ecological sustainability. The wood raw material from the plantations is of uniform quality, and this quality is being enhanced continuously. A new generation of trees has been cultivated, superior to those of previous generations. Numerous eucalyptus species have been developed for use in pulp mills. Eucalyptus chips can normally be delignified uniformly, and the pulp brightens easily. However, wood species do differ from one another. For this reason, the raw material used by the mills must always be considered in the selection of technical process concepts and in dimensioning of the equipment. Additionally, eucalyptus wood has several features that differ from other wood species. For instance, the logs are normally debarked in the forest after harvesting. They can also be debarked at the mill site, but the storage period before debarking must not be longer than 4-6 weeks.

New developments in pulp mill technology

Wood yard

When eucalyptus wood began being used in pulp mills, the wood was debarked in conventional debarking drums on the mill site. Debarking performance varied a great deal, often producing poor quality and unsatisfactory separation of the bark detached. For this reason, the debarking stage was shifted to the forest to be performed after harvesting when the wood is fresh and the bark detaches easily. As a result of forest debarking, harvesters were developed to perform the debarking work. However, the debarking result does not come up to the standard required by the pulping process, and log washing drums or other systems are also needed on the mill site. Mill debarking also has certain benefits: The bark can be used as fuel in power boilers or gasification systems, and any sand, bark, and other impurities are removed from the logs before the chipping and pulping process. The rules for log storage times still remain the same. However, the downside is that biomaterial is removed from the forest and this must be compensated by fertilizers.

Chippers have developed over the years, and chip quality has improved remarkably. In some cases, chip screening can even be omitted and only the oversized chips need to be removed. A new challenge in chipping is the ever decreasing diameter of the logs: Chip quality can be maintained, but capacity is lost, or vice versa.

Over the years, the industry has recognized the importance of controlling chip size distribution and different types of gyratory and disc screens have been developed for chip screening. The new system to separate oversized chips and fines from the chip flow is known as impulse chip screening. Reducing the oversized fraction is the main focus when increasing the cooking Kappa.

Cooking process

Until the 1950s, batch cooking was the only method used. After that, the continuous cooking process started to develop. The key innovations in the birth and development of the continuous cooking process were the method of feeding chips to the pressurized digester (high-pressure feeder) and the cooling of pulp in the digester discharge. Nowadays, the dominant cooking method in new mills is continuous cooking, and batch cooking is only considered in special cases.

Today, there are two suppliers of continuous cooking equipment. Both basically have their roots in the same innovation, but the technical solutions and technologies have differed over the years. In principle, the cooking equipment is similar for SW and HW, but the different wood properties require different process conditions.

Until the 1980s, cooking systems were based on the conventional cooking method, which means that the entire quantity of cooking liquor is charged at the beginning of the cooking process. There was no profiling of chemicals or dry solids during the cook. The four rules for modified kraft cooking were published at the beginning of the 1980s /1, 2/.

- The alkali concentration must be controlled, i.e. it must be decreased at the beginning and increased at the end.
- The concentration of hydrogen sulfide ions should be as high as possible, especially at the beginning of bulk delignification.
- The concentration of dissolved lignin and sodium ions in the liquor should be as low as possible, especially in the final cooking phase.
- The temperature should be low, especially at the beginning and end of the cook.

Modern cooking systems generally obey these rules. Suppliers have developed and modified their solutions specifically for eucalyptus, and the research and development work has provided the following results:

- Pulping yield has increased.
- Power and steam consumption have decreased.
- Pulp bleachability has improved, and pulp strength has increased.

Due to increasing mill capacities, digester volumes and geometries have seen substantial changes over the years. Figure 1 illustrates the changes made from the 1960s up to the present day.

In recent times a central focus of development work has been the yield increase in cooking and over the entire fiberline and production of dissolving pulp/3, 4/. The increase in yield is achieved by means of polysulfide cooking and by the kappa increase linked to oxygen delignification and screening.

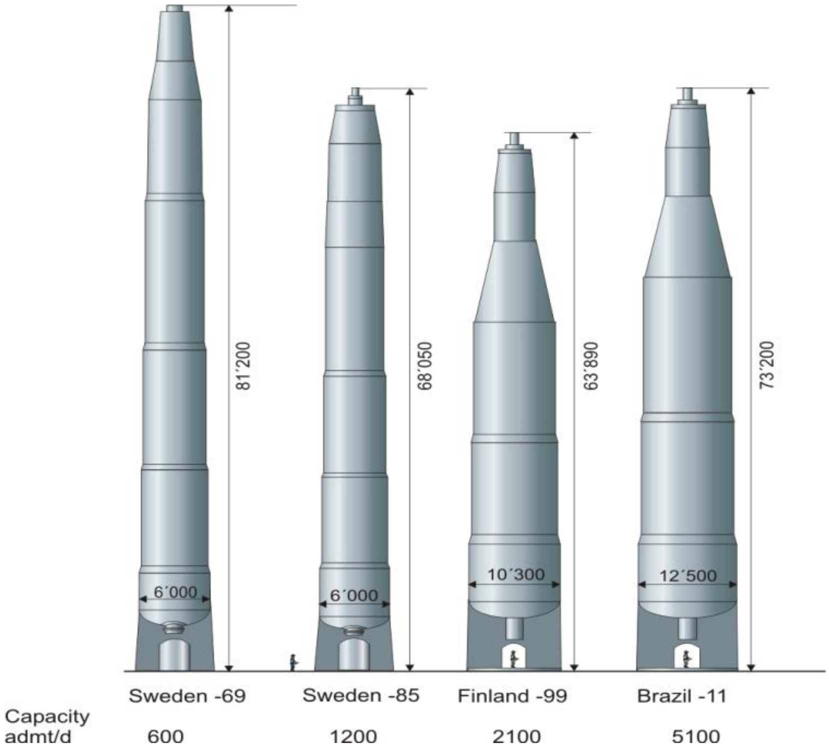


Figure 1. Development of digester geometry.

The cost of wood is generally the main production cost. There are several research efforts underway to find process alternatives for a further increase in pulping yield. The optional methods under investigation are:

- Preparing wood for pulping
- Improving modified cooking procedures
- Cooking additives
- Improving cooking chemistry
- Polysulfide cooking.
- Increasing the cooking Kappa
- Intensifying oxygen delignification
- Improving pulp screening system
- Improving the bleaching chemistry

Pulping yield

Figure 2 illustrates the importance of pulping yield in the operating cost. It is possible to achieve a significant benefit in wood cost with only a small yield increase in a mill producing 1.5 MT/a. The benefit is even greater if we consider that more pulp can be produced from the same amount of wood.

Figure 2. Annual wood cost saving in USD as a function of the wood price. Mill production of 1.5 MT/a.

Figure 3 illustrates the yield increase in laboratory cooking of eucalyptus as a function of Kappa. The improvement in yield is remarkable. The Kappa increase results in more uncooked shives. The screening concept has to be modified accordingly, i.e. provide more capacity for treating the reject fraction. When screen room operations are installed after the oxygen delignification stage, the reject can be processed to provide accept fiber by recirculating it partially to the oxygen stage/digester feed and thus increasing the yield.

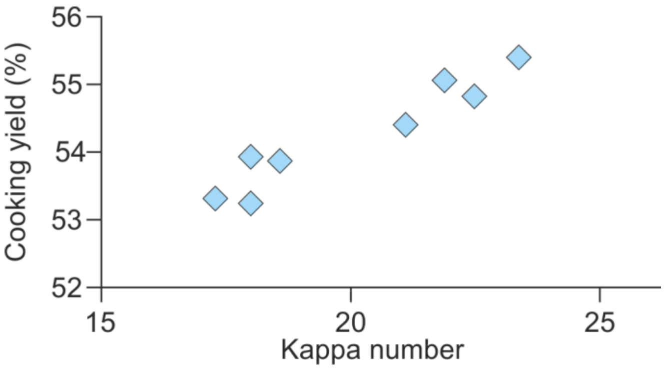


Figure 3. Cooking yield increase in eucalyptus laboratory cooking.

Polysulfide cooking

Polysulfide cooking is not a new innovation. The first installations were started up at the end of 1970, but the interest in polysulfide cooking has only risen again in recent years. Laboratory methods have been developed to simulate cooking under real conditions, which helps in the evaluation process. Figure 4 shows the operating principle for polysulfide cooking. Cooking liquor – orange liquor – is produced from white liquor by oxidizing it in a MOXY process. The higher is the white liquor sulfidity the higher the polysulfide concentration that can be achieved in the white liquor. The increase in yield depends on the polysulfide charge in cooking. The yield benefit is higher with SW than with HW. Around 1% of the polysulfide charge to the wood improves the yield by 1-2% with SW, and the higher the Kappa, the higher the increase. Figure 5 shows a MOXY oxidation system diagram, while Figure 6 shows the white liquor and orange liquor.

Sulfide reactions in MOXY reactor:

$2Na_2S + O_2 + 2H_2O \rightarrow 2S_0 + 4NaOH$

$2S_0 + 2Na_2S \rightarrow 2Na_2S_2$ (orange liquor)

Side reactions:

$2Na_2S + 2O_2 + H_2O \rightarrow Na_2S_2O_3 + 2NaOH$

$2Na_2S_2 + 4Na_2SO_3 + O_2 + 2H_2O \rightarrow 4Na_2S_2O_3 + 4NaOH$

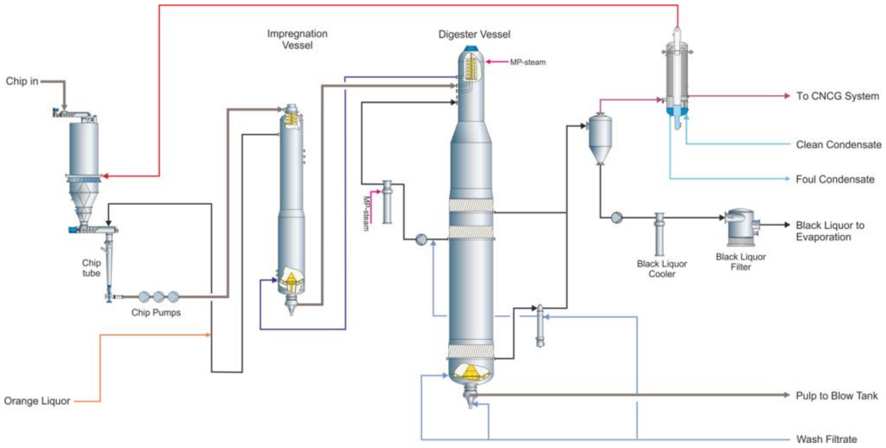


Figure 4. Continuous cooking using the polysulfide method

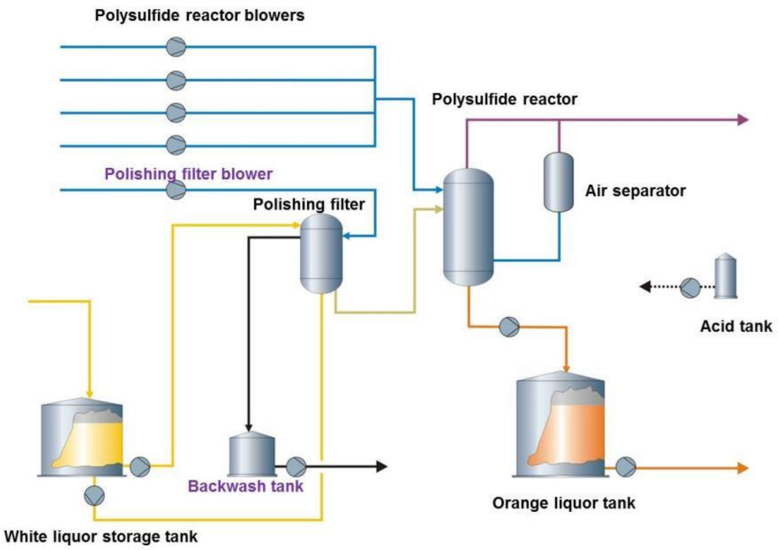


Figure 5. MOXY white liquor oxidation.

Figure 6. White liquor and orange liquor (right).

Dissolving Pulp

In the past, sulfite batch cooking has been pre-dominant in the production of dissolving pulp. Only a few batch-type prehydrolysis kraft cooking systems have been in operation. Since 2010, the demand for dissolving pulp and the market itself have been volatile. This is a consequence of the increase in consumption of textile fibers and of a fluctuating cotton harvest. Many kraft pulp producers became interested in this market opportunity and started to plan pulp plant conversions to implement the dissolving method. Traditionally, there was a belief that batch-type cooking systems are the only type suitable for this product. Only two continuous digesters were operated using this method (in Russia and Brazil). Many trials were conducted in the Varkaus mill at the beginning of the 1980s, but continuous production operations were never achieved.

Since the renaissance of the dissolving pulp market, new process solution has been developed for manufacturing dissolving pulp with a continuous cooking system and also gone into operation successfully. Figure 7 shows the operating principle for continuous cooking of dissolving pulp.

The process consists of an autohydrolysis step before cooking (Figure 8). Autohydrolysis is based on naturally forming acetic acid from the wood chips during water treatment. The prehydrolysis phase is controlled by the P-factor, which is similar to the H-factor in cooking. Dissolved and decomposed hemicellulose, water-soluble lignin and organic acids, as well as hydrolysate solution are removed by displacement after the autohydrolysis step. This is essential in order to save alkali input in the subsequent cooking process. Various by-products can be recovered from the hydrolysate /4/.

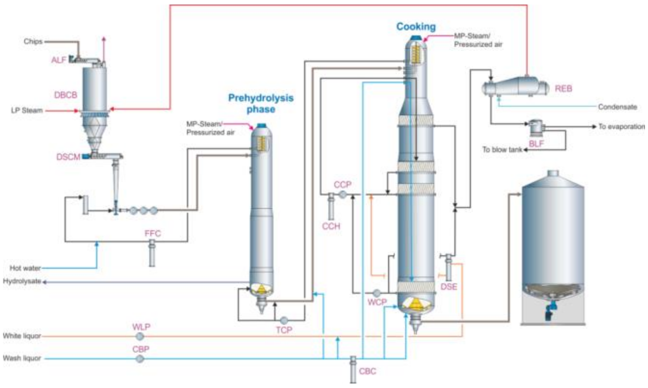


Figure 7. Continuous cooking of dissolving pulp

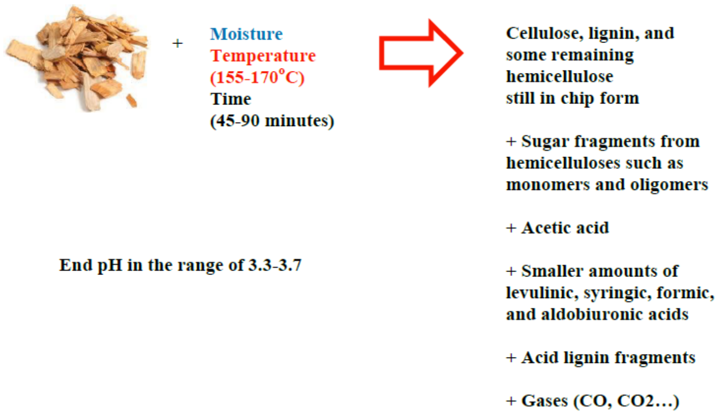


Figure 8. Autohydrolysis of wood chips

The quality properties of dissolving pulp differ a great deal from paper-grade pulp properties. Figure 9 shows typical properties, which are similar for SW and HW pulps. Alpha cellulose content is determined in prehydrolysis and cooking, where the hemicelluloses are dissolved. Other parameters, such as viscosity, brightness, brightness stability, cleanliness, and ash content are controlled in the rest of the fiber line. The Kappa number after cooking is significantly lower than in normal cooking. The pulp undergoes oxygen delignification under typical conditions to reduce the Kappa by 50%. Prehydrolysis pulp does not contain HexA. The bleaching sequence can vary, but it typically applies 3- or 4-stage bleaching. Ozone can be used successfully in bleaching of dissolving pulp and is very effective in viscosity control.

The continuous dissolving pulp concept is flexible in the sense that the same process facilities can produce both paper-grade pulp and dissolving pulp simply by changing the operating mode. Some plants produce dissolving and paper-grade pulp in the swing mode.

Brightness, % (ISO)	88-92
Viscosity, ml/g	450-550
Alpha cellulose, %	93-95
R10, %	>92
R18, %	>95
Kappa number	<0.5
Ash content, %	<0.1

Figure 9. Typical properties of dissolving pulp.

Heat recovery in cooking

Heat economy has become more and more important in the cooking system. Nowadays, the cooking system is often integrated into the evaporation system and the rest of the fiber line in order to reduce the overall steam consumption. The heat recovery options available today are:

- flash steam – contaminated black liquor flash steam to chip bin
- heat economizers for heating of wash water – low-pressure steam to chip bin
- kettle reboiler – clean steam to chip bin
- vapor reboiler – clean steam to chip bin
- digester evaporator – black liquor pre-evaporation steam to digester

Black liquor flash steaming is no longer recommended due to the unpleasant odor and for safety reasons. Nowadays, the most common heat recovery methods are the kettle reboiler and vapor reboiler (Figure 10) systems. A very new solution is the digester evaporator, where fresh medium-pressure steam is replaced by black liquor steam. In all modern heat recovery arrangements, the chip bin steam is clean, and all odorous emissions and explosion risks are avoided. In the new cooking systems, the black liquor temperature to evaporation is above 100ºC and thus, some flash steam benefits the evaporation process.

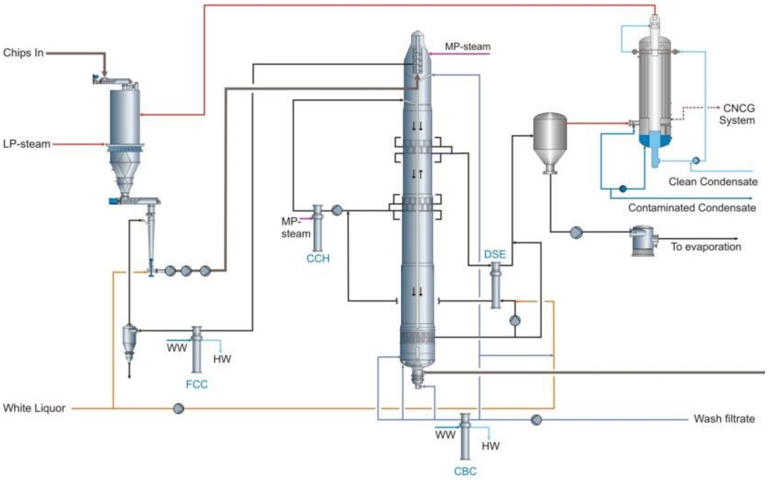


Figure 10. Continuous cooking with vapor reboiler heat recovery.

Washing, Screening and Bleaching process

Pulp screening

The pulp screening process has taken on a more important role in increasing cooking Kappa and, at the same time, improving pulp cleanliness with lower chemical consumption. A huge jump has been achieved recently with the Dolphin screening technology. Pulp consistency is raised beyond 5%, and narrow slots are used /5/. A high screening consistency saves energy, increases unit capacity, and benefits sizing of the overall process concept (Figure 11).

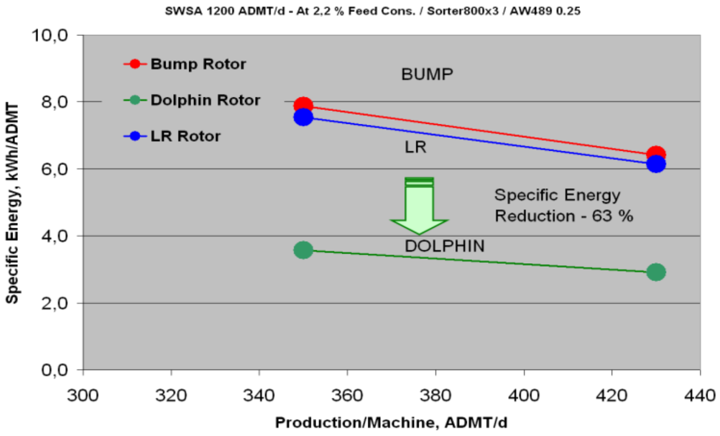


Figure 11. Specific power consumption of screen room with different screen concept.

Pulp bleaching

Only a couple of decades ago, pulp bleaching was mainly based on the use of chlorine and a minor amount of chlorine dioxide. The sequences normally included five or more bleaching stages. A little later, brown stock oxygen delignification, the oxygen-reinforced alkali stage, and peroxide as a bleaching agent were adopted in bleaching. Over the years, consumption of bleaching chemicals has decreased dramatically (Figure 12).

At the beginning of the 1980s, medium-consistency technology was developed and, in many respects, has opened up new opportunities in fiber line unit operations and development.

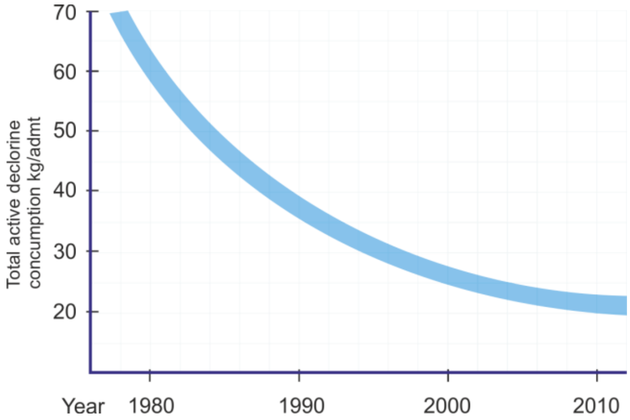


Figure 12. Active chlorine consumption in eucalyptus bleaching – brightness target level 90 ISO.

At the end of the 1980s, pulp mill effluents and organic chlorine compounds in effluents became a hot topic. This was followed by a period of intensive bleaching research. The first target was to move away from the use of elemental chlorine to the use of 100% chlorine dioxide. This bleaching technique was called ECF bleaching. The next target was to remove chlorine dioxide from the mill process and move to TCF bleaching technology. Thanks to the research and development activities at that time, oxygen delignification was enhanced, peroxide bleaching was intensified, and ozone bleaching technology went into industrial use at the beginning of the 1990s. Some mills introduced enzymatic pre-treatment of pulp, while peracetic acid (P_{AA}) and molybdate (P_{Mo}) were introduced as well, especially in TCF bleaching.

The development work conducted made it possible to bleach kraft pulp to full brightness using TCF bleaching, however TCF technology is not yet in general use. The question we must ask is why not? After all, the pulp quality and process economy appear to be similar to ECF technology, at least on laboratory scale. However, the use of oxygen, peroxide, and ozone has been established in modern ECF bleaching sequences. These sequences are referred to as light ECF sequences.

HexA removal in bleaching sequence

One of the most significant innovations for decades in pulp bleaching technology is the discovery of HexA removal from pulp /6, 7, 8/. Brightness reversion in bleached hardwood pulp, especially in eucalyptus pulp, was a problem as long as the HexA was found to be one of the major causes. Simultaneously, consumption of bleaching chemicals was reduced dramatically. Nowadays, HexA removal is an established bleaching stage in all modern HW bleaching sequences.

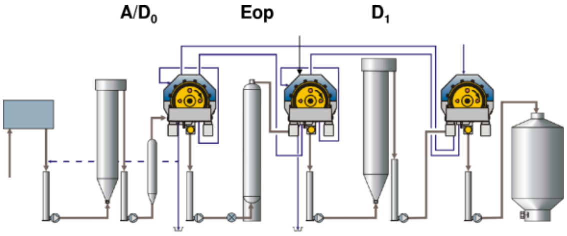
The two most common ways of achieving HexA removal in bleaching is to do so sequentially with chlorine dioxide (A/D) or to combine it with the dioxide stage (D_a). The best possible benefit from the process point of view can be achieved by sequential HexA removal. Chlorine dioxide can target lignin and impurities in pulp more effectively. Besides the process results, operational and investment costs need to be considered when selecting a concept.

ECF bleaching is a dominant concept, but there are several variations in the configuration of the bleaching sequence. Various factors such as target brightness, the chemicals to be used, costs, and emissions must be kept in mind when specifying the bleaching sequence. With eucalyptus pulp, the basic starting point is almost invariably a high HexA content so the bleaching sequence should begin with the removal of HexA. With a brightness target of 91-92+ ISO, four-stage bleaching is the most advantageous alternative in terms of operating costs, in spite of the fact that the investment in equipment is higher than for bleaching in three stages. Ozone is an efficient bleaching chemical, either alone or in combination with chlorine dioxide. Its benefits must be assessed separately in each case, taking the energy price and pulp quality requirements into account.

Bleaching effluent management

Recent mill experience has shown that pulp washing is very important in terms of the final bleaching result. Pulp cleanliness in the first stage of bleaching is especially important. The contaminants may originate from washing in the oxygen stage or from circulating bleaching impurities. Research has shown that the COD entering the system with the pulp and the COD circulating in bleaching both have a detrimental effect. The effect of the COD originating from the Do stage is especially detrimental. It increases the chemical consumption and it also impairs brightness development, possibly even bringing it to a halt.

Bleaching is the main water consumer and effluent generator in a pulp mill. The target is always to reduce water consumption and effluent flows. How then should water consumption in bleaching be lowered if the consequence is a significant increase in the consumption of bleaching chemicals and a brightness ceiling? The solution is fractional washing. The first stage of bleaching is kept clean, and the filtrates in the subsequent stages are circulated in fractions. The COD level of the bleaching stages will increase to some extent, but this can be compensated by a slight increase in the chemical dosage, which eliminates any brightness ceiling. An example is shown in Figure 13. The total COD output in bleaching effluent is 20-28 kg/adt, depending among other things on the brightness target and closure of the filtrate system.



Total COD in pulp kg/adt

	A/D_o	Eop	D_1	DM
Bleach Plant Effluent 15 m^3/adt	5	8.9	5	1.9
Bleach Plant Effluent 10.8 m^3/adt				
Segregated washing	5	22.8	14.5	3.6
Non-segregated washing	17.9	16.6	11.5	5.4

Figure 13. A 3-stage bleach plant with fractional and non-fractional washing at normal and reduced effluent discharge.

The next step to reduce bleaching effluent could be to recycle part of it in a recovery loop. Completely closed filtrate cycles were studied couple of ten years ago, but the corrosion and scaling, among other problems, then stopped this development. Fractional washing can provide new tools with which to design filtrate circulation in a new way. It is also possible to select a different bleaching sequence in order to improve ways of closing filtrate loops. TCF sequences have already been designed with closed filtrate loops, but this bleaching technology is still only emerging.

Light ECF sequences with ozone and peroxide are interesting options, both from the process point of view and for effluent reduction by lowering the chlorine dioxide usage. When bleaching effluent is recycled in a recovery cycle, it introduces chlorine into the loop. The chlorine has to be removed to prevent the content building up to a harmful level. In chlorine removal, chemicals are lost, and this increases the operating costs. Thus, it is essential to weigh up the benefits and drawbacks of recycling on a case-to-case basis.

Closure of the filtrate system increases the concentrations of ions and anions, which can cause scaling and incrusting. Thus, it is important to analyze the risks carefully and take decisions accordingly. Barium and calcium precipitates are the most common forms of scaling. An interesting innovation for calcium removal was presented recently, where calcium could be removed from acidic bleaching filtrate by means of precipitation with sodium salt /9/.

The re-use of purified process water in the fiber line has shown promising results in laboratory studies /4/. Encouraging results were obtained in the reduction of mill effluent by re-using biologically purified waste water in bleach plant washing. In addition, positive experience was gathered in mill-scale operation over a period of one year. Figure 14 shows schematic alternatives for filtrate coupling when using purified effluent in the fiber line.

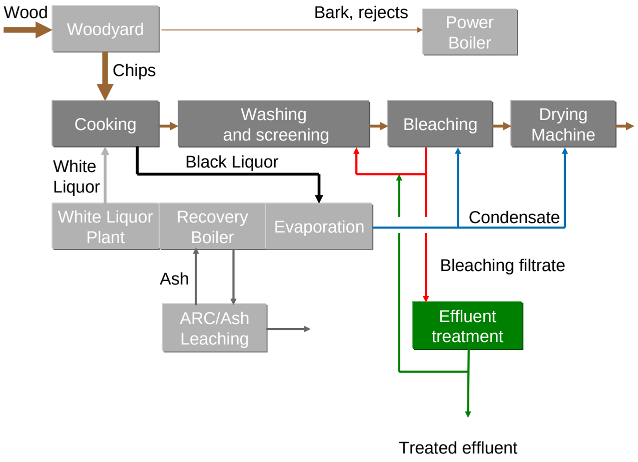


Figure 14. Schematic alternatives for filtrate coupling when using purified effluent in fiber lines.

Conclusions

Ten to fifteen years ago, the eucalyptus fiber line was different to the process used today. In another ten to fifteen years, it will be different again. But in what way?

Over the years, different driving forces have accelerated development of the pulping process. However, investment and production costs have always been the main drivers in research and development, in addition to the environmental aspects. For pulp producers, the new task is to integrate the entire pulp mill more closely into the energy generation process. Opportunities for the production of completely new products are also undergoing intensified research and development.

Increasing the cooking yield by using polysulfide and a higher Kappa number has become a reality. Dissolving pulping has returned and been produced successfully in a continuous cooking system.

The screening consistency has been raised to a new level, improving the power and process efficiency.

Reducing the effluent emissions from a fiber line is a continuous process, and improvements have been achieved by means of internal circulation. Efforts in the industry to further reduce the effluents occurring by re-using purified effluent and recycling part of the effluent have reached a promising phase.

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