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Sulfate cooking – now a dominating wood pulping process, still under further development

Göran Annergren and Ulf Germgård
Department of Technology and Chemical Sciences
Karlstad University
SE 651 88 Karlstad, Sweden

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Summary

Sulfite pulping was earlier the dominating pulping process but sulfate pulping (or kraft pulping) is today the most important pulping process for the production of both unbleached and bleached chemical pulps and of unbleached high-yield pulps. One important reason for this development of the kraft process has been its ability to efficiently use different wood species, in particular hardwood species, primarily for the production of bleached hardwood pulps. The latter grade has become a strong competitor to bleached softwood sulfite pulps.

This paper deals with the significance of a high sulfidity in the cook for a high bleached pulp quality in both continuous and batch systems, as a starting-point for a high degree of closure of the mill system, and of an efficient use of available hardwood resources.

Introduction

Cooking of cellulose-containing fibrous material in alkaline media, in order to produce fibers for papermaking, has been practiced for a very long time (in its very beginning mainly on materials easy to process), at first cooking with lime, then with sodium hydroxide and eventually also softwood with the cooking in a mixture of sodium hydroxide and sulfide (1), as well as such a mixture with a high share of sulfide (2, 3), the process then called kraft pulping, which to a very high extent has been applied in Sweden on the pulping of wood. The word kraft refers to strength in both German and Swedish and relates to the high strength of paper made from this kind of fibers, then produced from softwoods.

An interesting advantage for kraft cooking of wood has been that the process made it possible to cook also a great many different wood species, which were otherwise considered too difficult to process (3-5), in Sweden pine (*Pinus silvestris*), for a long time not accepted in the early sulfite pulping industry, where spruce (*Picea abies*) was the preferred wood species. However, methods have later on been developed to pulp also pine in somewhat modified sulfite processes. But these sulfite processes have on the other hand had some difficulty in competing commercially for the pine wood with a well balanced kraft process. Later on, when kraft pulping became dominating, also spruce became an important raw material for the kraft industry, but then in considerable competition with mechanical pulping. The latter had, however, somewhat higher demands on the wood quality, so that part of the spruce wood ended up in the kraft industry anyhow, particularly after the 1960ies.

The dark color of the unbleached pulp, the difficulty to bleach the pulp to a high brightness, and the high charge of cooking chemicals have together been important obstacles in the initial

development of an effective kraft process. However, in this case it was also realized that the relatively dark color of unbleached pulp was combined with a unique strength (4, 6), so that this color in unbleached kraft paper could even give a positive impression of strength in the marketing of the paper. This gave no doubt the unbleached kraft pulp the required niche for a further development.

The Second World War needed efficient packaging of different material for transport to remote seats of war, which promoted a development in North America of packaging paper, in which case strong unbleached kraft paper was a suitable choice. The kraft pulp industry in North America had thus an opportunity to develop efficient mill concepts (with an appropriate recovery of the cooking chemicals) also for relatively large scale mill operation, which has been important in the following development of the kraft pulping industry.

The development of the kraft industry in Sweden did not have equally strong incentives during the 1940ies, and it was only at the end of the 1950ies that the production of kraft pulp became larger than the total of different kinds of sulfite pulps, cf. table 1 (7).

Table 1. Production capacity in Sweden during the period 1930 to 2000 for different kinds of pulp. The more or less continuous increase of the kraft pulps and the mechanical pulps should be noted (7).

Pulp type	Capacity, Mt/a			
	1930	1960	1980	2000
Unbleached kraft pulp	0.650	1.336	1.560	2.100
Bleached kraft pulp	0.000	0.534	4.100	5.100
Unbleached sulfite pulp	1.000	0.982	0.310	0.150
Bleached sulfite pulp	0.040	0.248	1.230	0.450
Dissolving pulp	0.050	0.370	0.200	0.100
Semichemical pulp	0.000	0.040	0.440	0.300
Mechanical pulp	0.468	1.040	2.180	3.300
Total	2.208	4.550	10.020	11.500

The production of bleached kraft pulp had a modest development up to the end of the 1950's, mainly due to patent restrictions regarding the use of chlorine dioxide in the bleaching sequence (8, 9), in that case used for the production of strong high-brightness pulps. But after these problems had disappeared in the late 1950's, a rapid introduction of new bleach plants with chlorine dioxide bleaching stages took place (8, 10).

In 1960 the production capacity of different kraft pulps in Sweden was nearly 1.9 million tons whereas that of sulfite pulps was about 1.4 million tons, of which only about 30 % was bleached. Full bleaching of kraft pulps was relatively new at that time but had still reached about 30 % of all the kraft pulps. During the second half of the 1960ies and the first part of the 1970ies a large part of the sulfite mills and some kraft mills were shut down, mainly because they were old, and it was difficult to adjust their technique to the economic and environmental challenges during that period.

An important incentive for the use of hardwood for pulp production was that the hardwoods were available at a comparatively low price since the alternatives, mainly burning for different energy requirements, at that time had a low ability to pay for the wood. But once the pulping alternative had been established, a much higher wood price was expected by the wood suppliers. And this marks a transition to more normal commercial conditions, although the investment costs were often quite high in the case of green field mill establishments. These high investment cost were, however, to a considerable extent matched by the lower operating costs in the modern mills and in general a more effective technical standard (11).

Furthermore, sulfate cooking was the natural choice for hardwood pulping to chemical pulps, in most cases followed by full bleaching, whereas sulfite pulping of the hardwoods gave only weak paper pulps, usually characterized as filler in papermaking circles and then used primarily as bleached pulp in mixtures with other bleached pulps of considerably higher strength, so that the hardwood sulfite pulp would then stand primarily for bulk and opacity of the mixture (6, 12). The hardwoods are also used for dissolving pulp production, either in acid sulfite pulping or in prehydrolysis-kraft pulping, in which case sulfite pulping is the natural choice for low alfa dissolving pulps, because of the high cellulose yield in the cooking process of these sulfite pulps (13), whereas prehydrolysis-kraft cooking has primarily been used for high alfa pulps (13-15).

Bleached hardwood kraft pulp has been established as an important competitor to bleached softwood sulfite pulps, with most papermaking properties well matching those of the softwood sulfite pulps, except for the wet strength of the web in the paper machine (8, 16, 17). And the latter can be attended to by changes of the paper machine concept as well as by some reinforcement through softwood pulp in the furnish.

Figure 1, with the types of pulp fibers produced in 2007 in the world (7), illustrates the result of the far-reaching changes that have taken place since 1960, when much of the old post-war industrial structure still remained. Of particular interest is the dominance of kraft cooking in 2007. The importance of mechanical pulps and of non-wood pulps should also be noted. And bleached pulp dominates the kraft pulp sector, in which bleached hardwood kraft pulp now is the largest category.

And bleached pulps are now to a large extent referred to as so called ECF, ECF light or TCF, elemental chlorine-free bleaching in general, with only very small amounts of chlorine-containing chemicals in the bleaching sequence, and totally chlorine-free bleaching, all usually applied after a modified and more selective kraft cook and oxygen delignification in one or two stages (18-21). This kind of classification of bleached pulp, in ECF and TCF, is, however, not unequivocally related to the ecological situation for the corresponding pulp production, since it does not include

- the balancing of the chemicals in the bleaching sequence (important for the degree of chlorination of the effluent substances),
- the volume of the mill effluent (especially in the relation to the volume of the receiving water)
- mechanical, biological and chemical treatment of the effluent before the discharge to the receiving water
- and in general the ecological conditions in the receiving water.

World production of pulp

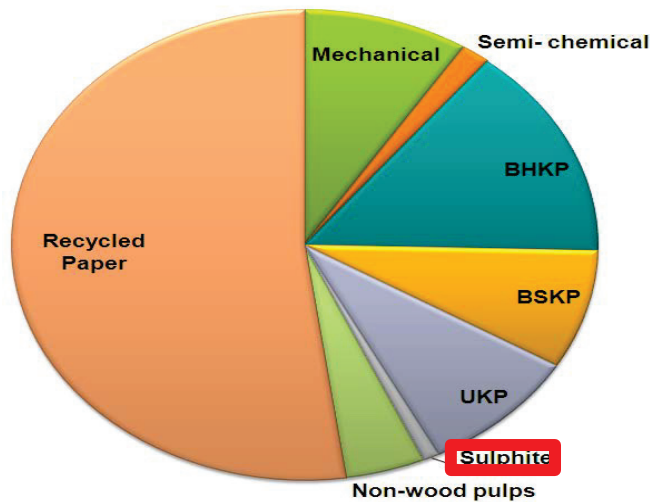


Figure 1. World production of pulp in 2007, which shows the present dominance of kraft cooking (7). The importance of mechanical pulps and of non-wood pulps should also be noted.

Kraft cooking conditions in general – the significance of sulfide in the cooking liquor

The active cooking chemicals in kraft cooking are sodium hydroxide and sodium sulfide, usually represented by active alkali (all NaOH and all Na₂S recalculated to an equivalent amount of NaOH) or effective alkali (with only half of the recalculated Na₂S compared to the case of active alkali) (22-23). The actual effect of the alkali in the cook lies somewhere in between those two concepts since SH⁻, which is not included in the effective alkali concept, will also itself influence the course of the cook, then not only as an alkali source (24a-d, 25).

Either one of the mentioned alkali concepts can be used for the control of the cook. And in the development stage of the sulfate process (after the process had been established in an industrial scale) the cooking conditions could therefore be reasonably well characterized by charge of active alkali and sulfidity (sulfide calculated as % of the total active alkali), together with time and temperature in the cook.

In mill operation, the charged cooking chemical solution (the charged white liquor) is diluted to the desired liquor-to-wood ratio in the cook by means of so called black liquor (spent cooking liquor and wash water from a late stage of the pulp washing after the cook), and not just water, as has often been the case in many laboratory studies of kraft cooking. It was originally assumed in normal mill practice that the organic substance in the black liquor (the black liquor fraction recovered at the end of the pulp washing, after most of the black liquor substance has been extracted and sent to the recovery system) could be expected to consume

mainly only the normal residual alkali in the black liquor. The charge of cooking chemicals could then, with reasonable accuracy, be represented by the charge of new chemicals only.

The development of a continuous cooking technique, sometimes with all the different phases of the cook in the same vessel at the same time, has made the original, quite simple kraft cooking concept much more complicated. In that case there is two somewhat different time concepts in the process, then related to the downward rate of cooking liquor following the chips (liquor inside the chips and outside liquor adhering to the chips, thereby also following the chips) and that of free liquor surrounding the chips but moving at a rate that may differ from that of the chips, a rate then depending on the liquor-to-wood of the charge to the digester in the beginning of the cook, cf. (26, 27).

Thus, with a high liquor-to-wood ratio, the free liquor moves faster than the chips and then, at equilibrium, gives an alkali gradient on a fairly high alkali level, whereas a low liquor-to-wood consequently gives a low alkali level, all at the same total alkali consumption in the cook. As long as the liquor-to-wood is held at a constant level, the cook behaves in a normal way in both cases. But disturbing changes in the liquor-to-wood will then change the rate of the free liquor, which in turn will change the relation between free liquor and liquor bound to the chips. During a period when a new equilibrium is being established, quite considerable changes in delignification may be experienced and has then to be dealt with in a suitable way in the process control.

Similar changes in the sulfide gradient would also be experienced. But the effect is less important since the main effect of the sulfide can be expected to concern the conditions in the beginning of the cook (25-27), that is a period with a very rapid chemical consumption, often covering at least half of the charged alkali.

Grade changes in a batch digester are mainly only a matter of changes in the original charge of chemicals and in the time/temperature schedule. In continuous cooking, grade changes/changes in production capacity may have a more important role in the process control since both cooking temperature and alkali gradients must then be adjusted, each in an individual mode (26, 27). After a time of transient conditions, the process may then adapt a new equilibrium state. But the pulp produced during the period of transient conditions may then be off-grade pulp. In many cases it can, however, be mixed into normal pulp at a suitable rate without serious consequences.

Modern trends in kraft cooking

The development after the Second World War has been characterized by gradually increased demands on both environmental protective measures and an economically sound pulp production, in the latter case to a large extent because of economic pressure from new pulp mills with new technique and at least initially low wood prices. The wood prices will however usually be adjusted to about the normal level on the world market when the new mill has left the starting phase and reached a high production level.

New wood species were used for pulping during this period, which for customer guidance lead to a quality classification on the softwood pulp side, then with Scandinavian and certain Canadian market softwood pulps at a very high level, in the latter case primarily mature wood, with a density about 350-400 kg atw/m³ moist wood (2, 26, 27), as compared to the Scandinavian level of about 370-420 kg atw/m³. Typical characteristics were here a

reasonably good beatability (low beating energy required to reach a high tensile strength) and a competitive relationship between for instance tear strength and tensile strength.

After the initial development of the sulfate process towards so called kraft pulping, relatively few further process modifications were introduced during the Second World War period. But the introduction of commercial continuous cooking in 1950 and further development of the continuous cooking concept during the 1950ies and the main part of the 1960ies laid the basis of some modified kraft cooking concepts (27-28).

Basic concepts for modified kraft cooking of pulp in general were then developed at the Swedish Forest Products Research Laboratory and the Royal Institute of Technology (KTH) in Stockholm (28-31). Four general principles were presented:

- The alkali concentration should be leveled out.
- The concentration of hydrogen sulfide ions should be as high as possible in the beginning of the cook.
- The concentration of sodium ions and dissolved lignin should be low.
- The temperature should be relatively low.

These principles, although all four are very difficult to fully consider within the same process technology, emerged in a modified kraft cooking technology, cf. (32).

The large original hydraulic continuous digester (with all the cooking phases in only one digester body) became very high at high production capacities (especially in the case of a long hi-heat countercurrent washing zone in the bottom of the digester) and had therefore to be designed for a very high pressure in the bottom of the digester (the hydraulic pressure in the top plus the pressure of the liquor column in the digester). The impregnation phase was therefore moved to a separate impregnation vessel in new digesters so that the height of the digester could be reduced considerably and consequently also the operating pressure in the bottom of the digester. This made it easier and less expensive to build digesters for large production capacities and would also facilitate the introduction of the different kinds of modified kraft cooking processes. (27).

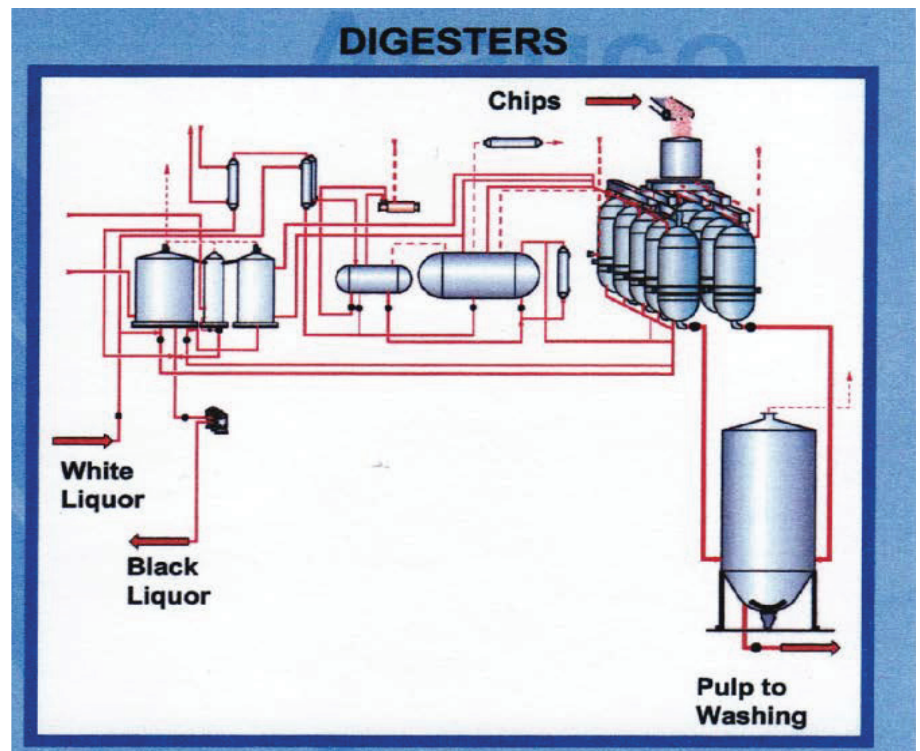
The original kraft cooking concept was batch cooking in fairly small digesters, usually with only the volume $\leq 100 \text{ m}^3$, which would mean a large number of digesters for the coming development towards very large total production capacities of the kraft mills. Heating of liquor and wood should be made in a sufficiently homogeneous way over the whole digester volume for a reasonably homogeneous cooking result. But that cannot be achieved by means of only a normal circulation system in batch digesters (with extraction of liquor from the digester and external heating before the heated liquor was brought back into the digester), which as such inevitably creates significant temperature gradients from the inlet of the liquor to the outlet via extraction strainers.

These gradients can, however, cause secondary movements of the liquor in the digester, which will level out at least part of the inhomogeneous temperature distribution. In order to promote such equalizing liquor movement, a short pressure relief at the top of the digester was made after some time of heating so as to bring about steam relief from the liquor phase in the digester towards the top of the digester (33, 34),

- either through steam discharge from the top of the digester
- or through a pressure drop by injecting a small amount of cold black liquor at the top,

in both cases creating a lower pressure at the top, and consequently also creating an equalizing steam relief from the lower part of the liquor in the digester towards the top.

Modern batch cooking system with accumulator technique for modified batch kraft cooking and extensive heat recovery (brochure material, Arauco, Chile).



Another important problem in the development of well-functioning digesters for kraft cooking was the strength loss that was obtained in the initial development of the continuous Kamyr digester and was at least partially solved by means of cooling the processed chips with wash water before discharge from the digester, cf. (26, 27). But the development towards very large digesters at high production capacity, improved steaming through atmospheric steaming in the chip silo with rather hot chips before the low-pressure feeder, and a following steaming in the low pressure system, has made it necessary to thoroughly examine possible negative effects on the final pulp from narrow passages in the system, particularly in the inlet system to the digesters, so as to guarantee a good so called strength delivery, cf. (35). Very high production, well over the design capacity, is particularly problematic in this respect.

Also batch cooking systems have experienced significant problems with the pulp strength because of mechanical damage on the fibers, mainly in connection with emptying the digester through blowing at fairly high temperature. Displacement of the hot liquor, by means of wash liquor at fairly low temperature, and pump discharge of the pulp at this reasonably low temperature have improved the situation to a great extent, a direct parallel to the cold blow in continuous cooking.

Modified kraft cooking – new ideas applied to an old process

The four general principles for modified kraft cooking (as mentioned above) have no doubt inspired the development ideas regarding modified kraft cooking of softwoods. But these ideas had to be adjusted to the available digester equipment and to the current system technique, factors which required certain compromises. On the other hand, modern mill scale operation offers also the possibility to adjust the time-temperature schedule in such a way that a certain yield increase is obtained through decreased hydratization of the carbohydrates at

high temperature at an early stage, before the major carbohydrate-degrading/dissolving reactions have speeded up. A high temperature already in the beginning of the cook, after only a very short initial impregnation with cooking liquor at high pressure, makes the carbohydrates less accessible to chemical attack and decreases the solubility of polysaccharide chains somewhat. But this will in turn affect the papermaking properties towards a somewhat lower tear/tensile strength relationship because of a somewhat higher hemicellulose content (26).

In continuous cooking, with an inlet cooking liquor circulation at 110-120°C and further heating at the top of an impregnation vessel (mainly through reaction heat from the corresponding, quite considerable alkali consumption), conditions for decreased hydratization are obtained already in the beginning of the cooking process, conditions which give a small increase in pulp yield at a given delignification or counteracts other factors, which otherwise would tend to decrease the pulp yield. Part of this was in fact tested already in a pilot plant in the Billerud mill at Jössefors (27). But it has later on been worked out in more detail in large scale operation (for instance in the small steam/vapor phase digester at SCA, Munksund (36)).

A similar effect can be obtained in batch cooking when the cooking liquor charging and time/temperature schedule are adjusted in an analogous way by means of cooking liquor accumulators. This has in fact been made possible through the development of a modern technique for cooking with such a use of cooking liquor accumulators (32).

An important issue in the production of bleached softwood kraft pulp has been the effects on the pulp quality of the measures that had to be taken to minimize the ecological problems of the mill effluent in the receiving waters. Transition from the previous rather well functioning bleaching sequences stages with elementar chlorine to

- sequences without elemental chlorine
- and in extreme cases also sequences without any kind of chlorine-containing chemicals,

in both cases after a balanced modified kraft cook and oxygen delignification as far as the final pulp quality standard permits, has required a very well reasoned production strategy, in particular how far you can go in each process stage without jeopardizing the final pulp quality (in the initial stages kappa number and later on brightness and pulp viscosity), cf. (37-38).

A normal standard has been to classify the bleached softwood kraft pulp in the quality control of the mill in question in accordance with the assumption that the main pulp quality variations will be adequately represented by the variations in pulp viscosity. There are of course several disturbing factors, but the normal case is that the viscosity of the bleached pulp quite well describes the paper-making strength potential of the pulp in a reasonably well run mill, as long as the wood to the mill is reasonably well under control (6, 12, 13, 17, 21, 32, 34, 40).

The relevance of pulp viscosity for pulp quality control has from time to time been questioned. It must, however, be stated that it has been shown to be the most important variable of the pulp quality parameters in a well functioning mill (statistical work on pulp quality test data from Östrand kraft pulp mill at the SCA R&D laboratory in the beginning of the 1980ies). The effect of a rather homogeneous DP on the strength is illustrated by the relationship between tensile strength of cellulose acetate films and the DP of the material, cf. figure 2 (39). The application of this kind of relationship must, however, also take into consideration a more pronounced variation in DP of the fiber material than in a normal pulp case and lokal defects in the fiber wall, which weaken the fibers, then superimposed on other

effects. But as the figure illustrates, the mean DP of the pulp is still a strong quality indicator when classifying the pulp quality. The main issue will then be to establish a suitable pulp viscosity target at otherwise well balanced process conditions.

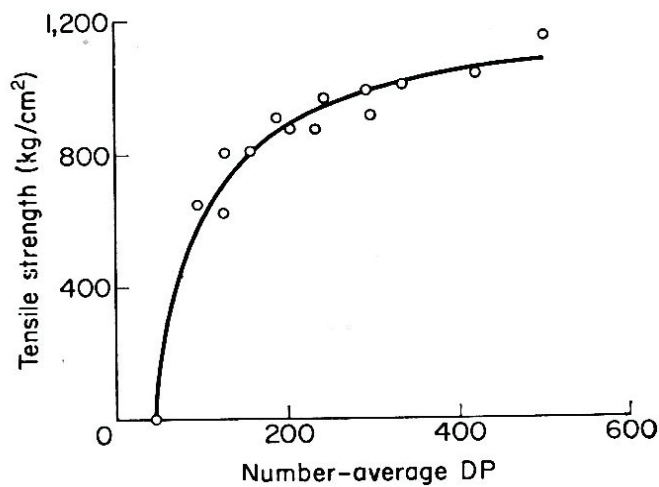


Figure 2. Tensile strength vs. DP of cellulose acetate films (39).

Furthermore, a normal standard has been to control the papermaking properties of the pulp at suitable interval by means of tests on laboratory paper sheets after standard laboratory beating and sheet preparations (cf. SCAN C 24:67, 25:76, and 28:76) and relate the results to a primary quality control based on pulp viscosity in the mill, thus updating the relationship between papermaking properties and pulp viscosity.

For the customers from paper mills, the main issue is to get a guarantee

- that the delivered pulp has expected properties in accordance with how the pulp is being used in the paper mill and
- that the pulp mill has been run according to expectations.

And this can be attained through a classification of the pulp based on frequent pulp viscosity measurements, with the relationship to papermaking properties adequately controlled at less frequent laboratory beating and determination of papermaking properties, which cover a broader spectrum of paper-properties.

The relevance of pulp viscosity measurements has from time to time been questioned. The measurements relate to an average DP of the cellulose in pulp, cf. figure 2 (39) and does not take into account actual variation in DP distribution, local mechanical damages of the fiber wall and kind of fiber material used in the pulp production. But for given conditions in a pulp mill, with reasonably well controlled wood to the mill and with a normal process control, in other words a well operated mill, the experience is that pulp viscosity takes care of a major part of the variance of individual papermaking properties of the pulp. The pulp viscosity will then give a good ground for quality classification of a certain pulp grade in the pulp mill and is therefore quite practical in the pulp mill quality control, provided the specific relationship between papermaking properties in the mill versus pulp viscosity has been determined and the relationship has been updated at regular intervals. It should be kept in mind that it is primarily the cellulose (its DP and its content), which determines the pulp viscosity. This means for instance that a low cellulose content will give a low viscosity, irrespective of the DP of the cellulose itself.

Hardwood pulp quality is somewhat more difficult to control in a simple way, both in the pulp mill and in the paper mill, in those two mill cases with different kinds of targets in the control. Variation in the cooking conditions have usually a more significant influence on the paper-making properties of the pulp, particularly since the short fibers require especially good inter-fiber bonding to compensate for the short fiber length when producing reasonably strong papers in paper mills. Pulp viscosity is then only weakly related to the paper strength. The main issue in the paper mill is here usually to know how variations in the pulp properties shall be balanced by changes in the furnish to the paper machine, a furnish which in this case should also contain some long-fibered pulps for reinforcement of the paper and possibly also other short-fibered hardwood pulps for commercial reasons.

Concluding remarks

Bleached sulfate (kraft) pulps are today a dominating pulp category where bleached hardwood is the largest pulp grade. Bleached softwood kraft pulps has at the same time become mainly a reinforcement pulp in different pulp furnishes for paper production.

The modern trend towards modified kraft cooking, oxygen delignification in one or two stages and final bleaching with mainly chlorine dioxide or in some cases with only chlorine free bleaching chemicals is quite intricate and requires a careful balance between the cook, the oxygen delignification and the following bleaching stages. This balance concerns both softwood and hardwood sulfate pulping, although the hardwood pulps are easier to bleach and the relative balance is therefore different in the two cases. The papermaking properties of the hardwood pulps are however more depending on the cooking conditions and on the choice of kappa number target in the cook since the dissolution of hemicelluloses is more pronounced when cooking to low kappa number. The reduction in strength can in extreme cases be quite dramatic.

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Sulfate cooking - a commercially dominating and continuously improving pulping process

Sulfite cooking was earlier the dominating pulping process but sulfate (kraft) cooking is today the most important process for the production of chemical pulps and high-yield pulps. One important reason for this development of the sulfate process is its ability to efficiently use different wood species, in particular different hardwood species. Another reason is that bleached hardwood sulfate pulps have become a strong competitor to bleached softwood sulfite pulps. The pros and cons of sulfate cooking are discussed in this report and compared with sulfite cooking.

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