**INFLUENCE OF PROCESS PARAMETERS ON BRIGHTNESS REVERSION -*A MULTIVARIATE ANALYSIS APPROACH***

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## ABSTRACT
High brightness and good brightness stability are desired properties for bleached hardwood kraft pulps. The presence of hexenuronic acids in pulp is known to be one contributing factor to brightness reversion. The application of multivariate data analysis on process data proved to be a useful tool in the work to identify which parameters in Celbi's fiberline that had the largest impact on the control of brightness reversion and also their relative importance. Cooking conditions at Celbi are designed to promote high yield and good runnability not to minimize hexenuronic acids content. The level of HexA in the bleached pulp must be controlled in the two D-stages in OQ(PO)DD sequence. It was shown that the temperature had a major influence on reversion and particularly in the second D-stage. The results of the studies made at Celbi show that it is possible to optimize the bleaching conditions for both brightness development and control of brightness reversion.

## INTRODUCTION
Stora Enso Celbi mill is located in Figueira da Foz, Portugal and produces 300 000 ton per year of bleached eucalyptus hardwood kraft ECF-pulp. The wood raw material is domestically grown *Eucalyptus globulus*. In September 1999 Celbi completed a major retrofit of the fiberline comprising a new digester from Kvaerner of Compact Cooking design and a rebuild of the bleach plant by Metso.

The investments increased the capacity and also changed the pulping process conditions. The old digester was heavily overloaded and cooking temperature was 168-172 °C. In the new digester cooking is made at a temperature in the range 140-145 °C. The bleaching plant was rebuilt and the sequence was changed from $ODE_{OP}DD$ to OQ(PO)DD.

The changes in process conditions had positive effects on yield and chemicals consumption but also some undesired effects on the pulp properties. Brightness reversion increased as did kappa number of bleached pulp and its hexenuronic acid content. Celbi has worked intensively with developing and optimizing the performance of the new digester and rebuilt bleach plant to exploit its full potential. The paper presents analysis and actions taken in the mill to investigate and control the brightness reversion while at the same time maintaining the benefits given by the new process conditions on yield and pulp properties.

There exists to date no complete scientific explanation of the causes for and reactions that lead to brightness reversion of chemical pulps. Both carbohydrate and lignin components in pulp can undergo changes in chemical structure when they are exposed to heat or light induced ageing [1]. The extent of brightness reversion varies depending conditions as temperature, pH, humidity and presence of some metals.

Hexenuronic acid (HexA) is known to be one contributing factor in brightness reversion [2]. HexA is created under alkaline cooking conditions through conversion of 4-O-methylglucuronic acids [3], figure 1. The glucuronic acid side groups are abundant on the xylan chains. Eucalyptus also has a higher degree of substitution of these groups than birch. The conversion to HexA is also said to help to preserve the xylan yield [4,5].

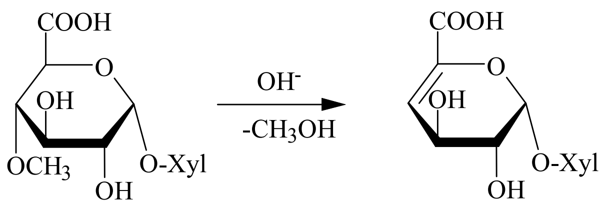


Figure 1. Conversion of 4-O-methyl glucuronic acid to hexenuronic acid

According to literature the HexA content in hardwood pulp increases when cooking kappa number decreases until a certain kappa level when the degradation/dissolution of HexA takes precedence and HexA content start to decrease [6,7]. The rate of formation and dissolution/degradation depend on cooking conditions and wood species. The content of HexA in unbleached eucalypt pulp can typically be in the range 40-80 mmol/kg [8]. HexA also contribute to kappa number measurement. Different numbers but of similar magnitude are reported in the literature [9,10]. According to Gellersted and Li 1 kappa unit corresponds to 11.6 mmol HexA. This means that at a level of 50 mmol HexA/kg in unbleached pulp of kappa 15, 29 % can be attributed to HexA.

HexA is degraded under acidic conditions as in an A-stage or acidic and oxidative as in D, Z or Paa stages. It is not degraded in alkaline oxygen or peroxide bleaching [5,11]. The manner and rate at which HexA is degraded differ depending on which chemicals and conditions that are used.

## METHODS

Data used in analysis of the process and trial results originate from on-line and Celbi mill laboratory measurements. Hemicellulose content and hexenuronic acids were analyzed by Stora Enso Research. Hexenuronic acid content was determined by ion chromatography preceded by enzymatic pretreatment of the sample according to a method developed at VTT.

In lab, reverted brightness was measured after 3 h in dry conditions at 105 °C. In the mill, it was used 20 min, 120 ºC. Pulp and paper testing was made according to SCAN standard methods.

Software used for multivariate data analysis was SIMCA 8.0 from Umetrics. Data was sourced from the historical database of the mill information system server.

## RESULTS AND DISCUSSION

### Impact of the project

The main effect of the digester investment and bleach plant rebuild compared to the old digester and bleach plant was a decrease in wood consumption as a result of increased pulping yield and part of this could be attributed to increased yield of hemicellulose in pulp. The number of D-stages had been decreased from previously 3 to 2 in the new sequence. Bleaching chemicals demand did change. The results are summarized in Table 1.

Table 1.

| Parameter | Difference; New compared to Old |
|---|---|
| Yield, [%](pulp production) | +2 % |
| Hemicellulose in pulp [%] | + 0.7 %-units |
| Bleaching chemicals consumption<br>-Chlorine dioxide [kg/t]<br>-Hydrogen peroxide [kg/t] | <br>-25 %<br>-13 % |

Soon after the startup it could be seen that brightness reversion had increased compared to before and that the level also varied. Hexenuronic acid content and bleached pulp kappa number had increased somewhat. There were few historical data of hexenuronic acid content in unbleached or bleached pulp from before the rebuild since this was not an issue then.

Several trials were performed to analyze and improve the brightness stability namely,

- Cooking kappa number
- A-stage trials
- Industrial trials, D-stage optimization

**Cooking kappa number variation**

Analysis of cooking kappa number showed that brightness reversion co-varied with unbleached kappa number so that brightness reversion decreased when cooking kappa number decreased, figure 2.


Figure 2. Variation of brightness reversion (machine sheet) with digester k number

The mill results indicated that the peak (or plateau) in HexA content in the cook had already been passed. This is somewhat contrary to results from laboratory studies presented in the literature for the kappa range in question but the conditions in a full scale cooking operations, although principally similar, are not identical to the laboratory case. Liquor composition, solids concentration and alkali profile differs which can very well influence kinetics and equilibriums.

According to the results one way to control and decrease the brightness reversion would be to decrease the cooking kappa target. However lower cooking kappa number means poorer pulp yield with a detrimental effect on production economy and paper properties.

**Trial with an A-stage in the bleaching sequence**

To increase the bleaching sequence’s capacity to reduce HexA, the conditions in the Q-stage were temporarily converted to an acidic stage (A), temperature 90 °C, pH 3 and retention time >2 h. In this case it was possible to see that brightness reversion decreased and also HexA content and the residual kappa in bleached pulp, figure 3. However this was achieved at the expense of lower yield, higher organic load to the effluent and especially with a detrimental effect on strength properties, figure 4.

The effect of the A-stage on paper properties is an important issue. Viscosity loss might be low to moderate but this is not a sufficient indicator for quality. It has been shown that too harsh conditions cause losses of pentosans [12]. This might very well result in an increased beating demand. Conditions within which the A-stage can be run must be chosen with great care in order to maintain the quality performance of the pulp. This might put limits to the obtainable HexA reduction. In the case of the mill the retention time in the Q (or A) stage varies within certain limits since the tower used as Q (or A) stage also functions as a storage tower and is used to buffer variations in production rate.

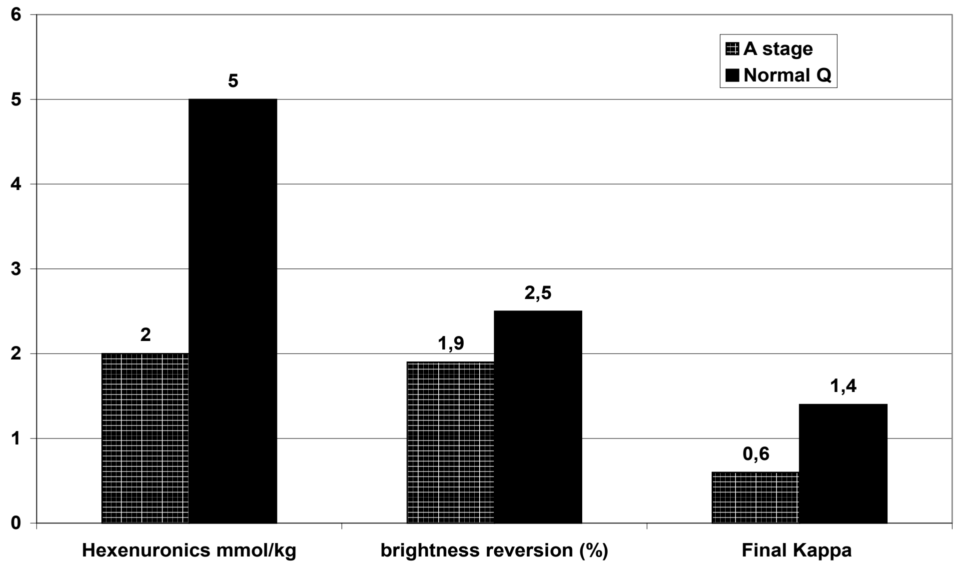


Figure 3. Comparison of properties of bleached pulp produced with normal Q-stage or with and A-stage.

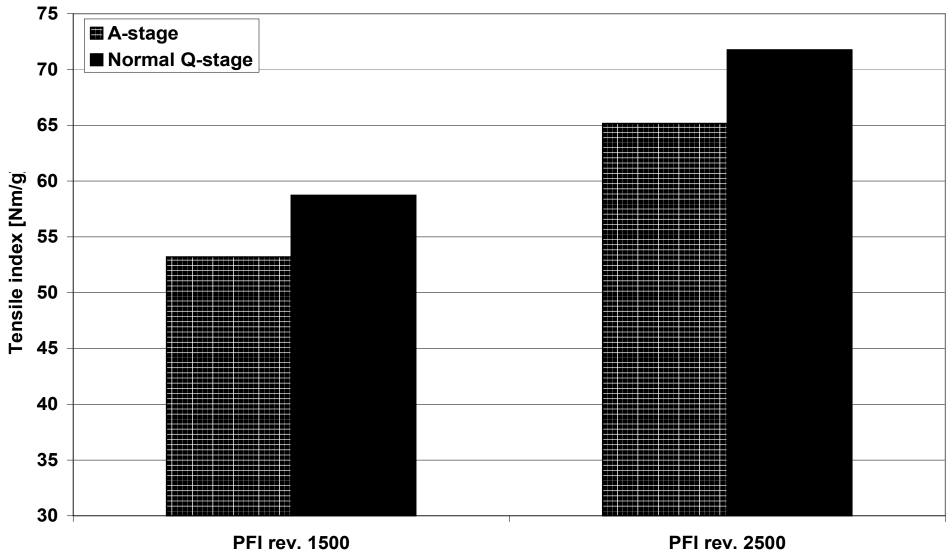


Figure 4. Comparison of tensile index of bleached pulp produced with a normal Q or with an A-stage.

**Bleach plant optimization work**

At a point in time some disturbances occurred in the bleach plant, which did cause variation in brightness reversion. These events prompted us to make a thorough analysis of the influence of process parameters on brightness reversion. A multivariate data analysis (MVDA) comprising a list of relevant process parameters was performed based on the available data stored in the historical database of the mill information system server, table 2.
Originally a list of 37 variables was used and after some runs of the MVDA those with minor influence were removed, so the total number was reduced to 18.
The number of observations was 1200.

Table 2. Process parameters included in the multivariate data analysis.

| | | | |
|---|---|---|---|
| P1- Sulfidity | P2-Liquor/wood ratio IV | P3- Liquor/wood ratio Dig | P4- Extract. alkalinity |
| P5- Extract. temperature | P6- ITC alkalinity | P7- Kappa number | P8- Viscosity dig |
| P9- Alkaly charge O2 | P10- Dilution factor | P11- Viscosity after O2 | P12- Q stage pH |
| P13 – H2O2 charge | P14- D1 temperature | P15- D1 ClO2 charge | P16- D2 temperature |
| P17- D2 ClO2 charge | P18- D2 pH | | y - Brightness reversion |

Partial least squares (PLS) analysis was made with brightness reversion selected as the y-variable. The PLS analysis resulted in a set of variables that had a big influence on the brightness reversion level, figures 5 to 7.

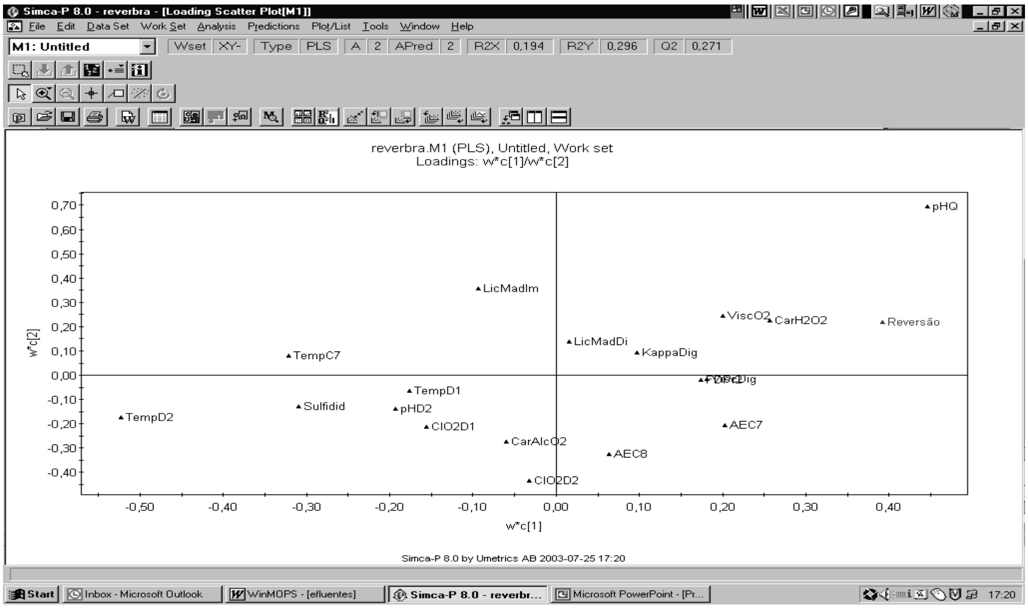


Figure 5. MVDA- correlation between variables

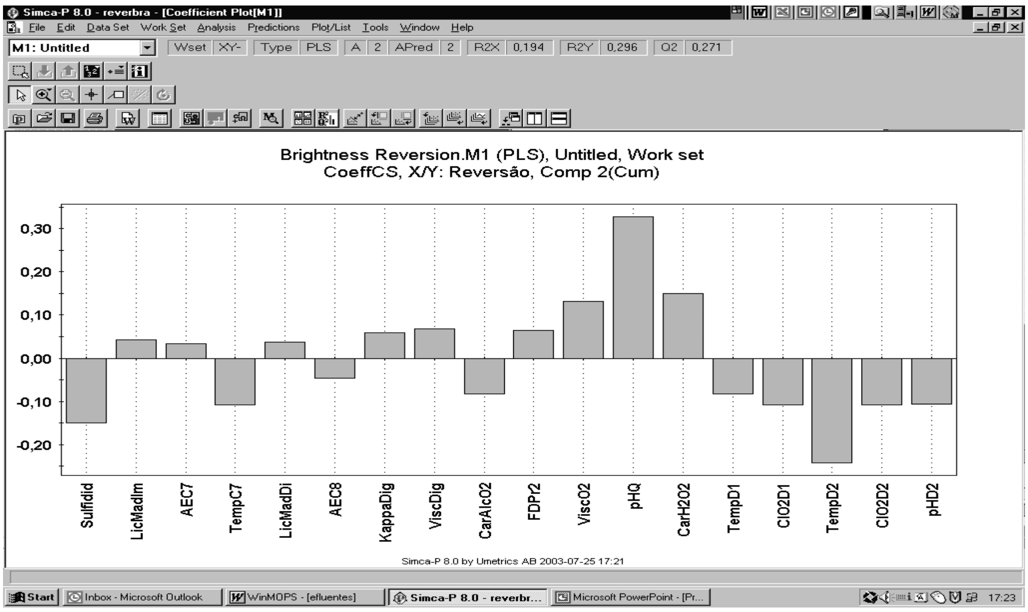


Figure 6. Influence of the variables on brightness reversion

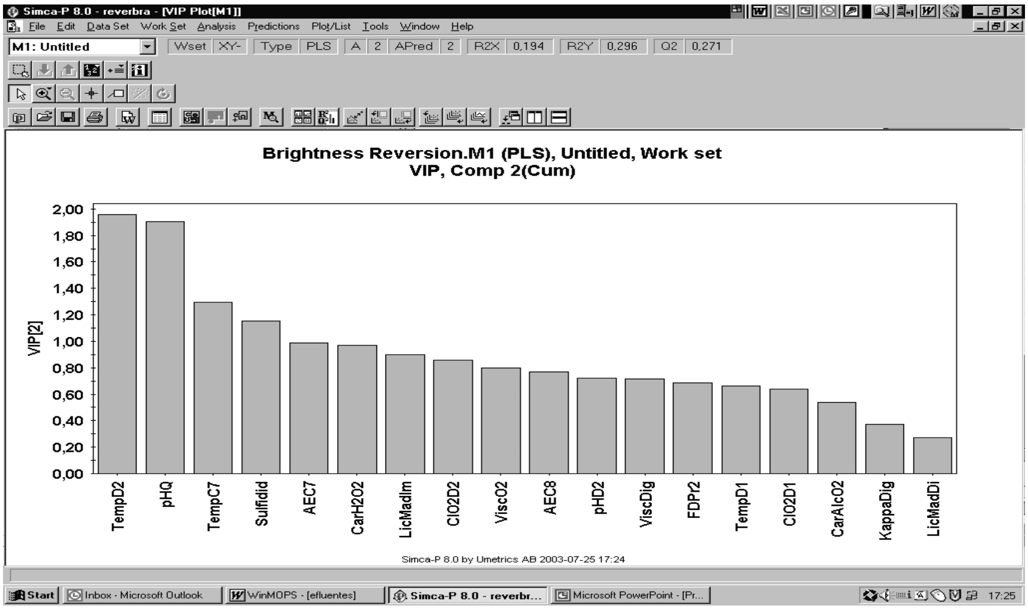


Figure 7. Variables contribution to the model

Especially temperature in the last (second) D-stage showed to be important but also the temperature in the first D-stage even though at a lower level. The influence of some of the other variables was already known, like for instance, the pH in Q stage. As mentioned before, when this stage was converted to an A stage by decreasing the pH from 5,5 to 3, a substantial reduction in brightness reversion was obtained, from 2,5 to 1,9.

According to StoraEnso internal results the reduction of hexenuronic acids in a D0 stage can be in the range 50-65% for eucalypt pulp. In a following D-stage, preceded by an EP stage the reduction was found to be between 70-90% [8]. Mill and lab results show that it can be possible to reduce HexA to a level of around or below 5 mmol/kg in two stages given that the conditions are the right ones and that they are well controlled. As is the case for all chemical reactions the rate of degradation also in D-stages depend on conditions as temperature, pH and residence time. In chlorine dioxide bleaching these conditions also influence which chlorine species that are present. In addition, the content of lignin with which the hexenuronic acid degradation competes is of importance. Celbi's pulp from the PO-stage has a kappa number between 7 and 8. The lignin kappa on the other hand entering the first D-stage is only about 1/3 while the hexenuronic acids represent 2/3. This emphasizes the conclusion that it is equally important to optimize the D-stages with respect to hexenuronic acid control as well as for brightness increase.

## Industrial trials

Based on these findings, a set of trials was performed to confirm them. Temperature in the last D-stage was varied between 70 and 84 °C. A decrease in the brightness reversion level of 0.5 to 0.6 % was obtained when increasing the temperature from 70 to 84 ºC, figure 8. No major impact could be seen in chlorine dioxide consumption, effluent load and strength properties.

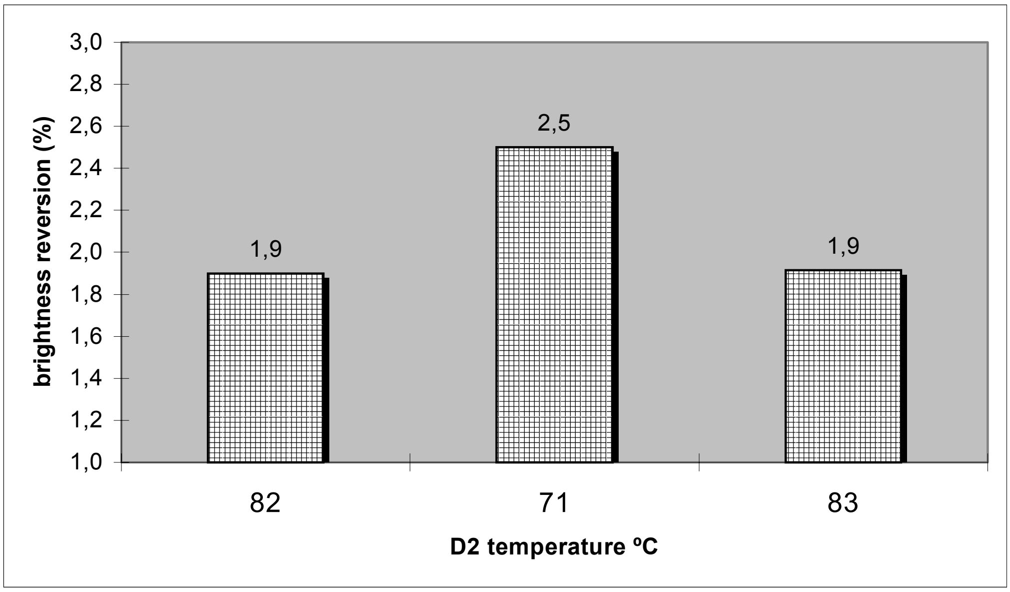


Figure 8. Influence of D2 temperature on brightness reversion

The conditions in the D2-stage proved to very be important for the control of brightness reversion of bleached pulp.
Analysis of pulp showed that total acid groups and final kappa number couldn’t explain the variation in the brightness reversion (fig 9-10); only in the case of hexenuronic acids, there was a slight increase when D2 temperature was decreased, fig. 11.However, it is not known if this HexA content decrease is sufficient to justify the results obtained.

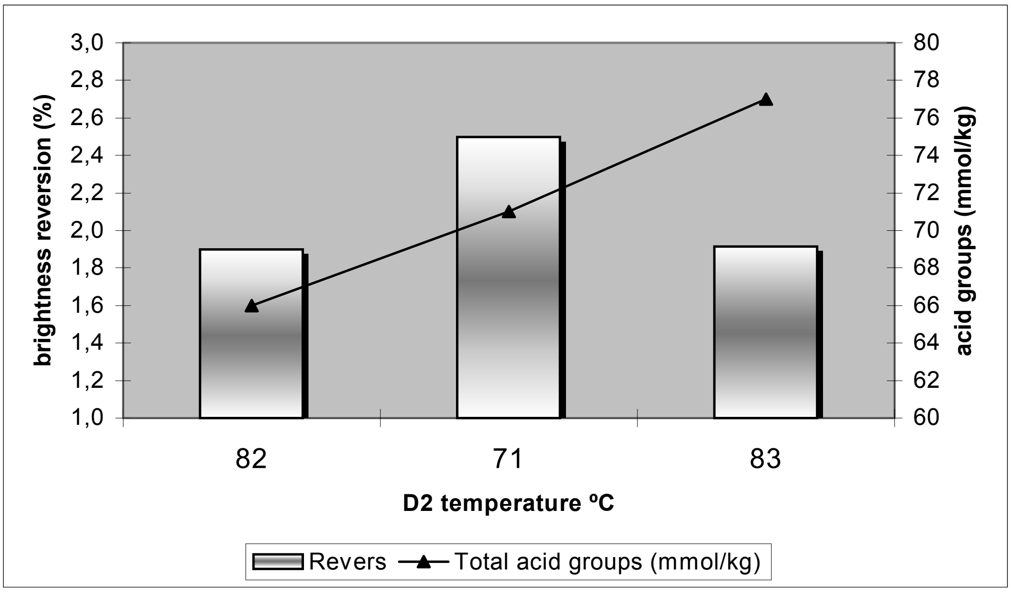


Figure 9. Influence of D2 temperature on brightness reversion and total acid groups

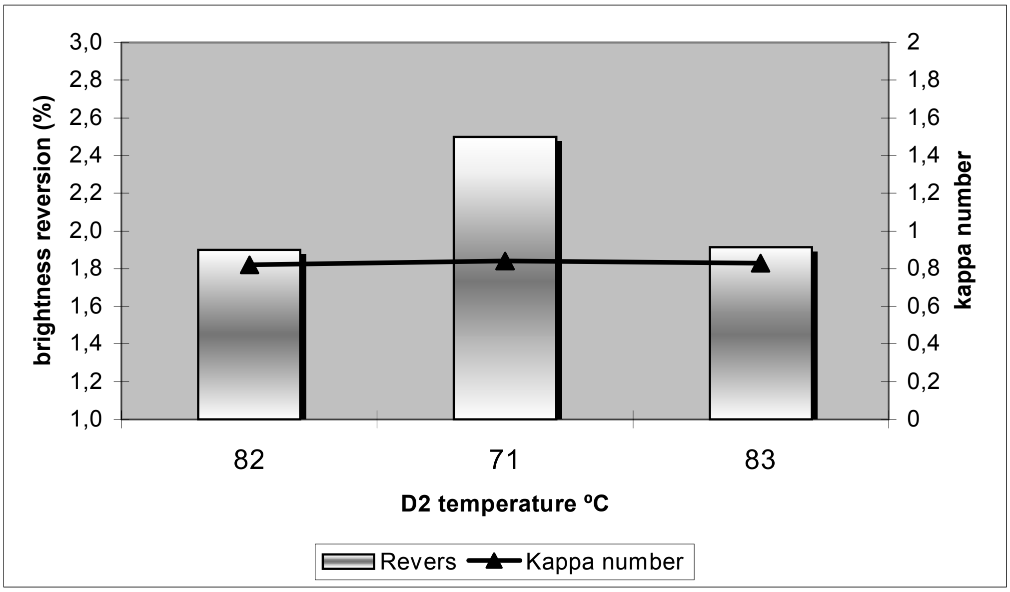


Figure 10. Influence of D2 temperature on brightness reversion and final kappa

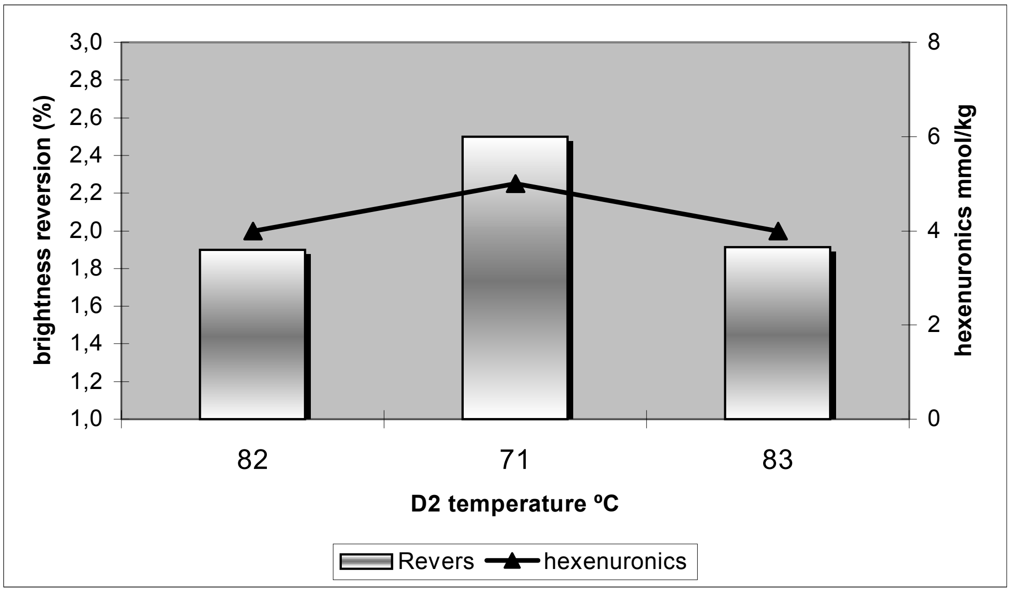


Figure 11. Influence of D2 temperature on brightness reversion and hexenuronic acids

## CONCLUSIONS

The goal of mill control is to keep the process parameters stable and the pulp quality uniform. With the multitude of parameters that exists it can be difficult to single out strong correlations between parameters and results. The use of MVDA can provide a better utilization of process data, avoid unnecessary and expensive trials and set guidance for new research activities.

The application of multivariate data analysis on process data proved to be a useful tool in the work to identify which parameters in Celbi's fiberline that had the largest impact on the control of brightness reversion and also their relative importance.

Control of brightness reversion is a complex issue that cannot be attributed solely to the presence of a single chemical component or a single process stage. Control brightness and also brightness stability is a ‘multiparameter’ task. In the case of brightness stability the parameters that work in favor of low reversion can work against the main targets as high yield, low bleaching chemical consumption and good paper properties. The process must be designed and optimized with this controversy in mind.

It is Celbi’s choice to favor high yield and runnability in the digester. Cooking conditions are not designed to minimize the HexA content. Good control of the conditions in the digester is nevertheless of outmost importance for keeping also HexA a stable level, which is a prerequisite for good control in the bleaching. The two D-stages are the key positions where the level of HexA in the pulp must be controlled. These two stages must then fulfill the demands on both brightness development and control of hexenuronic acid content. Temperature in the D-stages proved to very important for the resulting brightness stability.

However, as can be seen by the results, the brightness reversion behaviour cannot only be explained by the HexA content. Other influences must be present.
The chemical composition of the bleached pulp is the product of the raw material and the pulping process. Research is needed about the specific conditions and chemical components involved in brightness reversion so that the pulping process can be further developed and optimized. In this research it is necessary to include the impact also of mill conditions as compared to laboratory studies. It is then important to consider the role of each process stage.

## REFERENCES


1. Tenkanen, M., Forskåhl, I., Tamminen, T., Ranua, M., Vourenvirta, K., Poppius-Levlin, K.; Heat induced brightness reversion of ECF-light bleached pine kraft pulp; 7th European workshop on lignocellulosics and pulp
2. Ek, M., Buchert, J., Bergnor, E., Lindblad, G., Viikari, L.; The role of yellowing of xylan and glucomannan in yellowing of kraft pulps; 8th ISWPC Helsinki 1995, p 43-48
3. Buchert, J., Teleman, A., Harjunpää, V., Tenkanen, M., Viikari, L., Vuorinen, T.; Effect of cooking and bleaching aon the structure of xylanin conventional kraft pulps; Tappi Journal Vol 78 (1995); 11, 125-130
4. Pinto, P., Evtuguin, D.V., Pascoal Neto, C.; Chemical structure and kraft pulping behavior of xylans from three different hardwoods: A comparative study; 7th European workshop on lignocellulosics and pulp, p 313-316
5. Jiang, Z.H., van Lierop, B., Berry, R.; Hexenuronic acid groups in pulping and bleaching chemistry; Tappi Journal Vol 83 (2000) No.1, p 167-175
6. Daniel, A. I. D., Evtuguin, D. V., Silvestre, A. J. D., Pascoal Neto, C; Influence of pulping conditions on hexenuronic acid contents of *Eucalyptus globulus* kraft pulp, 7th Brazilian Symposium on ligni chemistry and other wood components, Belo Horizonte, Brazil 2001; p 137-144
7. Kadiric, J; Kinetics of the formation and dissolution/degradation of hexenuronic acid during kraft pulping of *Eucalyptus globulus*; Master thesis 2001, Royal Institute of Technology Stockholm Sweden, Department of Pulp and Paper Chemistry and Technology
8. Stora Enso internal investigations
9. Gellersted, G., Li, J.; The contribution to kappa number from hexenuronic acid groups in pulp xylan"; Carbohydrate Research, v. 302, 213-218, 1997
10. Colodette, J. L., Costa, M. M.; The effect of kraft pulp composition on its bleachability; Tappi Int. Bleaching Conference 2002, p 195-213
11. Buchert, J., Tenkanen, M., Ek, M., Teleman, A., Viikari, L., Vuorinen, T.; Effects of pulping and bleaching on pulp carbohydrates and tehcnical properties; Tappi Int. Bleaching Conference, Washington DC, USA 1996, Proceedings Vol 1, p 39-42
12. Primo, C. A. P. et. al.; Acid treatment applied to Portuguese *Eucalyptus globulus* kraft pulp before bleaching: Effects on quality and on hexenuronic acids and metal contents., Poster presentation
13. Colodette, J. L., Eiras, K. M. M., Oliviera, R., Ventorim, G.; The effect of wood supply and bleaching process on pulp brightness stability; 28th EUCEPA conference Lisbon, 2003, Proceedings p 165-173
14. Gellersted, G., Li, J., Sevastyanova, O.; The distribution of oxidizable structures in unblheached and bleached kraft pulps; 28th EUCEPA conference Lisbon, 2003, Proceedings p 158-164
15. Wennerström, M.; Decreasing brightness reversion with powerful ozone bleaching; Tappi Int. Bleaching Conference 2002