ECF Bleaching of Softwood and Eucalyptus Pulps - a Comparative Study

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INTRODUCTION

This paper deals mainly with a comparison in ECF bleaching and effluent characterization of kraft pulps based on softwood and eucalyptus. The study is made for both conventional and oxygen delignified pulps. The paper also briefly reviews the bleaching technology development and the chlorine dioxide production technology.

There are similarities in the bleaching of softwood and eucalyptus looking at the bleaching parameters. In mill scale there are however normally differences in the number of bleaching stages for conventional and oxygen delignified pulps when bleaching to 90 %ISO brightness. Conventional pulps are mainly bleached in a five stages sequence with peroxide reinforcement in the alkaline stages, D (EOP) D (EP) D. Oxygen delignified pulps are mainly bleached in a four stages sequence, D (EOP) D D, especially softwood pulps. A three or four stages sequence, D (EOP) D D or D (EOP) D, is usually used when bleaching oxygen delignified eucalyptus pulps. For brightness levels of 88 %ISO a three stages sequence can be used for both oxygen delignified softwood and eucalyptus pulps.

In the ECF bleaching optimization study we have used a five stages sequence for all pulps. The same bleaching sequence was used in the effluent characterization study except for the oxygen delignified eucalyptus pulp where a three stages sequence was used.

Combined effluents from all bleaching stages were characterized and exposed to biological treatment. Characterization studies were carried out both prior to and after the biological treatment.

The characterization of the main COD components; lignin, carbohydrates, methanol, low molecular acids and extractives prior to and after external treatment, corresponded well with the calculation of the total organic composition. The results showed that the organic composition varies for effluents from different pulps.

The COD compositions of softwood and eucalyptus effluents were significantly different, which explains why the effluents from the eucalyptus pulps were more biodegradable.

BLEACHING TECHNOLOGY DEVELOPMENT

The classic pulp mill produced a semibleached pulp with a brightness of 65-70% ISO in the sequence C E H H. The kappa number of the unbleached pulp into the bleach plant at that time was 35-40 and the related AOX in the effluent at the level of 8 kg/ton.

In the beginning of the 40's chlorine dioxide was introduced and the sequence C E H D was used to increase the final brightness. For a production of a 90% ISO brightness pulp the sequence C E H D E D was introduced. Still the kappa number of the unbleached pulp was in the level of 35-40.

In the early 70's a big environmental step was taken when oxygen delignification was introduced. The reason for this introduction was a demand from the authorities to reduce the COD (chemical oxygen demand) in the pulp mill effluent. After oxygen delignification the kappa number of the unbleached pulp was reduced to 18-20. The COD was reduced with 40% when the effluent from the oxygen delignification stage was recirculated to the recovery system. With the introduction of the oxygen delignification and a reduction of the kappa number the common bleaching sequence was O C_D E D E D with 50% reduction of elemental chlorine and without hypochlorite. The AOX in the effluent was reduced from about 7 kg/ton to about 3 kg/ton.

The ECF bleaching was introduced at the end of the 80's and was a result of extensive environmental research in different countries. It was, however, also a result of increased market demands in the big pulp consuming countries in Europe for elemental chlorine free bleaching. 1994 all the Nordic pulp mills had changed the bleaching to ECF.

However, 1989 Eka Chemicals announced the Lignox process, Q P, for totally chlorine free bleaching, TCF. The final brightness for softwood and hardwood pulp at that time was 75-85% ISO respectively. Later the brightness was improved to 85-90% ISO. In the beginning of the 90's complementary chemicals like ozone and peracetic acid were introduced to produce fully bleached TCF pulps.

BASIC BLEACHING CHEMISTRY

Chlorine gas or hypochlorite bleaching is the traditional way of bleaching pulp. The method is efficient but has the drawback of producing harmful effluent. In aqueous solutions chlorine reacts with water and forms hypochlorous acid. Both chlorine and hypochlorous acid are oxidative components and react with aromatic compounds in the lignin via substitution reactions. After the chlorine substitution the lignin will become soluble in water, to a limited extent. But after introduction of hydroxide groups (NaOH) the solubility increases dramatically. The amount of chlorine determines the bleaching effect. Increased amounts of chlorine will also generate increased amounts of high chlorinated organic compounds, which is well known to have a negative impact on the environment.

Chlorine dioxide has high oxidation power and is used commercially for pulp bleaching. The reaction pattern is different from chlorine in the way that it has mainly addition reactions with aromatic lignin compounds. The amount of chlorinated organic compounds is only 20 % of what is found in chlorine bleaching but most important is that not high chlorinated toxic compounds are formed.

PRODUCTION OF CHLORINE DIOXIDE

Chlorine dioxide has been commercially used for bleaching pulp since the mid 1940's. Until 1969, the only chlorine dioxide processes that were available produced a waste acid by-product. As the demand for this by-product diminished, our technology kept pace. The SVP® process was developed to eliminate the waste acid effluent and to produce a dry saltcake. The first commercial SVP® unit for producing chlorine dioxide went on stream in 1969, at Union Camp's Mill in Virginia, U.S.A. It did not take long for other mills to recognize the value of a system that could produce low-cost chlorine dioxide with no sulfuric acid effluent. With energy costs rising and pollution controls stiffening, the SVP® process was a product for the time. As a result, by the end of 2002 more than 100 SVP® units have been installed, modified or are presently under construction, throughout the world.

The development of the SVP-LITE® process is an outgrowth of this continual improvement and implementation. To meet the ever changing requirements of modern pulp mills, a process was required that minimized a standard SVP®'s by-product chlorine and saltcake. The chlorine by-product is eliminated completely and the saltcake is reduced 40%. The SVP-LITE® process utilizes the same high quality equipment and design that is used in the normal SVP® process, the only basic difference is in the chemistry.

The SVP-LITE® process is an ideal choice for pulp mills:

- That want to eliminate the chlorine in the chlorine dioxide water to produce ECF pulp
- That have low saltcake make-up requirements
- That want to economically expand the capacity of existing SVP®/R3 plants
- That can not utilize chlorine water or hypochlorite

Chemistry

The production of chlorine dioxide in the SVP-LITE® process is based upon the reaction between sodium chlorate, sulfuric acid, and methanol, per the following overall reaction:

$$9NaClO_3 + 2CH_3OH + 6H_2SO_4 \rightarrow$$
$$9ClO_2 + 3Na_3H(SO_4)_2 + 1/2CO_2 + 3/2HCOOH + 7H_2O$$

To maintain the highest yields and generator efficiencies possible, reactant concentrations are carefully controlled. The SVP-LITE® process, like the whole SVP® family of processes, can easily be converted to other modes of operation to meet the mill by-product requirements.

Chlorine dioxide generation

The heart of the SVP-LITE® process is an all titanium chlorine dioxide generator, a large vessel in which the sodium chlorate is reduced to form chlorine dioxide. The generator is sized to optimize reaction efficiency, promote saltcake crystal growth, provide efficient liquid-gas separation and to provide sufficient capacity for optimum control of chemical compositions.

A titanium pump circulates the generator solution through a titanium shell and tube heat exchanger, where water is evaporated, through indirect contact with low pressure steam. The vapor in turn leaves the generator combined with chlorine dioxide gas. The design of all the components in this loop is critical to eliminate boilouts and is unique to our process. The water evaporation rate is matched to the rate at which water enters the generator with the chemical feeds and from miscellaneous sources. Chemical feeds are injected into the recirculation cycle at the optimum points, to maximize and to insure adequate mixing. The entire generating system is operating under vacuum.

Chlorine dioxide recovery

The gas leaving the generator is a mixture of chlorine dioxide, water vapor and trace amounts of chlorine. The heat in this gas is removed in the generator condenser, where water vapor is condensed, thereby enriching the chlorine dioxide concentration of the gas. The chlorine dioxide is absorbed in a packed tower, the chlorine dioxide absorber, where water is forced into intimate contact with the gas. The resulting product is a strong solution of chlorine dioxide with a trace amount of chlorine. This solution is then pumped to storage tanks for further use in the bleaching process.

Contrary to other SVP® processes the gas from the chlorine dioxide generator does not contain any diluting gases like air or chlorine. This means that the absorption efficiency will be high. Chlorine dioxide concentrations up to and even exceeding 10 g/l can easily be reached when using chilled absorption water.

LABORATORY ECF BLEACHING

The ECF laboratory bleaching trials were carried out on both conventional and oxygen delignified softwood and eucalyptus pulps. The unbleached pulp characteristics and the chemical charges are given in Table 1. The charges of chlorine dioxide are calculated as active chlorine throughout this paper. The pulps were bleached to a final brightness of above 89% ISO, using optimum bleaching conditions (1, 2, 3) and a typical five stages bleaching sequence.

Table 1 Unbleached pulp characteristics, bleaching sequences and chemical charges

Kraft Pulp	Conventional Softwood	O_2 del. Softwood	Conventional Eucalyptus	O_2 del. Eucalyptus
Kappa No	28	12	13	8
Brightness, %ISO	22	38	42	56
Viscosity, dm^3/kg	996	1000	1127	993
Bl. Sequence	D (EPO) D (EP) D	D (EPO) D (EP) D	D (EO) D (EP) D	D (EO) D (EP) D
ClO_2 (aCl), kg/t	86	39	45	25
Kappa factor	0.20	0.15	0.15	0.15
H_2O_2, kg/t	7	3	1	1

Evaluation of the proper bleaching conditions

A study of the appropriate bleaching conditions for the individual stages of the ECF bleaching sequence was carried out with emphasis being placed on the importance of the final pH in all the stages. This parameter seems to be the one, which is fairly easily adjustable and may influence pulp and effluent characteristics. At each pH level of the D stages the time and temperature were adjusted to maintain a residual chlorine level of less than 0.5 kg/t.

Effects of final pH in the DØ stage

The effects of varying the final pH in the DØ stage were evaluated after a constant EO stage. For the conventional softwood and eucalyptus no noticeable effects on either the brightness or the kappa number were observed within the pH range of 2 to 4 in the DØ stage. The curves are very similar with differences in the brightness level related to the differences in the kappa number and the unbleached brightness. Considering the viscosity drop in the EO stage a recommended final pH in the DØ-stage is about 3, Figure 1.

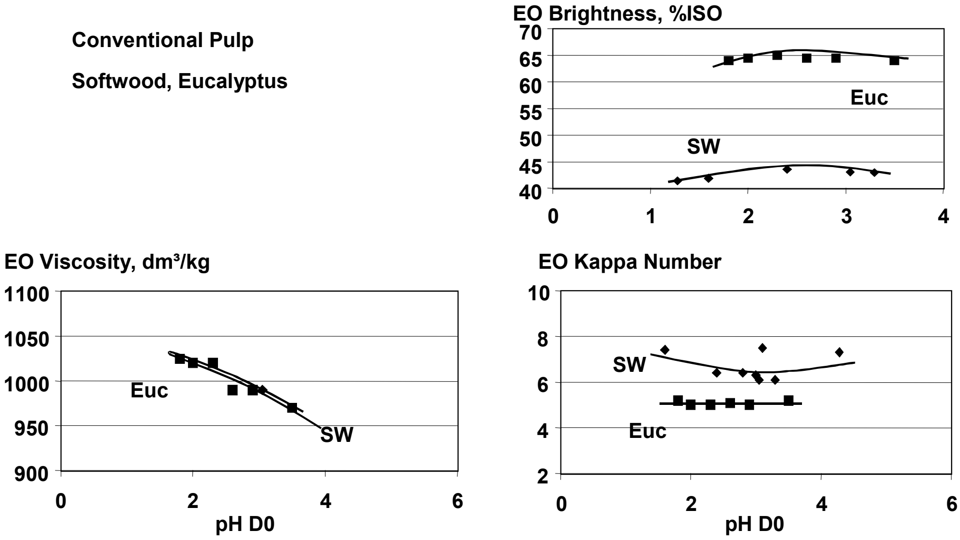

Figure 1 Effects in the EO stage related to final pH in DØ stage – conventional pulp

This trend was similar for the oxygen delignified pulp, but the drop in viscosity after the EO stage occurred at a higher pH level of about 3.5, Figure 2.

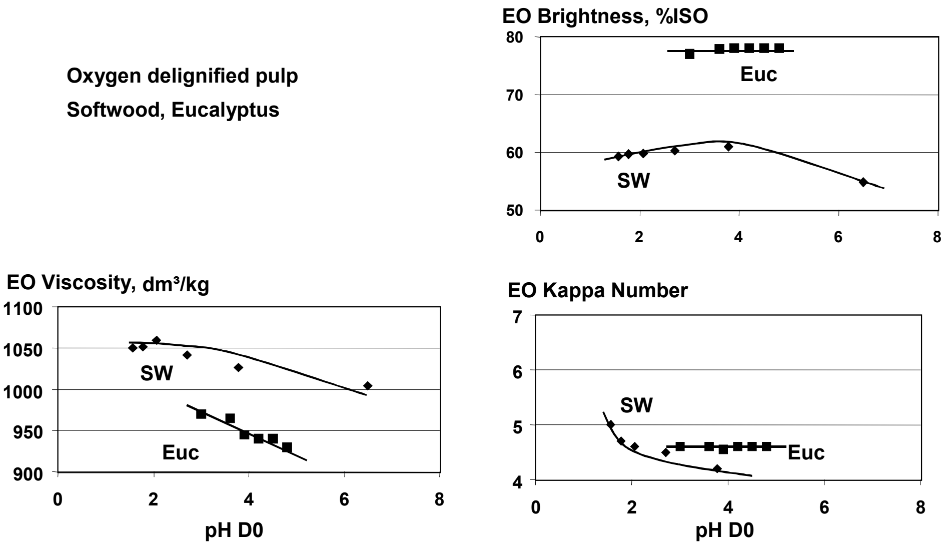

Figure 2 Effects in the EO stage related to final pH in DØ stage – oxygen delignified pulp

Effects of final pH in the EO stage

When studying the effects of pH in the EO stage on conventional pulps, it was found that between pH 9 to 12 there is a continuous increase in the brightness especially for the eucalyptus pulp, and a decrease in the kappa number at a very limited drop in the viscosity, Figure 3.

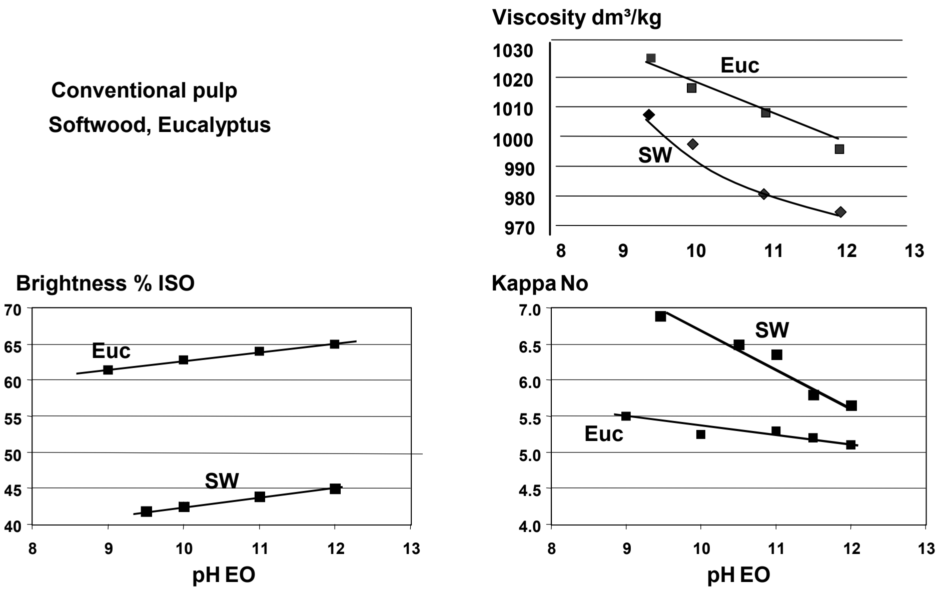

Figure 3 Effects of final pH on pulp characteristics in the EO-stage – conventional pulp

These effects were almost the same when bleaching the oxygen delignified pulps.

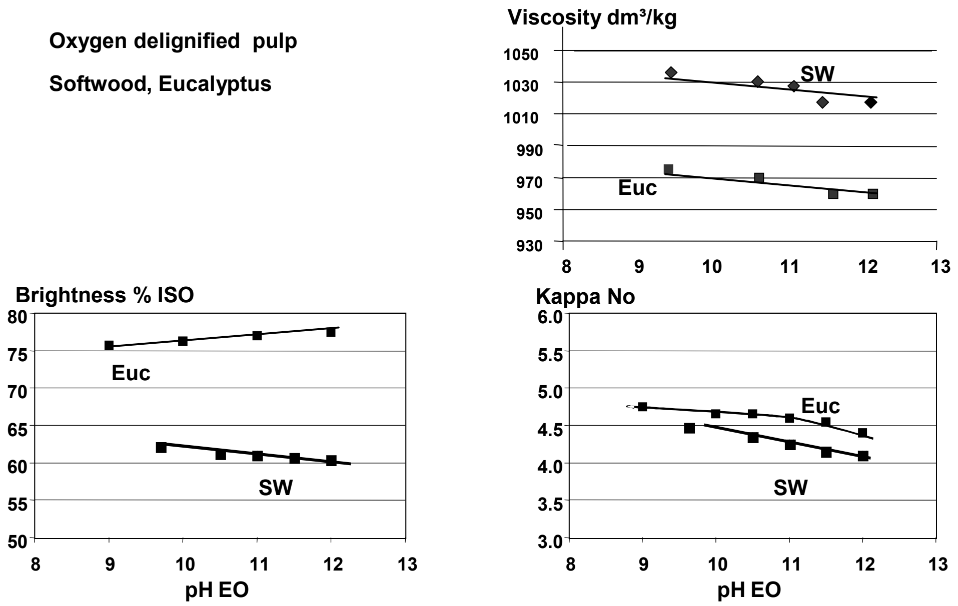

Figure 4 Effects of final pH on pulp characteristics in the EO stage – oxygen delignified pulp

The effect of pH in the EO stage was also studied in terms of COD formation. The COD level in the effluents then became the determining parameter in the EO stage for finding the optimum pH in this stage, Figure 5.

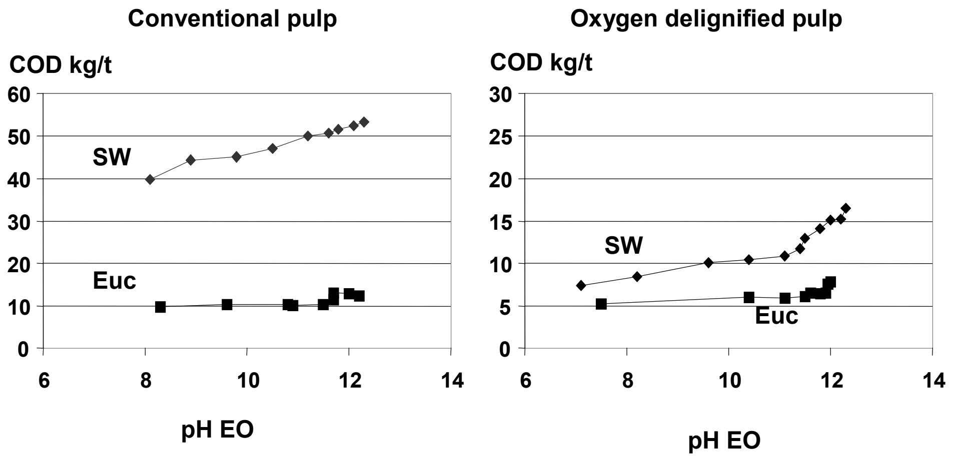

Figure 5 Effects of final pH on COD formation in the EO stage

There seems to be no justification for going above the pH level of about 11, without contributing unnecessarily to the formation of COD. The differences between softwood and eucalyptus is the level of COD related to the difference in unbleached kappa numbers.

Effects of final pH in the D1 stage

In the D1 stage, altering the pH was observed to have limited effect on the brightness levels at given charges of ClO_2 when bleaching conventional pulp. The viscosity, however, tended to drop as the pH increased, Figure 6.

Conventional pulp

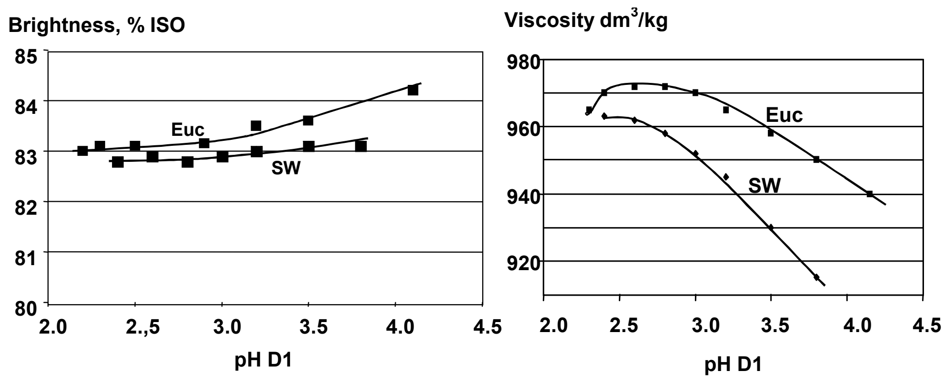

Figure 6 Brightness and viscosity related to pH in D1 stage – conventional pulp

The same type of optimization was also performed on the oxygen delignified pulps. In the case of the oxygen delignified pulp increasing the pH gave an increase in brightness. The determining factor for optimization became the effect of pH on the viscosity, Figure 7.

Oxygen delignified pulp

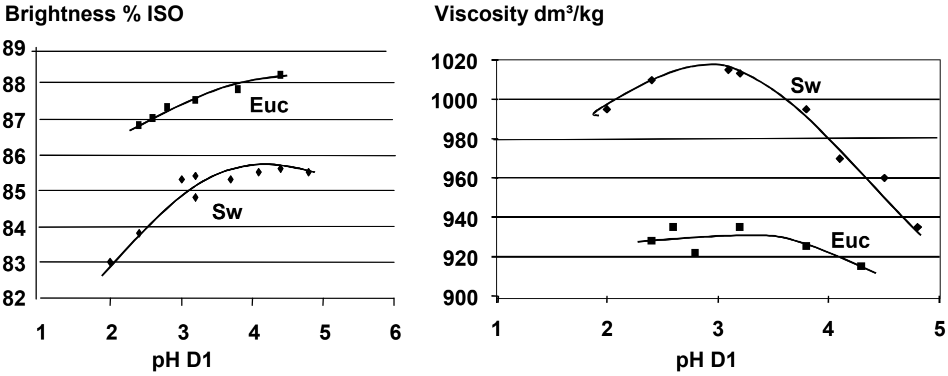

Figure 7 Brightness and viscosity related to pH in D1 stage – oxygen delignified pulp

The optimal pH for both softwood and eucalyptus is 3.0 – 3.2. From other laboratory tests we know that each charge of chlorine dioxide in D1 may have its own optimum pH.

Effects of final pH in the E2 stage

In the peroxide reinforced E2 stage the brightness and viscosity is in a certain level affected of a pH increase. Between the pH of 10 to 11.5 the brightness for conventional pulps increases 2 to 2.5 %ISO. For oxygen delignified pulps the brightness increase is less or between 0.6 to 1.0 %ISO within this pH range. The viscosity drops slightly as the pH increase from 10 to 11.5 for all pulps. However, the conventional softwood seems to be more affected in the viscosity when the pH exceed 11.2, Figure 8 and 9.

Conventional pulp

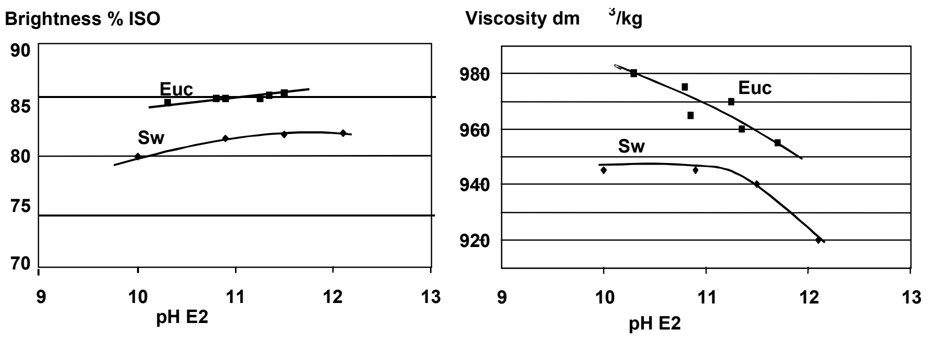

Figure 8 Brightness and viscosity related to pH in E2 stage – conventional pulp

Oxygen delignified pulp

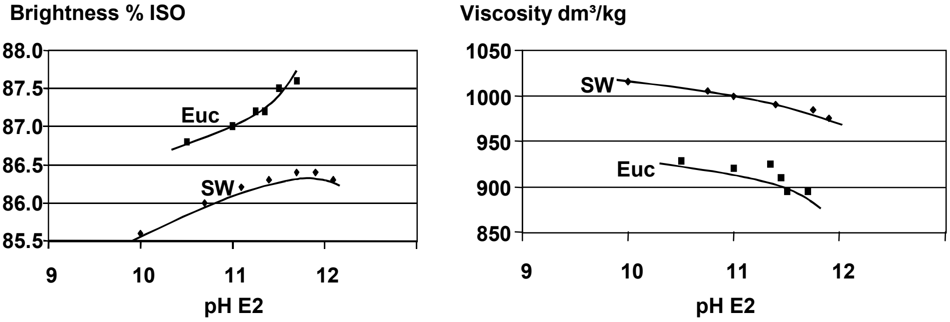

Figure 9 Brightness and viscosity related to pH in E2 stage – oxygen delignified pulp

Effects of final pH in the D2 stage

Also in the final D2 stage the effects of pH was studied in terms of brightness and viscosity. The charge of chlorine dioxide was 15 kg/t on the conventional softwood pulp and 10 kg/t on the conventional eucalyptus pulp. For the conventional pulps the brightness optimum related to the pH is similar for softwood and eucalyptus. Within the pH level 3 to 4 there is no or a minor drop in the viscosity but at higher pH:s the viscosity drop increases, Figure 10.

Conventional pulp

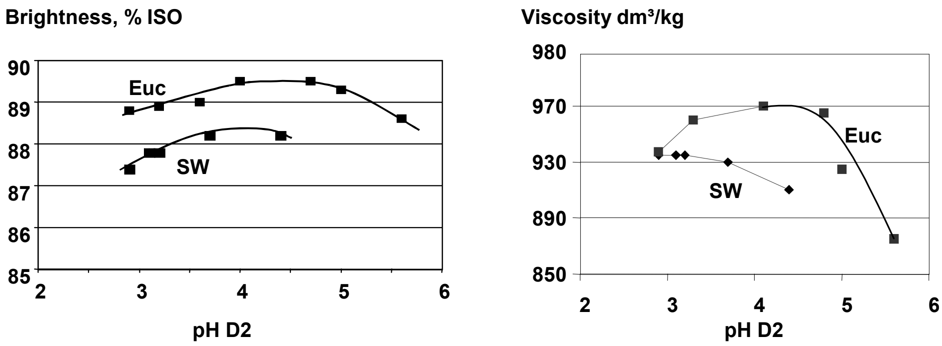

Figure 10 Brightness and viscosity related to pH in D2 stage – conventional pulp

For oxygen delignified pulps there is a different brightness optimum for softwood and eucalyptus related to the pH, but also for different charges of chlorine dioxide. This is shown in Figure 11, where two charges of chlorine dioxide, 5 and 10 kg/t, were used on the eucalyptus pulp. The chlorine dioxide charge was 5 kg/t for the softwood pulp.

Oxygen delignified pulp

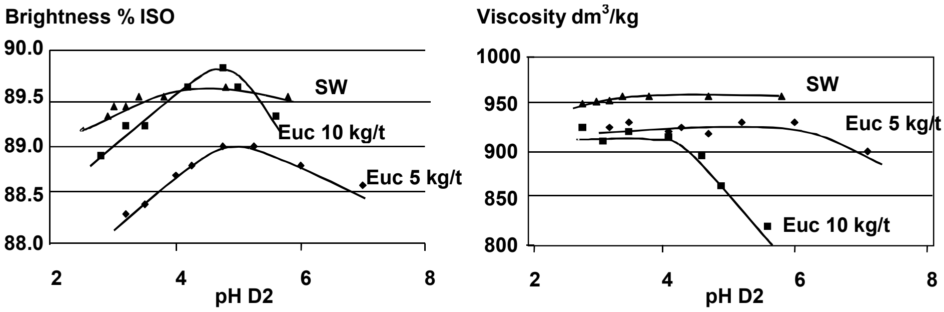

Figure 11 Brightness and viscosity related to pH in D2 stage – oxygen delignified pulp

Within the pH level 3 to 4 there is no viscosity drop on softwood or eucalyptus at a chlorine dioxide charge of 5 kg/t. However, for a higher charge of chlorine dioxide the viscosity drop is more obvious when the pH exceed 4.

Final results of the bleached pulp

The final bleached pulp characteristics for the pulps are listed in Table 2. A final brightness of between 89 to 90 %ISO was reached using optimum bleaching conditions in all bleaching stages.

Table 2 Bleached pulp characteristics

Kraft Pulp	Conventional Softwood	O_2 del. Softwood	Conventional Eucalyptus	O_2 del. Eucalyptus
Kappa No	0.8	0.6	0.8	0.8
Brightness, %ISO	89.5	90.2	89.3	89.3
Visc. drop, dm^3/kg	130	115	85	85

The viscosity drops were normal for all pulps and the final kappa numbers were of between 0.6 and 0.8 for all pulps.

COMPARATIVE CHARACTERISATION OF COMBINED BLEACH PLANT EFFLUENTS

The characterization studies were carried out on combined effluents from laboratory ECF bleached softwood and eucalyptus pulps, according to Table 1 and Table 2, except for the oxygen delignified eucalyptus pulp which was bleached in a three stages sequence to a final brightness of 89.5 %ISO (4). The combined effluents from all pulps were exposed to biological treatment and characterized both prior to and after the treatment (5, 6, 7).

The parameters studied were AOX, COD, BOD, organics including resin acids and sterols, inorganics and the acute toxicity measured as Microtox. When characterizing the effluents after the biological treatment even bioassay studies were carried out using the green alga Selenastrum and the crustacean, Ceriodaphnia, Table 3.

Table 3 Parameters studied in the effluents

Combined effluents **prior to** Effluent Treatment	Combined effluents **after** Effluent Treatment
AOX, COD, BOD5, Chlorate and Color Organics Resin acids Sterols Microtox	AOX, COD, BOD5 Chlorate Organics Resin acids Sterols Microtox; Selenastrum; Ceriodaphnia Dubia

The type of laboratory biological effluent treatment used was a continuous two-stage process schematically depicted in Figure 12. The treatment was chosen to give the best possible degradation thus showing the potential of biological treatment. It consisted of an initial 2-hour anaerobic stage, aimed at eliminating the chlorate content, and of a final 12-hour aerobic activated sludge stage (3), aimed at reducing the organic compounds measured as COD, AOX etc.

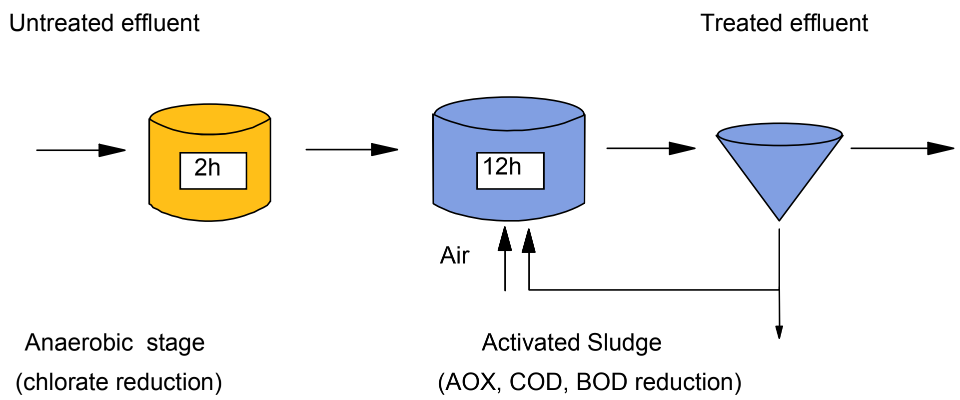

Figure 12 Laboratory effluent treatment

Effluent characterisation prior to effluent treatment

A comparison of the effluents from eucalyptus and softwood pulps shows the same pattern concerning the AOX levels. For both conventional pulps, the AOX levels were 1 kg/t, whereas for the oxygen delignified pulps, the levels were between 0.6 and 0.7 kg/t, Figure 13. In the case of the COD, the total levels are dependent on the initial kappa numbers. The trends for the levels of BOD_5 and color in the combined effluents are also shown.

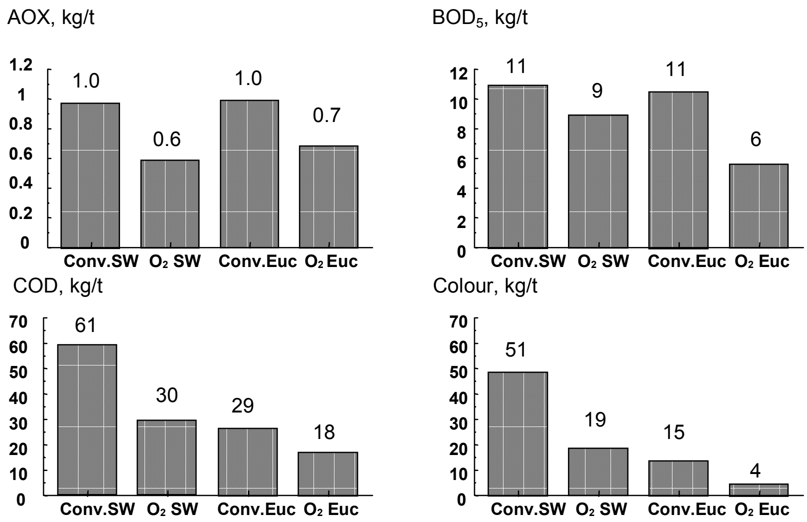

Figure 13 Effluent characteristics prior to treatment

The soluble organic compounds were further characterized as lignin, carbohydrates, methanol, extractives and various low molecular acids and their contribution to the total COD levels were calculated (7) using the conversion factors listed in Table 4.

Table 4 Conversion factors used in the COD characterisation

Compounds	Factors*
Lignin	1.9
Carbohydrates	1.2
Methanol	1.5
Formic acid	0.4
Acetic acid	1.1
Extractives	2.7

*from substance to COD

Figure 14, shows the percentages after conversion to COD for the individual effluent parameters and for the different types of pulp, with the numbers above each column representing the actual quantity in kg/t. The most important difference, when comparing the softwood effluents with the eucalyptus effluents, is the higher lignin content in the softwood effluents.

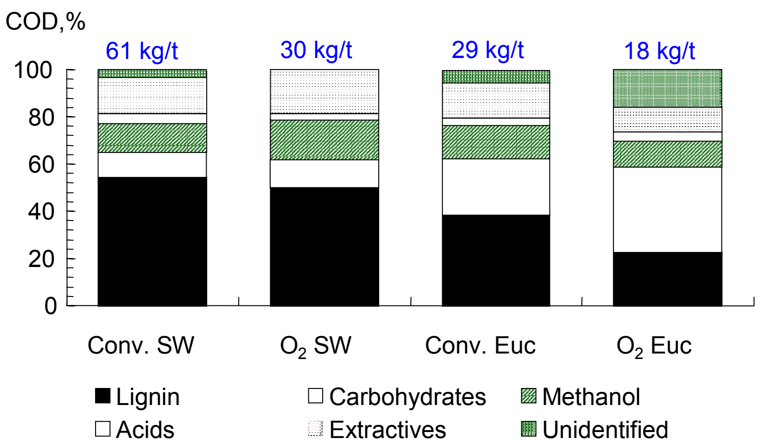

Figure 14 Effluent COD characteristics prior to treatment - combined effluents

Whereas for the softwood effluents, the COD levels varied, 61 kg/t for the conventional pulp and 30 kg/t for the oxygen delignified pulp, the distribution of lignin, carbohydrate, methanol, acids and extractives were very similar. On the other hand, the effluents from the oxygen delignified softwood and the conventional eucalyptus pulps had about the same total COD level, but their distribution of the COD components were quite dissimilar.

Effluent characterisation after effluent treatment

This part of the paper deals with the effects of the biological treatment on the combined effluents. Figure 15 shows the level of AOX and COD after the biological treatment.

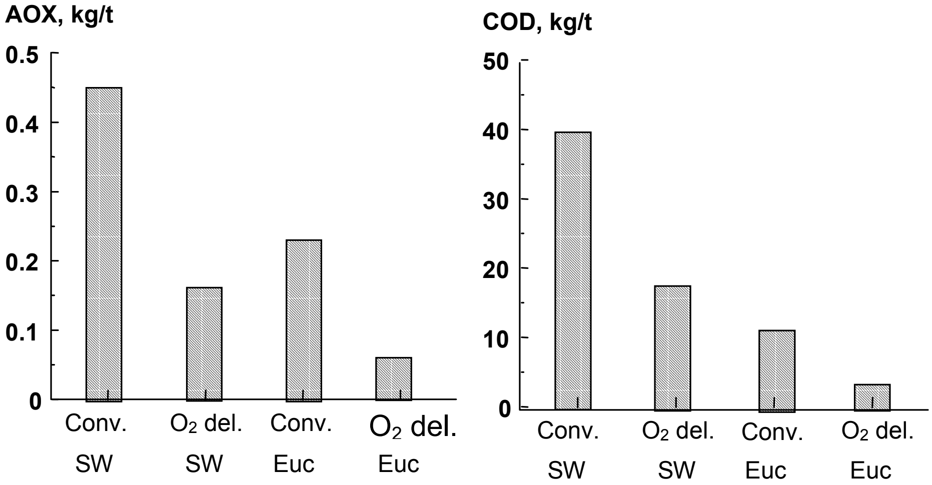

Figure 15 Levels of AOX and COD after effluent treatment

The AOX levels achieved were between 0.1 and 0.5 kg/t and for the COD, apart from the first column which represents the combined conventional softwood effluent, all the levels were below 20 kg/t. The explanation for the higher level of COD in the softwood effluents, especially for the conventional pulp, is that, whereas biological effluent treatment readily decomposes carbohydrates, methanol, acids, etc. it has very little effect on the lignin, resulting in good treatability for the effluents with low lignin content, Table5.

Table 5 Reductions in laboratory effluent treatment

Compound	Reduction
Lignin	0 – 30
Carbohydrates	85 – 100
Methanol	100
Acids	100
Resin Acids	60 – 100
Sterols	60 – 100

Environmental aspects

Many parameters are needed to evaluate the environmental aspects of the effluent characterization (8, 9). In this study Microtox was chosen as an indicative parameter and since compounds, such as sterols and resin acids which originate from the extractives, are suspected of having effects on fish for example, it is of environmental interest to measure even these compounds. As further bioassays, the green alga Selenastrum and the crustacean Ceriodaphnia Dubia were used.

In Figure 16 the levels of resin acids and sterols in the combined effluents both prior to and after effluent treatment are depicted.

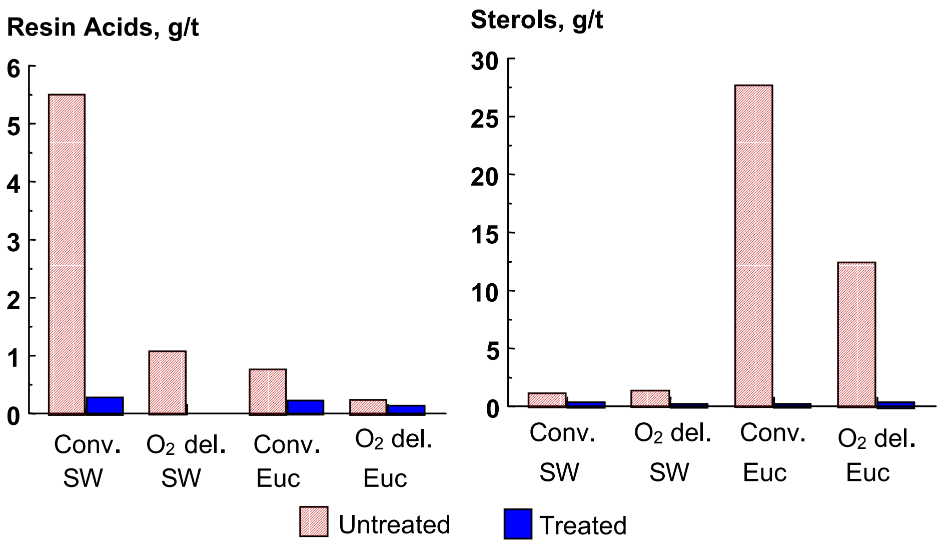

Figure 16 Levels of resin acids and sterols in combined effluents prior to and after effluent treatment

Whereas the levels of sterols and resin acids, prior to treatment, differed somewhat depending on the pulp etc., after treatment, these differences were eliminated, due to the almost total removal of both resin acids and sterols by the biological treatment. As expected, prior to the effluent treatment, the levels of sterols were lower and the levels of resin acids, higher in the softwood effluents compared to the eucalyptus effluents.

The bioassay test results were recalculated to Toxic Equivalent Factors, with the TEF values based on EC50 or LOEC values.

♦ EC50 corresponds to the concentrations of effluent, where a 50 % effect in the test occurs, for example 50 % growth inhibition of green algae.

♦ LOEC is equal to the Lowest Observed Effect Concentration, which means the concentration where an effect first occurs.

♦ TEF is calculated in the following way: TEF = Effluent Flow *100/(EC50 or LOEC). When the EC50 or LOEC values are equal to one hundred – the TEF values are defines as zero.

Some minor response was observed in the Microtox test on the untreated effluents but for all treated effluents tested, no response was observed, either for Microtox and Selenastrum on the EC50 levels or on the LOEC level for the Ceriodaphnia Dubia, Table 6.

Table 6 Bioassay results after treatment – combined effluents

	Conv. SW	O_2 SW	Conv. Euc	O_2 Euc
Microtox TEF (EC50)	0	0	0	0
Selenastrum TEF (EC50)	0	0	0	0
Cerio. Dubia Repr. TEF (LOEC)	0	N/A	0	0

CONCLUSIONS

Conventional and oxygen delignified softwood and eucalyptus pulps were successfully bleached in five stage sequences to over 89 % ISO.
There are obvious similarities in bleaching both the conventional and the oxygen delignified softwood and eucalyptus pulps in terms of bleaching conditions for optimum bleaching results.

The lignin content in the softwood effluents is significantly higher compared to eucalyptus effluents. The COD reduction in the effluent treatment is therefore lower for softwood effluents, since lignin is very little affected of the biological effluent treatment.

Due to the almost total removal of both resin acids and sterols by the biological treatment no response was observed, either for Microtox and Selenastrum on the EC50 levels or on the LOEC level for the Ceriodaphnia Dubia.

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