

2.1 Wood fibre sources

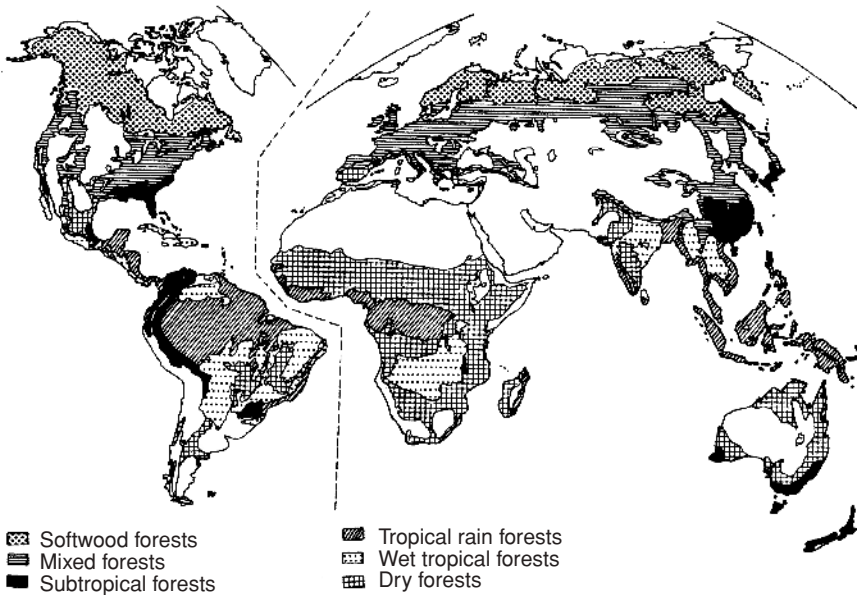
The main natural fibre source worldwide comprises various softwood and hardwood species. The softwood forest belt of the northern hemisphere covers Russia, the Nordic countries, Canada, and parts of the northern United States, see Fig. 2.1. The main softwood species of these forests in Asia and Europe are larch (*Larix sibirica*) in eastern Siberia, Scots pine (*Pinus silvestris*) and Norway spruce (*Picea abies*). In North America some other species occur, for example white and black spruce (*Picea glauca* and *P. mariana*), balsam fir (*Abies balsamea*), and jack and lodgepole pine (*Pinus banksiana* and *P. contorta*). In the USA hemlocks (*Tsuga* sp.) and Douglas fir (*Pseudotsuga* sp.) also occur, and pines growing in the west and south also deserve mention. These ‘Southern pines’ comprise among others *Pinus taeda*, *P. elliottii* and *P. palustris*.¹

The most important hardwood species of the mixed forests south of the true softwood forest belt are birch (*Betula* sp.), aspen (*Populus tremula* and *P. tremuloides*), oak (*Quercus* sp.), gum (*Nyssa* sp.), maple (*Acer* sp.) and beech (*Fagus* sp.).¹

In addition to these naturally grown wood species, there are some cultivated softwood and hardwood species that should be mentioned. The Radiata pine (*Pinus radiata*) is grown in Australia and New Zealand. A number of eucalyptus species are also cultivated in many subtropical areas and play an important rôle in the pulp and paper industry. *Acia* sp. is currently cultivated, and various nonwood fibrous raw materials representing mainly the *Gramineæ* family, for example cereal straws (rice, wheat etc.), sugar cane bagasse and bamboo form a significant fibre source not yet fully utilised.

2.2 Pulping methods

Chemical and mechanical pulping of wood raw materials dominate the paper and board industry worldwide, although other fibrous materials



2.1 Global forest belts.²

called nonwood are used in certain countries. The most common chemical pulping process is the Kraft pulping process, which is an alkaline process utilising sodium hydroxide and sodium sulphide as active delignification chemicals. The kraft pulping method is able to process a variety of fibre raw materials including both softwood and hardwood raw materials.

Another family of delignification methods comprises various sulphite pulping processes actually based on sulphur dioxide with varying cation, liquor pH and cooking temperature. The acidic calcium bisulphite pulping process spread all over the world, but because its use was limited practically to spruce wood only, and because the chemical regeneration produces insoluble calcium sulphate, its use has been limited. Later, so-called soluble cations, for example magnesium, sodium and ammonia, were introduced to increase the liquor pH from 1–2 typical for the conventional calcium bisulphite process up to 5 for the magnesium bisulphite process, and to even alkaline pH levels for the sodium bisulphite/sulphite processes.

Acidic bisulphite processes and modified two- or three-stage sodium sulphite processes, for example the Rauma process, played an important rôle as dissolving pulp methods for a long period of time, and the acidic bisulphite process is still valid. The main feature of the multistage processes was to alternate between more or less acidic bisulphite/sulphite and alkaline

stages. A process could start or end with the alkaline stage, which latter alternative led to a kind of alkaline extraction to diminish the residual hemicelluloses.

2.3 Dissolving pulp processes

2.3.1 Introduction

The pulping process has to dissolve the main bulk of the lignin and modify the residual lignin for successful bleaching. Bleaching then has to remove this residual and increase the pulp brightness and cleanliness. The final result should be a technical cellulose as free as possible from lignin and hemicelluloses as well as extractibles. The α -cellulose content of the final dissolving pulp may normally vary between 90 and 96%, dependent upon the pulping and bleaching processes.

2.3.2 Bisulphite processes

Sulphur dioxide-based pulping processes can be used to produce pure dissolving pulp grades for chemical cellulose. The final result is very much dependent upon liquor pH, bound and total SO_2 contents of the liquor, the time taken to reach cooking temperature and the maximum temperature. The solubility of the cation base determines first of all the pH level, which typically is 1–2 for acidic calcium bisulphite pulping processes, 4.5 for magnesium bisulphite processes and finally up to 14 for sodium sulphite processes because of the high solubility of sodium salts in water. The bound SO_2 must be about 1% and the total SO_2 must be 7–10% of the liquor to guarantee optimum sulphonation and to prevent lignin condensation reactions. Sulphonation begins at temperatures exceeding 110°C , and normally the maximum temperatures are kept at 140 – 160°C depending on the acidity of the liquors; acidic pH requires lower temperatures, while bisulphite pH allows some higher temperatures.^{3,4}

Dissolving pulp grades should practically be lignin free and contain only certain low quantities of hemicelluloses. This can be achieved for spruce and hardwoods under the conditions mentioned above, but as sulphonation of the α -carbon in the side chain of the phenyl propane (lignin) unit forms strongly acidic sulphonates, the pH may be reduced and simultaneously increase the risk of lignin condensation. Condensation is evident particularly when the SO_2 level is low and if phenolic substances other than lignin are available. Pine heartwood contains a type of stilbene called pinosylvine (3,5-dihydroxy-*trans*-stilbene), which is thought to be partly responsible for lignin condensation, and therefore pines are normally not recommended for sulphite pulping processes.^{3,5}

2.3.3 Sulphite–soda processes

These processes are worth mention, although they are not in use anymore. These normally two- or three-stage processes were conducted in specific steps for different tasks. Thus the Sivola (sulphite–soda) and the Rauma (bisulphite–sulphite–soda) processes were aimed at performing the delignification in the sulphite stage(s), because the soda stage finally had to control the level of α -cellulose content and viscosity. These levels depended on pH, temperature and time, which preferably were 5–10, 145–180°C and 1–4 h, respectively.³ The alkaline soda stage was thought to achieve some of the extraction which normally takes place in the alkaline stage of the bleaching sequence. The Rauma process delivered α -cellulose contents up to 96% easily.

2.3.4 Prehydrolysis Kraft processes

Because the Kraft pulping process dominates worldwide as a producer of paper and board pulp grade, it has been interesting to develop the current pulping concept with prehydrolysis before the Kraft cooking stage so as to produce dissolving pulp grades. The prehydrolysis stage is conducted by steaming the wood chips or cooking them in water at 140–170°C, or alternatively by treating the wood with some dilute mineral acid at 110–120°C. The steam or water treatment cleaves acetyl and formyl groups from the wood thus forming acetic and formic acids, which leads to pH 3.5 in the wood. Hence, true acid hydrolysis starts depolymerising the wood components, reducing the wood mass by 5–20% dependent on hydrolysis time and temperature.^{3,6} Up to half of the softwood hemicelluloses, mainly glucomannans, dissolve during the hydrolysis, but the lignin remains almost intact, while correspondingly significant amounts of hardwood lignin dissolve. By prolonging the hydrolysis, cellulose may be affected, resulting in a low cellulose yield and a more condensed lignin. This implies difficulties in the subsequent Kraft delignification, because more effective alkalis and higher temperatures would be required.³ The optimum α -cellulose content (95–96%) for beech (*Fagus silvatica*) was obtained at a wood loss around 20–22% in the prehydrolysis stage.⁷ Increased prehydrolysis and Kraft cooking temperatures resulted in shorter residence times in these steps for eucalyptus in a pilot plant producing 11–16 tonnes per day, and simultaneously the viscosity was reduced significantly at a comparable level of α -cellulose content.⁸ Further, under comparable overall conditions pine and birch produced the same α -cellulose content (slightly below 96%), while eucalyptus provided α -cellulose slightly above 97%. The viscosities were about the same for the hardwood pulps, but significantly higher than the pine pulp viscosity.⁸

2.3.5 Bleaching technology

2.3.5.1 Introduction

Pulp bleaching aims to remove the residual lignin. This can be done successfully by application of oxidative bleaching agents to depolymerise the highly condensed residual lignin. Moreover, to achieve high final α -cellulose contents, removal of the hemicelluloses* is also required. Further, the bleaching improves pulp purity, that is it decreases the extractives content, and particularly improves the pulp brightness. But bleaching does not significantly affect the cellulose properties, for example degree of polymerisation, viscosity and so on, whose levels are mainly determined in the cooking stage.

2.3.5.2 Elemental chlorine-free bleaching of sulphite pulps

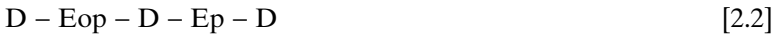
The bleaching sequence is performed in two main stages, an initial stage, where delignification mainly takes place, and a final bleaching stage, where brightness is improved. According to a Nordic Kraft mill survey there are a variety of elemental chlorine-free (ECF) and totally chlorine-free sequences mainly designed for paper pulp grades; the survey emphasises the current development trends in bleaching processes.¹¹ Delignification in modern bleaching sequences is conducted in the form of ECF processes by application of chlorine dioxide followed by alkaline extraction, which might be strengthened by oxygen and/or hydrogen peroxide. Both oxygen – after being reduced – and hydrogen peroxide produce hydroperoxide ions in an alkaline system, according to the following equilibrium reaction:



The hydroperoxide ion is considered to be responsible for a number of lignin depolymerisation and bleaching reactions, which initially involve attachment of hydroperoxide ions to various types of phenoxy radicals thus forming intermediate organic hydroperoxides. Subsequent reactions cause side chain elimination and opening of the aromatic ring to form carboxyl groups.¹² The first type of reaction contributes to delignification and the second type to bleaching and ‘hydrophilisation’.

* Chemical pulp fibres dissolve partly when treated in a 10% NaOH solution, but leave a residue (denoted by α -cellulose or R_{10}). The dissolved part (S_{10}) contains low molecular weight cellulose (β -cellulose) and hemicelluloses (γ -cellulose). The last-mentioned can be determined as the substances dissolved in 18% NaOH (S_{18}), and hence the β -cellulose is the difference between the alkaline soluble materials ($S_{10} - S_{18}$).^{9,10}

Hydrogen peroxide is subject to decomposition caused by heat, the presence of transition metal ions and radical reactions, where hydroxy and hydroperoxy radicals are involved.¹² Thus, for effective utilisation of the hydrogen peroxide, the temperature should be limited to 110°C and acid washing or chelation should be introduced to eliminate Cu^{2+} , Mn^{2+} and Fe^{2+} particularly.¹³ Typical ECF bleaching sequences for full bleaching of softwood pulp, Equation [2.2] and hardwood pulp, Equation [2.3], respectively, may appear as follows:



where D stands for chlorine dioxide and E for alkaline extraction, while the subindices o and p indicate strengthening by oxygen and hydrogen peroxide, respectively. The short sequence [2.3] might be useful for bleaching dissolving pulps. It has been demonstrated for dissolving pulps made from spruce wood by the acidic bisulphite process that replacement of the conventional bleaching sequence CEHH by D/CEHH (C for chlorine and H for hypochlorite) – where part of the chlorine is substituted by chlorine dioxide – led to some higher α -cellulose content, but a lower filtration value, R_v .¹⁴ Acidic Na bisulphite pulps made from softwood (type A) were bleached by CEH and CDEH, and it was revealed from the compiled results that CEH pulps had more low-molecular cellulose (given by $S_{10} - S_{18}$, which represents substances soluble in 10% and 18% NaOH, respectively), and a lower degree of polymerisation (DP) than the CDEH pulps.⁹

2.3.5.3 *Totally chlorine-free bleaching of sulphite pulps*

Totally chlorine-free (TCF) bleaching is performed without any chlorine chemicals whatsoever. Instead the delignification part of the process may be effected by ozone followed by alkaline extraction as outlined above. The later part of the sequence may also contain ozone or peracid stages in addition to peroxide stages, but since sequences evidently are developed for specific needs, they do not look the same, mainly because the chelation now plays a very important rôle in the bleaching sequences.¹¹ Acidic bisulphite pulp made from spruce resulted in the same α -content, but with a clearly higher DP and a lower R_v value, when the bleaching was changed from D/CEHH to a pure TCF sequence, EopPEP.¹⁴ Acidic Na bisulphite pulp of softwood (type A) – with an α -cellulose content level around 97% – produced higher viscosity and DP, but definitely lower brightness, when the bleaching system was changed from DPZE (Z for ozone) to a pure TCF system PZE.⁹ For beech, acidic bisulphite pulp of κ number 6–7, changing

the bleaching process from CEHH to EopPP provided about 1% unit lower α -cellulose content and higher R_v value, while viscosity became slightly higher.¹³ Acidic bisulphite pulp of birch wood maintained the α -content, brightness and viscosity roughly at the initial level, when the DEH bleaching sequence was changed to OH, where O stands for oxygen treatment (8 bar oxygen, 6% NaOH, 100°C and 1 h). The pentosans increased, but fortunately the dichloromethane extractives reduced to half of the reference level.¹⁴

2.3.5.4 Bleaching prehydrolysis Kraft pulps

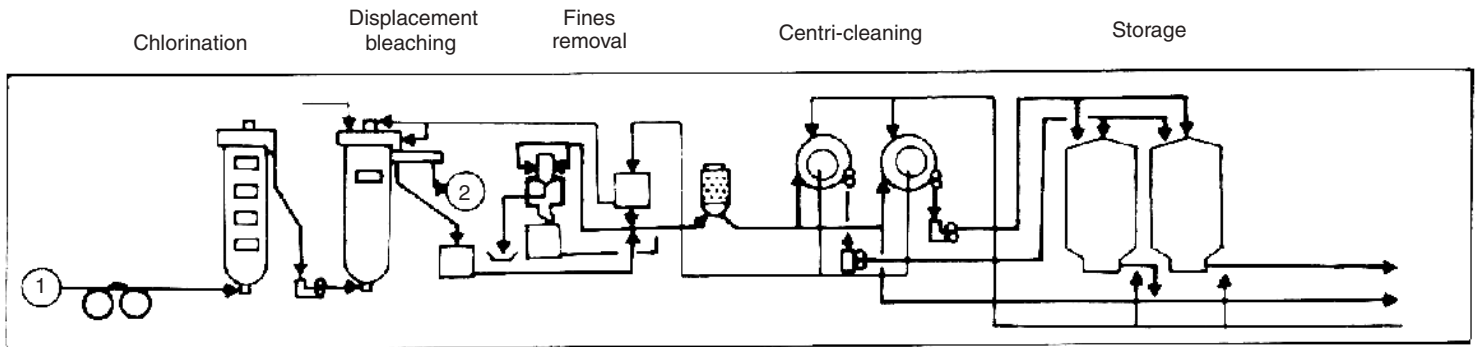
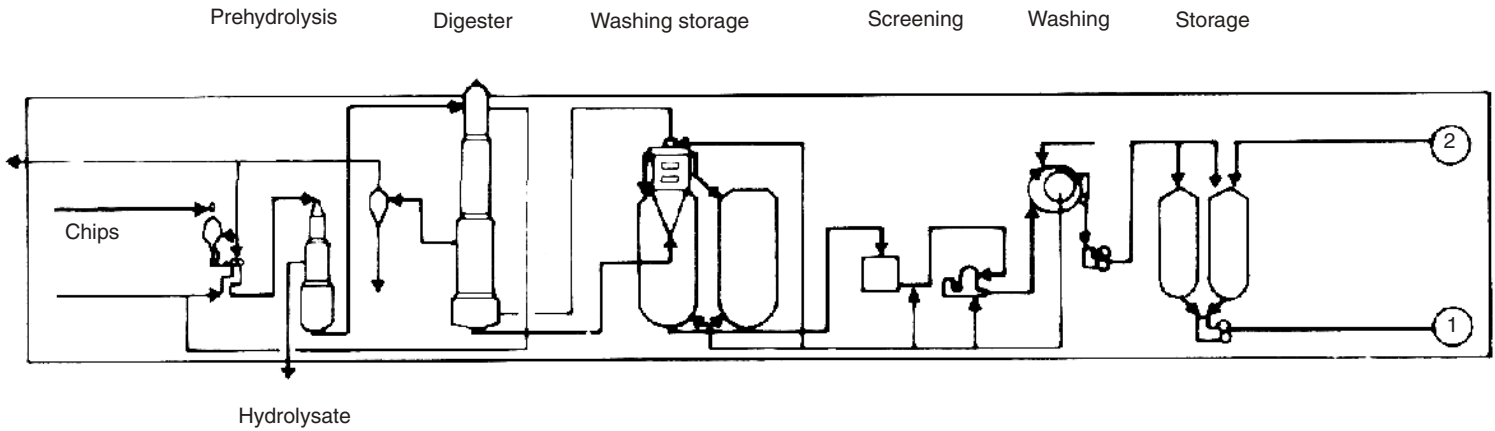
The conventional CEH bleaching sequence provided a much lower viscosity than the chlorine-free DED sequence, when applied to prehydrolysed beech Kraft pulps (see Fig. 2.2).¹⁶ Simultaneously it was found that the ECF bleaching sequence significantly improved the reactivity of the pulp, expressed as solubility in emulsion xanthation.

Oxygen treatment as a part of the bleaching sequence may reduce the pulp extractives content, as indicated for sulphite pulps.¹⁵ This was also tested on birch prehydrolysis Kraft pulps by application of various sequences. DEoDH was replaced by ODEoDH, which led to a higher α -cellulose content, a halved BOD (biological oxygen demand) discharge and a more than halved extractives content, while replacement of the short DH by ODH, changed the pulp properties only moderately, but still reduced the extractives by 30%.¹⁷

Ozone displays four mesomeric forms, and it is a dipole and acts as an electrophilic agent. It adds to aliphatic and aromatic double bonds in both free and conjugated phenolic structures, and hence forms polyoxides which after several steps finally end up as carbonyl or carboxyl groups.¹² As a consequence of this, ozone will not only delignify and bleach due to aromatic ring opening, but also attack aliphatic structures. The ozone bleaching stage should preferably be used in the initial stages of the bleaching sequence. This is because ozone, with its high reactivity and relatively low selectivity, affects cellulose fibrils which do not have much protection because of the low residual lignin content at the end of the bulk delignification or at the end of the bleaching sequence.¹⁸

2.4 Environmental assessment

The acidic bisulphite process is applicable to spruce wood and a number of hardwoods, mainly beech, eucalyptus and birch. However, owing to difficulties separating spruce and pine, and because of the relatively high (neutral) extractives content of many hardwoods, there has been increasing interest in using alkaline pulping processes for production of dissolving



2.2 Typical prehydrolysis Kraft pulping followed by modern displacement bleaching.⁴

Table 2.1 Development of bleaching sequences applied to soft- and hardwood acidic bisulphite and hardwood prehydrolysis Kraft dissolving pulps

Wood material	Pulping method	Bleaching sequence	Year	Reference
Spruce	Acidic bisulphite	(C + D)HEDEH ^a	1983	4
		CEHD	1977	19
		ECHD ^b	1977	19
		EopPEP	1992	14
Softwood (A)	Acidic bisulphite	DPZE	1994	9
		PZE	1994	9
Beech	Acidic bisulphite	CEHH	1992	14
		EopPP	1992	14
Birch	Acidic bisulphite	OH	1976	15
Beech	Prehydrolysis Kraft	CEHD H	1968	7
		DED	1986	17
		ODEoDH	1986	17
		ODH	1986	17
Eucalyptus	Prehydrolysis Kraft	OOAZQP	1999	20

^a High grade viscose pulp. ^b BOD discharge 60% lower than for CEHD.

Key: C = chlorine, D = chlorine dioxide, H = hypochlorite, E = alkaline extraction, P = hydrogen peroxide, Z = ozone, O = alkaline oxygen, A = acidification and Q = chelation; subindices: o = oxygen enhanced, p = hydrogen enhanced.

pulp grades. Since the mid-1980s tremendous changes have occurred in the wood pulping industry. The entire dissolving pulp process including cooking and bleaching has been developed and often employs a soluble base in acidic cooking to ensure a reasonable recovery of the cooking chemicals. This is not possible for a Ca base and thus Mg or preferably Na or NH₄ bases should be used. The prehydrolysis Kraft process employs a common recovery process which involves black liquor evaporation and incineration in the soda vessel to generate carbonate and sulphide for final regeneration into caustic and sulphide.

The bleaching sequences have been shortened in length, and they have become more or less chlorine-free, and in certain cases employ sequences containing oxygen, ozone and/or hydrogen peroxide stages. This implies that modern dissolving pulp bleaching sequences well may give an absorbable organic halide (AOX)-free discharge. Application of oxygen before the bleaching sequence as a rule reduces the discharges, particularly BOD, in direct proportion to the delignification or treatment in general. Table 2.1 indicates the dramatic changes in bleaching dissolving pulps made from soft- and hardwoods by application of acidic bisulphite and prehydrolysis Kraft methods.

2.5 Dissolving pulp production

2.5.1 Market share

Since the mid-1980s great changes have occurred in wood raw materials and the pulping processes used, as well as in dissolving pulp production. In 1985 the hardwood proportion made up less than 20%, but now is almost 60% of the total usage of dissolving pulp grades. Simultaneously prehydrolysis Kraft pulping increased and now produces about 40% of the total dissolving pulp worldwide.¹⁸ Total production of dissolving pulp was about 4.8 million tonnes in 1978, and in 1998 about 3.5 million tonnes.¹⁸ The main trend is towards a decrease, but after reaching minimum production in 1996 at about 2.8 million tonnes, it seems that some increase will take place.

In 1978 the entire world pulp production including all pulp grades was 127.7 million tonnes.²¹ In comparison with world pulp production, the proportion of dissolving grades appeared as 3.7%. In 1998 the corresponding world pulp production was 175.5 million tonnes, and consequently the dissolving pulp proportion was only about 2%.²² However, the situation is different if the chemical dissolving pulp is compared to the world chemical pulp production of 123.6 million tonnes in 1998, which would provide a share of 2.8% for the dissolving pulp grades.

2.5.2 Pulping economy

The development of the dissolving pulp market will, of course, be dependent on a number of factors, that is, raw material and particularly pulpwood prices, textile fibre demand and prices, production of natural fibres and particularly cotton, and finally production of synthetic fibres, for example polyesters.

The wood raw material costs are projected to be 31% of the total costs including variable, fixed and capital costs for a 500 000 tonnes per annum softwood chemical pulp mill.²³ The unbleached softwood and hardwood Kraft pulp yields are about 47% and 53%, respectively, calculated on the charged wood raw material, and as the high-grade dissolving pulp yield is well below 40%, it is understandable that the wood costs are significant for the dissolving pulp methods. The wood 'working-up' value when used in the pulping process may be computed by Equation [2.4], which gives the wood market price (P_w) in relation to the oil (energy) market price (P_o):²⁴

$$\frac{P_w}{P_o} = \eta \frac{P_p}{P_o} + (1 - \eta) \frac{H_B}{H_O} \quad [2.4]$$

where η stands for the pulp yield, P_p for pulp market price, H_B for energy content of the black liquor dry substance, and H_O for the energy content of

Table 2.2 Wood value deficit, expressed by model equation [2.4] as a function of the ratio between the prices of market pulp and fuel oil, P_p/P_o , varying from 2 to 8. The deficit is due to differences in pulp yield, which for hardwood Kraft pulp was put at 53% and for hardwood prehydrolysis Kraft pulp at 35%. Hardwood density was put at 500 kg/m³

P_p/P_o (tonnes oil/ tonnes pulp)	P_w/P_o (tonnes oil/ tonnes wood)	P_w/P_o (tonnes oil/ m ³ wood)
2	0.27	0.14
4	0.63	0.32
5	0.80	0.40
6	0.99	0.50
8	1.59	0.80

the fuel oil considered. Because the energy values are about constant, 20 and 40 GJ t⁻¹ respectively, the ratio $H_B/H_O \approx 0.50$ may be considered to be a material constant. If a reasonable value is taken for the ratio P_p / P_o 5:1, and the hardwood Kraft pulp yield of 53% and the prehydrolysis kraft pulp yield of 35% are considered, the following 'oil equivalent' values would be achieved: 2.88 and 2.08 tonnes oil/tonnes wood for Kraft pulp and prehydrolysis Kraft pulp, respectively. This means that 0.8 tonnes oil/tonnes wood or 0.4 tonnes oil/m³ wood is the value deficit due to the lower pulp yield, which must be considered in the dissolving pulp production to balance economically. This can be done by a decrease in the wood price or an increase in the dissolving pulp price, see Table 2.2. The use of dissolving pulp may thus be successful only where wood market prices are low and if the demand for pulp pushes the pulp market price up.

2.6 Future of dissolving pulp processes and pulps

As outlined above, the future of dissolving pulp processes and pulp production is not easily predictable; the long-term trend has been decreasing steadily, although there is a slight increase in dissolving pulp production at the moment. Better economy would improve the probability of the dissolving pulp methods surviving, but there is no definite way of making the pulping process cheaper. Better utilisation of the wood raw material and a cheaper pulpwood could improve the situation; the current acidic bisulphite and prehydrolysis Kraft pulps provide a dissolving pulp yield of about 35% only, which actually means that of necessity some of the cellulose material has also been removed during pulping, because the cellulose content of common wood raw materials is about 40%. It will thus be a task for the future to develop methods of producing high-quality celluloses, let's say

with an α -cellulose content around 96–98%, but at a significantly higher pulp yield than 35%.

Modern dissolving pulp processes (e.g. Visbatch, which is a displacement method) seem to employ the best of pulping technology including the wood raw material, and are therefore an alternative for the future.²⁰ It has been demonstrated that acidic bisulphite may produce about 96% cellulose (R_{18}) grades of eucalyptus, while the prehydrolysis Kraft process correspondingly would produce about 98% at the same yield of 35%.²⁰ Hence, there is a need for an additional alkaline step in the bisulphite process before the bleaching sequence to upgrade the cellulose to high-quality grades for acetates.

The current development of dissolving pulp processing from softwoods to hardwoods, and from acidic bisulphite to alkaline prehydrolysis Kraft methods is well motivated, as hardwoods may produce a high-grade α -cellulose pulp which is also easily bleachable with TCF sequences. The viscose process is still common, but there are new so-called direct spinning methods (Lyocell, Tencel etc.) under development that may change the prerequisites for the pulping processes and the dissolving pulp properties. Good regenerated cellulose properties, however, require high cellulose activity, high α -cellulose levels, narrowly distributed cellulose DP and hence a well-controlled solution viscosity.

The question is whether other possible dissolving pulp concepts, for example ASAM (methanol containing alkaline sulphite), prehydrolysis soda-AQ, IDE (ethanol containing soda), Milox and so on would provide considerable benefits. This may be clarified only by doing further research work.

Comparison of some of the alternative dissolving pulp technologies with Visbatch would be interesting, because this process is an actual process and it seems to work according to modern displacement pulping principles. The chips are neutralised after the prehydrolysis stage with white and black liquors, which is followed by a white and black liquor hot displacement delivering black liquor to the chemical recovery. This is followed by cooking and finally cold displacement with washing filtrate before the discharge. The hot black liquor coming from this cold displacement is then used in the next cook.²⁰

The ASAM cooking concept is an alkaline sulphite process catalysed by anthraquinone and finally strengthened by methanol, whose chemical designation forms the short name. When started with a common prehydrolysis prior to the digestion the process provides high-viscosity dissolving pulps in high yields of about 40%. Beech, however, constitutes an exception, and it seems to require a weak sulphuric acid prehydrolysis to reach the high yield level, although simultaneously the R_{10} level unfortunately reduces below 90%. Compared to Kraft this process requires a lot more total

cooking chemicals, 25% on o.d. wood, expressed as NaOH (but in the form of Na_2SO_3 and NaOH).²⁵

A modern approach to pulping involves sulphur-free pulping chemicals for several reasons. The base for these processes is the caustic soda which needs to be catalysed by, for example, anthraquinone and further strengthened by simple alcohols.^{26,27} The first mentioned method starts with prehydrolysis including methanol, but for quality reasons the subsequent alkaline cooking had to be stopped at κ number 30.²⁶ The other method called the IDE concept is an alkaline method starting with a strong impregnation followed by delignification and finally extraction, which is a special kind of ethanol washing effectively to remove all residuals.²⁷ The bleached IDE pulp made from birch wood was tested as such for dissolving, and it was suitable at least for sponges; the pulp had an R_{18} value of about 95% and a high viscosity.²⁸

Finally, there are acidic pulping methods aimed at dissolving pulp purposes. Mention should be made of the Milox concept, which is based on formic or acetic acid and hydrogen peroxide involving use of peracids.^{29,30}

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