Abstract

Over the years, different driving forces have been used to accelerate the development of the chemical pulping process. However, investment and production costs besides the environmental aspects 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 to energy generation. Possibilities to produce completely new products are also under intensified research and development.

A brief assessment of what forces were determinants in the development of each of these steps is an important point in understanding how we are today, and what the factors are that will determine the future steps of the pulping sector.

Keywords: kraft pulping, cooking, bleaching

Introduction

The first eucalyptus pulp mills were built decades ago. From the 1950’s onwards, eucalyptus wood began to play a role in pulp production. The 1980’s saw an intense increase in the use of eucalyptus as raw material for pulp. We then learned about the use of short-fibred pulp and its advantages in paper manufacturing and witnessed a dramatic increase in its demand. Since the 1990’s, there has been a huge jump in eucalyptus pulp production. Besides the growing pulp production, research and development activity, both in wood plantation and in pulping fields, has been established.

Today, eucalyptus pulp is the most desirable raw material for fine paper. This is thanks to its good fiber properties and, above all, its uniform quality. Approximately 20 million tons of eucalyptus pulp is produced annually today, and this quantity is rapidly increasing. The increase in the pulp production capacity has been in the southern hemisphere. In this area the fast-wood plantations produce advantageous pulp raw material of uniform quality and in the vicinity of the production plants. The circulation speed of these fast-wood plantations is between six and eight years, and, consequently, the wood supply areas do not need to be large. Hence, to lower the investments costs, efforts are made to dimension the mills’ production capacities as high as possible in single-line implementations. At this moment, the maximum size exceeds 1.5 million t/a, and the trend seems to be only growing. There is no seasonal variation in the wooden raw material as in the northern hemisphere and hence the maximum pulp production potential can be taken out of the mill equipment on a continuous basis.
The genetic development of eucalyptus wood has resulted in enormous improvements in wood growth and suitability in pulping, not forgetting the ecological sustainability (Figures 1, 2). The wooden raw material from the plantations is of uniform quality and this quality is continuously enhanced. Good care is taken of the plantations, which are under strict control. A new generation of trees has been developed, superior to those of previous generations. Numerous eucalyptus species have been developed for the use of pulp mills. Eucalyptus chips normally delignify uniformly and the pulp brightens easily. However, there are wood species that differ from each other in terms of pulping, brightness development, and drainage properties. For this reason, the raw material used by the mills must always be considered in the selection of process technical concepts and in the dimensioning of the equipment. Additionally, eucalyptus wood owns several features which differ from other wood species. For instance, wood log debarking is normally done in the forest in connection with harvesting. It can also be done on the mill site, but the storage time before debarking must be limited to 4-6 weeks.

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### Sustainable investments in the last 30 years

- genetic
- biogenetic
- raw material of high quality
- social and environmental planning
- forest management
- rotation of planted areas

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![Figure 1. Forest growth development over the past 30 years](source: Bracelpa)

**Brazil, wood for pulp production**

<table>
<thead>
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<th>Year</th>
<th>Eucalyptus</th>
<th>Pine</th>
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<td>19</td>
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<tr>
<td>2009</td>
<td>44</td>
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Source: Bracelpa

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![Figure 2. Current and potential forest growth](source: Pöyry)

**Hardwood - Forests of rapid growth**

<table>
<thead>
<tr>
<th>Country</th>
<th>Current</th>
<th>Potential</th>
</tr>
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<tr>
<td>Chile, Eucalyptus</td>
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<td>30</td>
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<tr>
<td>Indonesia, Acacia</td>
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<td>30</td>
</tr>
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<td>Uruguay, Eucalyptus</td>
<td>25</td>
<td>35</td>
</tr>
<tr>
<td>Brazil, Eucalyptus (*)</td>
<td>44</td>
<td>70</td>
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</tbody>
</table>

Source: Pöyry

(*) Source: Bracelpa
Main development steps in pulp mill technology

Wood yard

When eucalyptus wood was started to be used in pulp mills, debarking was done in conventional debarking drums at the mill site. The debarking performance was very variable and often poor and the separation of loose bark didn’t succeed well. For this reason, the debarking was moved to the forest to be performed in connection with harvesting when the wood is fresh and the bark loosens easily. Thanks to the forest debarking, harvesters have been developed to do the debarking work. The debarking result, however, is not as good as the pulping process requires and therefore log washing drums or other systems are required on the mill site. There is also a new method – the live bottom barking system, which unfastens and separates loose bark effectively. This kind of mill barking offers several benefits: the bark can be used as a fuel in power boilers or gasification, wood logs are more easily cleaned from sand, bark, and other impurities for the chipping and pulping process, and the harvesting capacity is increased. The rules of wood log storage times still remain the same. However, another side of the coin is that biomaterial is removed from forest and this must be balanced by fertilizers.

The wood log chippers have developed over the years. Chip quality after chipping has improved remarkably. A new challenge for chipping is the continuously shrinking diameter of the logs: the chip quality can be maintained but the capacity is lost, or vice versa.

There can be as much as several percentages of bark residuals after forest debarking. In chipping, bark residuals are loosened, causing chip screening difficulties. Over the years, the importance of controlling the chip size distribution has been recognized. Different types of gyratory and disc screens have been developed for chip screening. A new system to separate oversized chips and fines from the chip flow is the impulse in chip screening.

It is quite normal that pulp mills are using several eucalyptus species as their raw material. Different species behave differently in the pulping process. The wood yard and its operations are a part and parcel of the pulping process. In many respects, the chip quality dictates the quality of the cooking result and creates the preconditions for further successful pulp treatment steps and consumptions. The optimum way would be to treat each of the wood species separately to obtain the best suitable quality for processing. Then each wood species may need an own storage and chip blend prepared after the chip piles.

Cooking process

Until the 1950’s, the only cooking method was the batch cooking method. After that, the development of continuous cooking started. 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. Today the dominant pulping method for eucalyptus pulp is continuous cooking. Figure 3 illustrates the development steps of the continuous digester.
Figure 3. Development steps of the continuous digester

The first digesters had a chip and cooking chemical feed to the digester, heating to cooking temperature, cooking, and discharge. Their capacities were low, 100…300 admt/d. The first digesters were for softwood and, due to the high outlet temperature, the pulp strength quality was lost. One step forward was to cool the pulp by liquor displacement in the digester bottom before discharge. This made the cooking method acceptable for softwood pulping. The next step was to continue the pulp cooling displacement to digester washing, the so-called Hi-heat washing. Hi-heat washing zones were continued up to 4 hours in retention time. Under the best conditions, the long digester washing corresponded to the washing efficiency of 2…3 drum washers. When production capacities increased, long digester washing made the digester geometry unfavorable from the cooking process point of view and, therefore, the modern digester has a short washing zone only. Figure 4 shows the development of the digester geometry.
There are single-vessel and two-vessel digesters. The two-vessel digester system consists of a separate impregnation vessel and digester vessel whereas the single-vessel digester system has the required impregnation on top of the digester. For eucalyptus cooking, mainly single-vessel cooking systems are used.

In continuous cooking, hydraulic and steam phase digesters are also used. The difference is that the hydraulic digester is completely filled and pressurized by cooking liquor; the steam phase digester is pressurized and heated by steam.

There has been continuous development in the cooking unit operations. Figure 5 shows one typical example of the modern cooking system. The basis and precondition for a successful cooking process is efficient air removal from the chips. Chip feed to the digester can be carried out by a conventional high pressure feeder or by chip pumps. Cooking liquor is impregnated into the chips in a separate impregnation vessel or on top of the digester. Wood chip column heating, chip bed packing and movement are controlled by liquor flows through the chip bed.

Heat economy has become more and more important in the cooking system. Nowadays, the cooking system is often integrated to the evaporation and to the rest of the fiberline to reduce the overall steam consumption.
Figure 5. Typical example of the modern cooking system

Until the 1980’s, the cooking systems, both batch and continuous, were based on the conventional cooking method which means that the entire amount of the cooking liquor is charged at the beginning of the cook. There were no chemical or dry solids profiling during the cook. At the beginning of the 1980’s, the four rules for modified kraft cooking were published /1, 2/.

- The alkali concentration must be controlled – decreased in 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 at the end of the cook.

Later research has proved that some of these rules are more relevant than others depending on the raw material used.

The modern cooking systems are generally following these rules. Suppliers have developed and modified their solutions specifically for eucalyptus. The result of extensive research and development work has been:

- Pulping yield has increased/wood consumption decreased substantially.
- Power and steam consumptions have decreased.
- Pulp bleachability has improved and pulp strength increased.

Bleaching process

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, brownstock oxygen delignification, the oxygen reinforced
alkali stage, and peroxide as a bleaching agent were adopted in bleaching. Sequence chlorination was developed to solve the pulp quality problem caused by the increasing process closure and elevated pulp temperature in chlorine bleaching. Kappa number before bleaching was between 14 and 18 and the total active chlorine consumption up to 60-70 kg/adt. Pulp brightness was typically between 88 and 90 ISO. Since then, a dramatic decrease in chemical consumptions has occurred (Fig. 6).

Bleach line production capacities were limited to 1500 adt/d due to limited equipment capabilities. At the beginning of the 1980's, medium consistency technology was developed and in many respects this technology has opened up new opportunities in fiberline unit operations and development. Medium consistency pumping enabled an increase in the pumping volume and head, and high shear mixing improved the bleaching chemical homogeneity in the pulp. Vacuum washers were commonly used for pulp washing in bleaching. Diffuser bleaching and displacement bleaching systems were also developed. This period when the efficiency of pulp washing and chemical mixing became increasingly important passed by quickly. Fresh water was mainly used for pulp washing together with a split or jump flow principle of filtrates. Water consumption and effluent volumes from bleaching have decreased from 40 to below 15 m³/adt.

At the end of the 1980’s, pulp mill effluents and organic chlorine compounds in effluents became a hot topic. This was followed by an intensive bleaching research period. The first target was to move away from the use of elemental chlorine to the 100% use of chlorine dioxide. This bleaching technique was called ECF bleaching. The next target was to also take out chlorine dioxide from the mill process and transfer to the TCF bleaching technology. Thanks to research and development activities, oxygen delignification was enhanced, peroxide bleaching was intensified, and the ozone bleaching technology was industrialized at the beginning of the 1990’s. Some mills introduced the enzymatic pre-treatment of pulp. Peracetic acid (PAA) and molybdate (PMo) can be used as well, especially in TCF bleaching.

The development work that was conducted made it possible to bleach kraft pulp to full

Fig. 6. Active chlorine consumption in eucalyptus bleaching. Brightness target level 90 ISO
brightness using TCF bleaching. The total production economy of fully bleached pulp with TCF technology does not yet meet the total economy of ECF technology. However, the use of oxygen, peroxide, and ozone in modern ECF bleaching sequences has been established. These types of sequences are called light ECF sequences. Thanks to the abandonment of chlorine and the new way of using peroxide and oxygen, the AOX in bleach effluent has been reduced dramatically (Fig. 7).

![Graph of AOX in bleach effluent]粉碎

Fig. 7. AOX in bleach effluent. Brightness target level 90 ISO

One of the most significant innovations in decades in the pulp bleaching technology is the discovery of HexA removal from pulp /3, 4/. Brightness reversion in bleached hardwood pulp, especially in eucalyptus pulp, was a problem as long as the HexA was found to be a major reason. Simultaneously, bleach chemical consumptions were reduced dramatically.

ECF bleaching is a dominant concept, but there are several variations in the way of building the bleaching sequence. In specifying the bleaching sequence, various factors such as target brightness, the chemicals to be used, costs, and emissions must be kept in mind. With eucalyptus pulp, the basic starting point is almost invariably a high HexA content. Preferably, the bleaching sequence should be started with the removal of HexA. With a brightness target of 91-92+ ISO, four-stage bleaching (DA-EP-D-P) 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, alone or combined with chlorine dioxide. Its advantageousness must be assessed separately in each case taking the energy price and pulp quality requirements into account.

Recent mill experiences have shown that pulp washing is very important in terms of the end result of bleaching /5/. Especially important is pulp cleanliness in the first stage of bleaching. The uncleanliness may originate in oxygen stage washing or consist of circulating bleaching impurities. Research has shown that the COD that comes to bleaching together with the pulp and the COD circulating in bleaching have a detrimental effect. The effect of the COD originating in the Do stage is especially detrimental. It increases the chemical consumption and deteriorates brightness development and may even stop it. Figure 8 presents the effect of the D100 stage (100% chlorine dioxide) and post O2 stage filtrates on the result of the D100-Eop.
The results show that the COD affects both kappa number and brightness. In this case, the additions of 10 kg/adt COD from the post O$_2$ stage had an influence of one brightness unit. The addition of 8.5 kg/t COD from the D$_{100}$ stage, on the other hand, decreased the brightness by more than 3 units.

Bleaching is the main water consumer and effluent generator in a pulp mill. The continuous target is to reduce water consumption and effluent flows. How then shall the water consumption in bleaching be lowered if the consequence is a clear increase in the consumption of bleaching chemicals and a brightness ceiling? The solution is fractional washing /7/. The first stage of bleaching is maintained clean and the filtrates in the subsequent stages are circulated fractionally. The COD level of the bleaching stages will increase to some extent, but this can be compensated through a slight increase in the chemical dosage and the brightness ceiling can be prevented. An example is shown in figure 9. Total COD output in bleach effluent is 20-28 kg/adt depending on the brightness target and the closure of the filtrate system, among other things.
Recent mill results from a state-of-the-art eucalyptus pulp mill

Fray Bentos

The Fray Bentos pulp mill has now been running for more than three years (Fig. 10). This mill has proven that with intensive training, good co-operation with suppliers, and a strong organization, an unprecedented learning curve and design capacity can be reached.

The wood comes to the mill from the plantations as debarked logs selected according to the eucalyptus species. The wood logs are washed in washing drums and fed to two parallel chipping lines. The wood chips are stored in two chip piles according to species. Chip screening is located before cooking.

Excellent chemical consumption figures and pulp quality parameters have been achieved. Cooking kappa is 18 and the kappa into bleaching 10-11. The bleach sequence represents state-of-the-art technology, which can meet the requirements for high pulp quality, low chemical consumptions, and low effluent emissions. The ClO$_2$ consumption as active chlorine is below 20 kg/adt at the brightness of 91% ISO /8/.
What are the developing trends for the future pulp mill?

The present trends – to reduce the total production cost and improve sustainability – will be continued and emphasized in the future. The determination of the carbon and water footprints will also be used in the pulp and paper industry. This will demand further development in environmental issues, raw materials, and power and energy usage. There are no real new process technology entries expected in the near future. The soda cooking process has been developed to an industrialized phase, but it has not yet been adopted widely for economical reasons. Process options where wood sugars could be used as biofuel have been under intensive research. It is quite possible that a kraft pre-hydrolysis process will see a renaissance. Products extracted in the pre-hydrolysis stage will be recovered for further processing.

In recent years, potentials of nano and micro fibers have been under fundamental research. There is a variety of products where this new fiber based material is suitable. It may bring special requirements on the pulping process, but these are still unknown.

Energy and power efficiency will be a critical theme in existing and future pulp mills (Fig. 11). The target is to maximize the energy output from the biomass, the wood raw material used, by reducing the power and energy consumption in pulp production and improve the efficiency in energy generation. The goal is to increase the electricity net sales. The tools for reaching this goal are:

- Development and utilization of new technology and equipment
- Process integration
- Simplification of processes
- Reduction of water consumption
- Replacement of fossil fuels by biofuel
- Integration of the pulp mill with biorefinery production.
Ten to fifteen years ago, the eucalyptus fiberline looked quite different from what it looks today. It is easy to say that in another ten to fifteen years, it will again be different. But in what way? Through the cook it is possible to affect the amount of HexA generated and the pulping yield, through multi-chemical or a new bleaching agent the length of the sequence. The focus of research lies in this area.

The cost of wood is generally the main production cost. There are several research efforts going on to find process alternatives for a further higher pulping yield (Fig. 12). The optional ways which are under study are:

- Wood logistic and preparation for pulping
- Improve modified cooking procedures
- Cooking additives
- Improve cooking chemistry
- Increase the cooking kappa
- Reduce reject amount
- Intensify oxygen delignification
- Improve bleaching chemistry
It is very likely that pulp and paper mills will get plants where wood based biomass is treated for industrial or household usage in their neighborhood. Many facts support this development: wood supply, logistics, the availability of steam and power. The optional plants can be gasification of biomass, pelletizing, or the utilization of hemicelluloses from pulping.

An important area will be to improve the environmental image of the pulping industry. Air and water emissions and solid waste are in focus. The main effluent discharge from pulp mills comes from bleaching. The bleach sequences have been renewed and the effluent parameters may need to be reevaluated. Closure of the filtrate loops inside the bleach plant is a reality today but recycling to recovery is still an open question. Recycling of filtrates leads rather invariably to disadvantages in process economy and pulp quality. Separate treatment of bleach filtrates by means of evaporation or other techniques has not yet broken through.

The reuse of purified process water in the fiberline has shown promising results in laboratory studies /9/. Figure 13 shows schematic filtrate coupling alternatives when using purified effluent in the fiberline.
A great deal of development work has already been done in the modeling and simulation area. Bleach reactions in each bleach stage and soon through the whole bleach process can be modeled and simulated. This may leave the development and optimization of bleach process systems with much less laboratory work.

Conclusions

Over the years, different driving forces have been used to accelerate the development of the chemical pulping process. However, investment and production costs besides the environmental aspects 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 to energy generation. Possibilities to produce completely new products are also under intensified research and development.

The present trends – to reduce the total production cost and improve sustainability – will be continued and emphasized in the future. The determination of the carbon and water footprints will also be applied in the pulp and paper industry. This will demand further development in environmental issues, raw materials, and power and energy usage.

Overall, the forest industry image needs a raise in the future. It is important technology-wise to start in the forests and end with the final product, and to involve intelligent and motivated people in this development work.
References


