# ON THE ROLE OF XYLAN IN OXYGEN DELIGNIFICATION

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## ABSTRACT
Using modern cooking concepts for the manufacture of hardwood kraft pulp, a higher pulp yield is obtained, mainly as a result of higher xylan retention. The effect of the xylan content in the pulp on the oxygen delignification is the topic of the present study. An industrial Eucalypt Urograndis kraft pulp was subjected to xylanase treatment prior to oxygen delignification in order to obtain similar pulp differing primarily in their content of xylan. The results showed that up to 30 % xylan was removed from the eucalyptus kraft pulp by xylanase but the removed xylan had no effect on the delignification in the oxygen delignification. The pulps with high xylan content showed a slightly improved selectivity in the oxygen delignification compared to pulps with low xylan content. Thus it seems that the xylan acts as a protector for the cellulose degradation. The xylanase treatment seemed to have a slightly preference to dissolve high-substituted xylan rather than xylan not attached to HexA.

## INTRODUCTION
One efficient way to increase the overall yield of kraft pulp is to terminate the cook at a higher kappa number and continue with oxygen delignification and bleaching. The increased yield means that more carbohydrates have been retained in the pulp and in a hardwood kraft pulp it is mainly the xylan content that is higher. By terminating the cook at higher kappa number the pulp will also be less delignified and consist of a higher amount of lignin. The lignin should of course be removed in subsequent bleaching. Extending the oxygen delignification is a better alternative than extending the bleaching due to a lower cost and less environmental impact of the oxygen delignification. However, by oxygen delignification not all the lignin could be removed, at least not without a severe degradation of cellulose. The limits of oxygen delignification of hardwood kraft pulps have been explored in a number of studies, focusing on the structure of the residual lignin [1, 2], the importance of Lignin-Carbohydrate Complexes (LCC) [3], the importance of carbohydrates [4] and the importance of process parameters both in the cooking process [5] and in the oxygen delignification [6].

Recently, it has been shown by Näsman et al. [7] that the efficiency of oxygen delignification of a hardwood kraft pulp was markedly reduced as the cooking kappa number was increased. This effect was suggested to partly be a result of a higher yield of hemicellulose. The response to oxygen delignification of hardwood kraft pulp having a high hemicellulose content has also been study by Zou et al. [8]. It was then reported that pulps with a high xylan content were more difficult to delignify but showed a better selectivity compared to pulps with a low xylan content.

In this study the effect of xylan content of a Eucalypt Urograndis kraft pulp on the oxygen delignification process was investigated. The xylan content was varied by means of enzymatic treatment using endoxylanase degrading parts of the xylan. Oxygen delignification trials were performed on the treated pulps.

## EXPERIMENTAL
An industrially manufactured Eucalypt Urograndis kraft pulp (kappa number 18.1, limiting viscosity number 1400 dm³/kg) was obtained from Aracruz, Brazil. The pulp was treated with Pulpzyme HC, a 1,4-endoxylanase from Novozymes. The treatment was performed at pH 7 (0.02 mol/dm$^3$ phosphate buffer), 60 °C and at 4 % consistency for 2 h. Three different enzyme charges were investigated; 0.25 XU/g, 12.5 XU/g and 125 XU/g. A control without any xylanase added was also made. The xylanase treated pulps were oxygen delignified in teflon-coated stainless steel autoclaves, heated while rotating in a polyethylene glycol bath. The oxygen delignification trials were performed at 10 % consistency, at 105 °C with 0.5 MPa oxygen pressure for 90 min using an alkali charge of 20 kg sodium hydroxide/BDt [bone dry] pulp.

Kappa number was determined according to ISO 302:2004 and the limiting viscosity number according to ISO 5351:2004. The carbohydrate content of the pulps was determined according to Tappi T249 cm-85, except that ion-exchange chromatography was used instead of gas chromatography for separation. The HexA content of the pulps was determined according to a method described by Gellerstedt and Li [9].

## RESULTS AND DISCUSSION
Xylan was removed from a Eucalypt Urograndis kraft pulp by enzymatic treatment using xylanase. The carbohydrate composition of the enzymatically treated pulps is shown in Table 1.

**Table 1:** Carbohydrate composition in the pulps after xylanase treatment.

| | After enzymatic treatment | | | |
|---|---|---|---|---|
| **Xylanase** XU/g | **Xyl** Rel % | **Glu** Rel % | **Man** Rel % | **Gal** Rel % |
| 0 | 17.1 | 82.6 | 0.2 | 0.2 |
| 0.25 | 15.9 | 83.7 | 0.2 | 0.2 |
| 12.5 | 13.2 | 86.5 | 0.2 | 0.1 |
| 125 | 11.9 | 87.9 | 0.2 | 0.1 |

It can be seen that a xylose removal of up to 30 % was reached, but a complete removal of the xylan did not even seem possible at any charge. The reasons behind this behaviour could be many. One speculation is that the xylanase primarily removed re-precipitated xylan on the surface of the cellulose fibres, whereas xylan located more inside the fibres was not accessible for the enzyme, hindered by the cellulose or by covalently bound lignin.

The carbohydrate composition of the pulps after the subsequent oxygen delignification is shown in Table 2.

**Table 2:** Carbohydrate composition in the pulps after oxygen delignification.

| | After oxygen delignification | | | |
|---|---|---|---|---|
| **Xylanase** | **Xyl** | **Glu** | **Man** | **Gal** |
| XU/g | Rel % | Rel % | Rel % | Rel % |
| 0 | 16.5 | 83.1 | 0.2 | 0.2 |
| 0.25 | 15.4 | 84.3 | 0.2 | 0.2 |
| 12.5 | 11.8 | 87.9 | 0.2 | 0.1 |
| 125 | 10.1 | 89.6 | 0.2 | 0.1 |

During the oxygen delignification more xylan was dissolved from the xylanase pretreated pulp. The effect was most clear for the pulps subjected to the highest xylanase charge, thus having the lowest xylose content. This could be an effect of that all depolymerised xylan was not dissolved in the washing after the xylanase treatment and the alkali in the oxygen delignification enhanced the dissolution of the depolymerised xylan.

In order to investigate a possible impact of the xylan content of the pulp on the efficiency and selectivity of the oxygen delignification process, kappa number and limiting viscosity were determined. To obtain accurate lignin-related kappa numbers, all pulp samples were analysed for their content of hexenuronic acid (HexA) and the contribution to the kappa number by this structure was subtracted from the measured kappa number. This procedure, although providing a more accurate lignin-related kappa number, still suffers from the fact that other structures in the pulp also contribute to the kappa number [10]. Consequently, all lignin-related kappa numbers are slightly too high. The kappa numbers obtained for the pulps after xylanase treatment and subsequent oxygen delignification are shown in Table 3.

During the xylanase treatment, also some HexA was dissolved along with the xylan backbone. This removal of HexA resulted in a decreased kappa number. Small amounts of lignin were also dissolved during the xylanase treatment. One possible reason for the lignin removal is that some lignin originally hindered by the xylan was more accessible when some of the xylan was removed. Another possible explanation is that lignin bound to the xylan through covalent lignin–carbohydrate bonds (LCC) could be dissolved when some of the xylan was removed. However, the lignin removal was, compared to the removal of xylan, small.

Oxygen delignification does not degrade HexA, which was also confirmed in this study. The oxygen delignification trials in this study all led to a removal of around six kappa number units. Since the HexA content was almost unchanged, the decrease in kappa number was mostly due to the lignin removal. In the present study the xylan content seemed not to have any effect on the delignification in the oxygen delignification. It is difficult to draw any conclusions regarding how the xylan left in the pulp could affect the oxygen delignification.

The cellulose-related limiting viscosity number can be calculated according to equation 1.

$$\eta_{cell} = \frac{\eta c}{x_{cell} \cdot c} \qquad (1)$$

where $\eta_{\mathrm{cell}}$ is the corrected viscosity for the contribution of hemicellulose, $\eta c$ is obtained from the limiting viscosity analysis and should be close to 3.0 as possible, $\chi_{\mathrm{cell}}$ is the amount of cellulose in the sample (data taken from the carbohydrate analysis) and $c$ is the concentration of the sample solution (dried pulp divided by the volume of 50 ml solvent)

**Table 3:** Contribution from lignin and HexA to the total kappa number after xylanase treatment and subsequent oxygen delignification. The decrease in kappa number in the oxygen delignification is expressed as Δ kappa number.

| **Xylanase** | **Kappa No after enzymatic treatment** | | | **Kappa No after oxygen delignification** | | | **Δ Kappa No oxygen delignification** | |
|---|---|---|---|---|---|---|---|---|
| XU/g | Total | HexA | Lignin | Total | HexA | Lignin | Total | Lignin |
| 0 | 17.4 | 6.2 | 11.2 | 11.3 | 6.1 | 5.2 | **6.1** | **6.0** |
| 0.25 | 16.3 | 5.8 | 10.5 | 10.2 | 5.9 | 4.3 | **6.1** | **6.2** |
| 12.5 | 14.0 | 4.4 | 9.6 | 8.2 | 4.1 | 4.1 | **5.8** | **5.5** |
| 125 | 13.7 | 3.6 | 10.1 | 7.6 | 3.2 | 4.4 | **6.1** | **5.7** |

In Figure 1, the cellulose-related limiting viscosity number after oxygen delignification is plotted against the xylan content in the pulps after the xylanase treatment. The viscosity is corrected for the contribution from hemicelluloses according to equation 1.

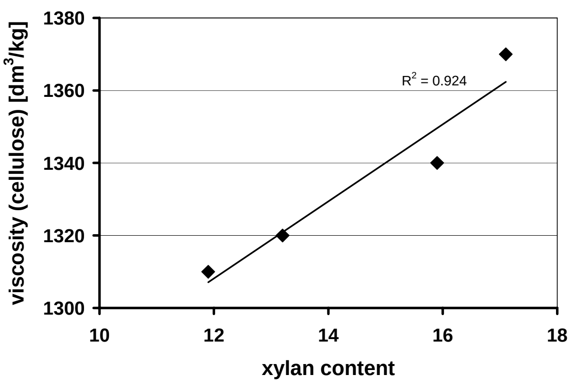


**Figure 1:** The effect of xylan content in the pulps on cellulose-related viscosity after the oxygen delignification.

The cellulose-related viscosity was not affected by the enzymatic treatment, which means that all the pulps started at the same cellulose viscosity of 1680 $dm^3/kg$ into the oxygen delignification. In Figure 1 it can be seen that a higher xylan content in the pulp seems to yield a slightly higher cellulose viscosity of the pulp after oxygen delignification. Since the kappa number reduction was the same for all the pulps in the oxygen delignification, the pulp with the highest xylan content showed a slightly better selectivity in the oxygen delignification. Thus a higher xylan content in the unbleached pulp gave a better selectivity in the oxygen delignification. Zou et al. has also seen that pulps with high xylan content has a higher viscosity after oxygen delignification and they suggested that xylan is protecting the cellulose in the pulp from degradation by hydroxyl radicals[8].

In Table 4, the degree of substitution of the xylan with HexA is presented. The degree of substitution provides some useful information of how the xylanase works.

**Table 4:** The degree of substitution of HexA in the pulps after enzymatic treatment.

| **Xylanase** | **After enzymatic treatment** |
|---|---|
| XU/g | HexA /100 xylose residues |
| 0 | 6.0 |
| 0.25 | 5.9 |
| 12.5 | 5.3 |
| 125 | 4.8 |

As the xylanase charge is increased the degree of substitution seems to decrease slightly. This could be an effect of the carboxylic acid groups in HexA, making the high-substituted xylan more easily dissolved.

## CONCLUSIONS

Some 30 percent of the xylan of the investigated Eucalypt Urograndis kraft pulp was readily removed by means of an enzymatic treatment with an endo-xylanase. However, the remaining 70 percent of the xylan seemed difficult to affect by this kind of a treatment. The removal of the 30 % of the xylan from the pulp did not markedly affect the efficiency of a subsequent oxygen delignification treatment. However, whether or not the xylan left in the pulp could exhibit such an effect was not possible to conclude in the present study. The pulps with high xylan content showed a slightly improved selectivity in the oxygen delignification compared to pulps with low xylan content. Thus it seems like that the xylan acts as a protector for the cellulose degradation. It was also found that the enzymatic treatment seemed to have a preference to peel xylan high-substituted with HexA.


## ACKNOWLEDGE

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