Challenges in Kraft Cooking of Eucalyptus

Mikael E. Lindström

Associate Professor Pulp Technology, School of Chemical Engineering and Science, KTH - Stockholm – Sweden
e-mail: mili@pmt.kth.se

ABSTRACT

The main development trend in kraft cooking of Eucalyptus has been to increase the cooking yield by lowering the concentration of hydroxide ions throughout the kraft cook. This results in a higher xylan content and thereby a higher overall pulp yield. A high xylan content in the pulp also positively affects physical pulp properties such as the tensile strength. However, the amount of slowly reacting residual phase lignin is increased by a lower hydroxide ion concentration. The delignification during the residual phase is extremely slow in hardwood pulping, i.e. the cook comes almost to a complete stop when this phase is reached

Due to the low defibration point of Eucalyptus, i.e. the low lignin content at which the fibers are chemically separated, and the high HexA content contributing to the kappa number there is a great risk that the later part of the kraft cook of Eucalyptus is actually performed where the unselective residual phase is dominating. This will result in a low overall pulp yield despite the favourable low hydroxide ion concentration when it comes to the xylan reactions.

It can be concluded that kappa number alone cannot serve as a measure to avoid entering the very slow residual phase for Eucalyptus kraft cooking. It has to be combined with the hydroxide ion concentration and the H-factor. One solution is, however, to increase the target kappa number after the cook to about 20-22. This should significantly help to avoid "over cooking". However, today the cooking kappa number is limited by the efficiency of the oxygen stage on hardwood and/or today's design of the bleach plant.

Keywords: Kraft cooking, Delignification, Eucalyptus, Pulp yield, Kappa number, HexA

INTRODUCTION

Hardwood contains a higher amount of the hemicellulose xylan than softwood. A large part of the xylan is dissolved during kraft cooking. One of the side-groups in xylan, methylglucoronic acids, making xylan souble is split off by time and temperature resulting in a xylan less souble at the later stage of the kraft cook. This xylan can re-deposit on to the fibers depending on the kraft cooking conditions. It is mainly the hydroxide ion concentration that will govern the dissolution of xylan and the re-deposition. A low hydroxide ion concentration during the kraft cook of Eucalyptus will result in a high xylan content and thereby a high overall pulp yield. A high xylan content in the pulp will also positively affect physical pulp properties such as the tensile strength.

Given this background the main development trend in kraft cooking of Eucalyptus has been to lower the concentration of hydroxide ions throughout the kraft cook. This will, however, also affect the desired delignification reactions taking place during the kraft cook. The delignification of hardwood can be divided into three parallel reactions, initial, bulk and residual phase, i.e. the same as for softwood but the rates and the amount of lignin reacting according to the different phases differ (Lindgren, Lindström 1998). The amount of slowly reacting residual phase lignin is increased by a lower hydroxide ion concentration. The delignification rate during the residual phase of a kraft cook is very slow resulting in poor selectivity and is therefore a limiting factor for lignin removal. Consequently, the kraft cook must be interrupted when the residual phase is reached, in order to maintain a high pulp quality and yield.

The content of hexenuronic acid (HexA) in the pulp is in many ways an important factor in the production of bleached chemical pulps. The HexA consume permanganate in the kappa number analysis of pulps and thereby appears as "false lignin" in the kappa number measurement (Vuorinen et al. 1996; Gellerstedt, Li 1996). Since hardwood contains higher amount of the hemicellulose xylan than softwood the influence of "false lignin" in delignification studies will be of greater importance.
Gellerstedt and Li reported that typically 3-6 kappa number units of an unbleached hardwood pulp and 1-3 kappa number units of an unbleached softwood pulp are due to HexA and not lignin (Gellerstedt, Li 1996).

Due to the low defibration point of Eucalyptus, i.e. the low lignin content at which the fibers are chemically separated, and the high HexA content contributing to the kappa number there is a great risk that the later part of the kraft cook of Eucalyptus is actually performed where the unselective residual phase is dominating. This will result in a low overall pulp yield despite the favourable low hydroxide ion concentration when it comes to the xylan reactions
The present paper will focus on the challenges to counteract this phenomenon.

RESULTS AND DISCUSSION

Delignification

Based on literature data (Santos et al. 1997, Sjödahl 2006) a kappa number of 15-20 for kraft cooking of

Eucalyptus is close to where the slow residual phase is dominating, see figure 1.

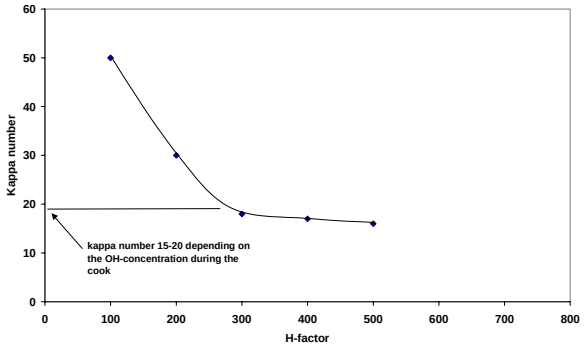

Figure 1. A generalised view of the bulk and residual phase delignification during eucalypt kraft pulping.

The kappa number where the residual phase starts to dominate is highly dependent on the hydroxide ion concentration (Lindgren, Lindström 1998). A lower hydroxide ion concentration will increase the amount of slowly reacting residual phase lignin.

In Figure 2 pulp yield versus kappa number for pulps produced at different hydroxide ion concentrations in the impregnation stage (Axelsson 2004) illustrates this important aspect for industrial application of hardwood kraft pulping. Kappa number alone is not always a good indication for how long the cook should proceed. The use of a very levelled-out alkali profile (as is customary in modern cooking applications) do result in an early introduction of the residual phase delignification. Therefore the use of a standard kappa (e.g. 15) might lead to a significant part of the cook being performed where the residual phase is dominating, leading to yield loss and pulp quality losses.

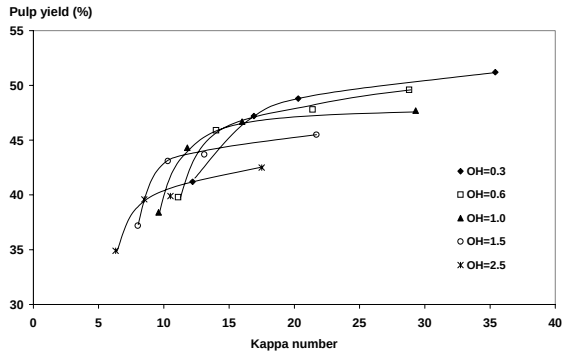

Figure 2. Pulp yield versus kappa number for pulps produced at different hydroxide ion concentrations in the impregnation stage (120 °C, 45 min, $[HS^-]$=0.2, $[Na^+]$=2.0) and similar conditions in the cooking stage (160 °C, $[OH^-]$=0.3, $[HS^-]$=0.2, $[Na^+]$=2.0) (Axelsson 2004).

Since hardwood contains higher amount of the hemicellulose xylan than softwood the influence of "false lignin" originating from carbohydrates will be of greater importance for the rate of delignification measured by the standard kappa number.

Figure 3 displays both the kappa number and the kappa number corrected for the contribution of HexA(kappa**) for a series of conventional hardwood kraft pulps produced at different H-factors using the same alkali charge (Axelsson 2004). The HexA contribution to the kappa number can be seen as a gap of 3-5 kappa number units between the curves. The kappa number suggests a very slow delignification in the residual phase, but the corrected kappa number indicates that the actual delignification comes to a complete stop. What is evaluated as a slow delignification by the kappa number is actually a HexA degradation.

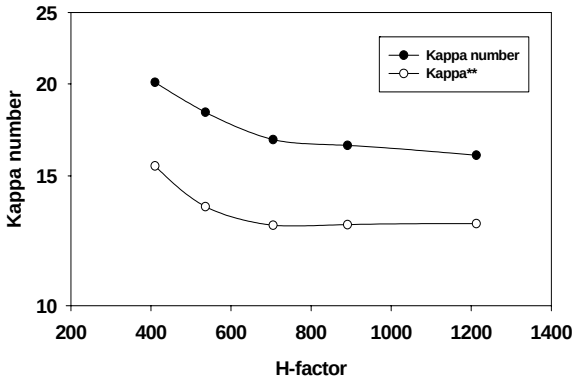

Figure 3. The kappa number and the kappa number corrected for the contribution of HexA(kappa**) for a series of conventional hardwood kraft produced to different H-factors using the same alkali charge. The kappa number is given on a logarithmic scale (Axelsson 2004)

Pulp quality

The importance of charged groups for beatability measured as tensile index at a given PFI revolutions is illustrated in Figure 4, which is a series of *Eucalyptus globolus* kraft pulps pulped at different conditions (Axelsson 1999). In this case the xylan content does not differ much between the different pulps. However, due to differences in selectivity of the cook, the uronic acid group content differs some 30%, which results in a difference in beatability of around 50%

The charged groups in a bleached kraft pulp are mostly of the uronic acid type. The amount of xylan can therefore be expected to be important, in the sense that the uronic acids are connected to the xylan. However, even more important is the ability to perform the cook in such a way as to preserve the methyl glucuronic acid groups in the xylan. Methyl glucuronic acids are converted to hexenuronic acids (HexA) at kraft

pulping conditions. HexA, also being a charged group will contribute to beatability of the unbleached pulp, however, the HexA is mostly degraded during bleaching. Therefore, it is the uronic acids that is not transformed to HexA, or degraded itself that contribute to pulp beatability in the bleached product.

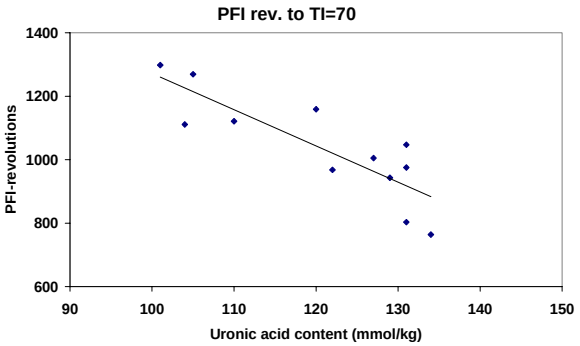

Figure 4. The number of PFI-revolutions needed for the pulp to reach Tensile Index 70 kNm/g for a series of *Eucalyptus globolu*s kraft pulps.

The conversion of methyl glucuronic acids to HexA and the subsequent degradation of HexA can be seen in Figure 5 which is a simplified figure based on literature data (Ek et al. 2001, Daniel et al 2003, Danielsson 2006). The amount of methyl glucuronic acid groups, HexA and the total amount of charged groups (here shown as total of uronic acids and HexA) are shown as a function of cooking time.

A decrease in pulping selectivity resulting in an increase in the need for H-factor from lets say 300 to 500 will not result in any significant change in the amount of HexA or the total amount of acidic groups, however, it will lead to a significant loss of methyl glucuronic acid groups. Based on this hypothesis it can be expected that a selective cook, that reaches target kappa with around 300 H-factors, will show only a minor improvement in tensile strength of the unbleached pulp, but a significantly higher effect on the bleached pulp.

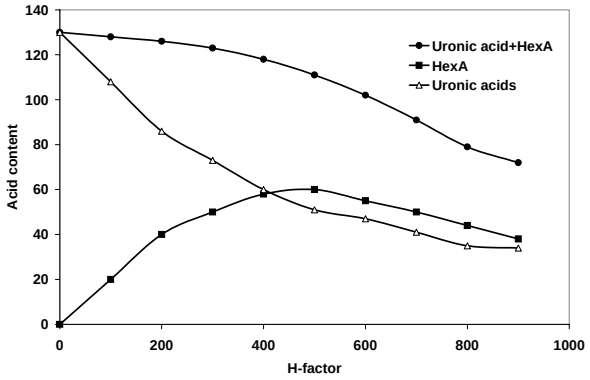

Figure 5. A hypothetical figure of the amount of methyl glucuronic, hexenuronic and total amount of uronic acid groups in pulp as a function of H-factor.

Process considerations

The relation between pulp kappa number and tensile index based on mill data for *Eucalyptus* (unpublished data) is shown in figure 6. It can be concluded that during this period the pulp in many cases was "over-cooked".

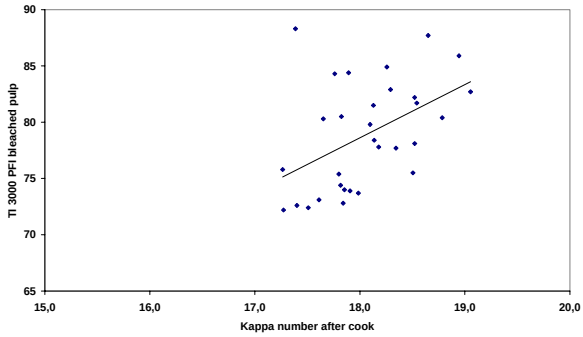

Figure 6. Tensile index at 3000 PFI of bleached pulp as a function of the kappa number of unbleached pulp (unpublished mill data on *Eucalyptus*)

It might seem as if a difference in kappa number of 17 to 19 is not very large. However, looking at figure 6 it can be seen that it has a significant effect. It should be remembered that the transition from bulk to residual phase delignification occurs in this kappa number region illustrated in figure 1. The kappa number level where this occurs, around 15 to 20, depends strongly on the hydroxide ion concentration during the cook. The delignification during the residual phase is extremely slow in hardwood pulping, i.e. the cook comes almost to a complete stop when this phase is reached. As a result it was possible to reach kappa number 19 with 300 H-factors, but the same cook extended to an H-factor of 500 might not decrease the kappa number more than an additional 2 kappa units i.e. ending up at kappa number 17 (cf figure 1). Even though the difference in kappa number is small, the effect on the carbohydrates, especially the charged groups, is significant (cf Fig. 5). Increasing the target kappa number after the cook to about 20-22 for Eucalyptus should significantly help to avoid "over cooking". However, today the cooking kappa number is limited by the efficiency of the oxygen stage on hardwood (Chirat, Lachenal 1999) and/or today's design of the bleach plant.

CONCLUSIONS

It can be concluded that kappa number alone cannot serve as a measure to avoid entering the very slow residual phase for Eucalyptus kraft cooking. It has to be combined with the hydroxide ion concentration and the H-factor. One solution is, however, to increase the target kappa number after the cook to about 20-22. This should significantly help to avoid "over cooking".

The great challenge of *Eucalyptus* cooking is produce a pulp which is possible to defibrate without entering the kappa region where the residual phase is dominating in combination with improved efficiency of the oxygen stage and/or design of the bleach plant.

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