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# INFLUENCE OF XYLAN CONTENT ON THE OXYGEN DELIGNIFICATION PERFORMANCE OF EUCALYPT KRAFT PULPS AS STUDIED USING PREHYDROLYSIS AND XYLANASE TREATMENTS

Helena Wedin,[a] Stefan Antonsson,[b,*] Martin Ragnar,[c] and Mikael E. Lindström [a,*]

Common metrics for evaluating the efficiency of oxygen delignification include the kappa number and Klason lignin content. As a change in xylan content often leads to a change in HexA content, the kappa number must be corrected for the HexA contribution before evaluating the degree of oxygen delignification when trying to understand the process in detail. Questions could also be raised about the accuracy of the Klason lignin method for oxygen-delignified hardwood kraft pulps, since the amount of residual lignin is small in such pulp. This study investigates the influence of xylan content on oxygen delignification efficiency in *Eucalyptus urograndis* kraft pulps. Xylan content was varied using two methods: treatment with xylanase and with acid prehydrolysis for various times before kraft cooking. The degree of oxygen delignification, expressed as the HexA-corrected kappa number, indicated no significant trend with xylan removal, and no significant trend was evident when expressed as Klason lignin content.

*Contact information: a: School of Chemical Science and Engineering, Division of Wood Chemistry and Pulp Technology, Royal Institute of Technology, SE-100 44, Stockholm, Sweden; b: Metso Paper Sweden AB, Box 1033, SE-651 15 Karlstad, Sweden; c: Svenskt Gastekniskt Center AB, Scheelegatan 3, SE-212 28, Malmö, Sweden; * Corresponding author: mil@kth.se*

## INTRODUCTION

Competition to sell bleached market hardwood kraft pulp is intense; because of this, pulp mills are seeking new ways to reduce production costs. Increasing the carbohydrate retention during kraft pulping is an attractive alternative, since it means more effective wood use. Several other measures could be taken to increase the yield. Controlling chip quality and size to avoid oversized chips and chips with knots and bark is one way. Other ways to increase the kraft cook yield include terminating the cook at a high kappa number, reducing the cooking temperature, avoiding alkali peaks, and/or adding yield-preserving additives (Kleppe and Kringstad 1964; Sanyer and Laundrie 1964; Jiang *et al.* 2002; Ragnar and Lindström 2002; Zou *et al.* 2002; Wedin *et al.* 2010).

Zou *et al.* (2002) demonstrated that increased carbohydrate retention, resulting from adding anthraquinone to the kraft cook, reduced the efficiency of subsequent oxygen delignification measured as the degree of delignification. Their study was performed on mixed northeastern US hardwoods. The pulp resulting from the trials had an increased carbohydrate yield and, of the carbohydrates, it was xylan that increased the most. The degree of delignification was expressed in three ways: kappa number, kappa number corrected for the first lignin extraction, and Klason lignin content. All three ways

indicated improved efficiency, as smaller amounts of hemicelluloses were present in the unbleached pulps. Increased degree of delignification (in terms of kappa number) along with xylan removal has also been reported for eucalypt treated with prehydrolysis before kraft pulping (Sixta *et al.* 2006b). The improved efficiency with lower xylan content is discussed in the aforementioned literature, and it may be related to competitive reactions consuming alkali, which would lead to decreased oxygen delignification. Alternatively, lignin–carbohydrate complex (LCC) could play a key role, as the presence of more hemicellulose, which could be linked to lignin, could retard lignin removal during oxygen delignification. The importance of LCC at standard cooking kappa numbers can be questioned, however, since regardless of pre-conditions (*i.e.*, kraft, prehydrolysis-kraft, or sulfite) resulting in different hemicellulose contents, the lignin contribution to the kappa number was similar after oxygen delignification (Antonsson *et al.* 2003).

The most common way of expressing the degree of delignification is by the reduction in the kappa number during oxygen delignification divided by the initial kappa number of the unbleached pulp. However, it is well known that hexenuronic acid (HexA) groups contribute to the kappa number. Hexenuronic acid is a side group in xylan, formed during the kraft cook from 4-*O*-methylglucuronic acid originally present in wood as a side group linked to the xylan backbone. The HexA content of the pulp results not only from the amount of retained xylan, but also from the applied kraft cooking conditions, of which alkalinity and cooking temperature have the greatest effects. In scientifically studying actual lignin removal during oxygen delignification, it is therefore important to correct the kappa number for the HexA content. Another way of expressing the degree of delignification is based on the Klason lignin content. Although the Klason lignin content would be a more correct way of expressing the lignin removal efficiency than would the kappa number, one could – and should – question whether this method really provides significant results, since the lignin content in an oxygen-delignified pulp is very low.

Reduced oxygen delignification efficiency could be an obstacle for high-kappa eucalypt kraft pulps (Näsman *et al.* 2007). Terminating the cook at a high kappa number, *i.e.*, in the 17 to 34 range for eucalypt, means that 30 to 40% of the yield gain is due to hemicellulose retention (Näsman *et al.* 2007; Wedin *et al.* 2010). If xylan retards the oxygen delignification, a large amount of xylan could limit extended oxygen delignification and the desired kappa number might not be reached. Hence, even harsher conditions with additional alkali charge and high temperature would have to be applied to reach the desired low kappa number. In other words, with harsher conditions, a great part of the retained xylan could be lost during extended oxygen delignification. It is therefore important to investigate the impact of xylan content as such on the oxygen delignification efficiency.

The present paper examines the influence of xylan content on the degree of oxygen delignification in terms of the HexA-corrected kappa number and the Klason lignin content of *Eucalyptus urograndis*. Two independent methods were chosen to manufacture unbleached eucalypt kraft pulps with different xylan contents: 1) an enzymatic process using xylanase and 2) using a prehydrolysis pretreatment. The advantage of these over other possible methods, such as autohydrolysis (*i.e.*, hot water extraction) or the use of polysulfide and/or anthraquinone as pulping additives, is the potential to obtain a broad interval in the amount of xylan without substantially affecting the residual lignin content or cellulose depolymerization. However, the literature reports that minor amounts of lignin become dissolved during xylanase treatment (Yang and

Eriksson 1992; Hortling *et al.* 1994) and that more lignin becomes dissolved during subsequent alkaline treatment as an effect of xylanase treatment (Hortling *et al.* 1994). Hence, xylanase treatment as such may increase the efficiency of oxygen delignification. Prehydrolysis conditions could also lead to undesirable condensation reactions, since lignin fragments are more soluble under acidic conditions (Sixta *et al.* 2006a). This could affect the subsequent kraft cook, thereby lowering the efficiency of the following oxygen delignification. On the other hand, prehydrolysis may break the glycosidic bonds between lignin and hemicelluloses in LCC networks (Lawoko *et al.* 2006), which may improve the efficiency of the oxygen delignification. Choosing two independent approaches to xylan removal should make it possible to evaluate the impact of xylan content despite the limitations of each method.

## EXPERIMENTAL

### Materials

Mill-chipped *E. urograndis* wood chips from a plantation in Bahia supplied by Bahia Pulp, Brazil, were used in the prehydrolysis kraft pulping experiments. Clearly oversized chips and chips containing bark, knots, or other deformations were rejected by hand sorting. For the xylanase treatment experiments, an industrial *E. urograndis* unbleached kraft pulp, supplied by Fibria from the Aracruz mill in Barra do Riacho, Brazil, was used. The pulp was carefully washed with deionized water before use.

Pulpzyme HC supplied by Novozymes, Denmark, was used for the xylanase treatments. This product, which contains endo-1,4-β-D xylanase activity (EC3.2.1.8), is produced from a selected strain of Bacillus. The product is standardized to 1000 XU $g^{-1}$ and the supplier-recommended dosage for helping delignify and bleach kraft pulp is 0.5–1.0 XU $g^{-1}$.

### Prehydrolyzed Kraft Pulping

The prehydrolysis treatment used in the prehydrolysis kraft pulping experiments was carried out in 2.5-L stainless steel autoclaves rotating in a heated polyethylene glycol bath. A quantity of 320 g of oven-dried (o.d.) wood chips was put in the autoclave and evacuated for 20 min. Sulfuric acid was then charged at a concentration of 0.02 mol $L^{-1}$ (0.8% $H_2SO_4$ of wood) and a liquor-to-wood ratio of 4:1. The autoclaves were immersed in the polyethylene glycol bath at 120 °C and the prehydrolysis treatment was performed at this temperature for various lengths of time, *i.e.,* 60 to 200 min. Next, the autoclaves were cooled in a bath containing circulating cold water. The free liquor in the autoclaves was removed using a wire-coated Büchner funnel. The volume and pH of the free liquor were noted, as was the weight of the wet prehydrolyzed chips. The wet chips were put back into the autoclaves and evacuated for 10 min before adding white liquor. The kraft cooking was performed in a conventional way, in which all the white liquor was added at the beginning of the cook. The concentration of hydroxide ions in the white liquor was expressed as effective alkali, which is the sum of sodium hydroxide and half of sodium sulfide measured on a common basis and equal to the concentration of hydroxide ions due to the complete hydrolysis of the sulfide ion. Two amounts of effective alkali were used: a moderate charge of 18% EA (as NaOH) and a high charge of 31% EA (as NaOH); the sulfidity and liquor-to-wood ratio were 35% and 4:1, respectively, in the two

cases. The white liquor charges were based on the starting wood weight with no corrections for remaining sulfuric acid or lost wood components during prehydrolysis. The autoclaves were put back into the heated polyethylene glycol bath for 240 min at cooking temperatures of 150 °C for 18% EA (as NaOH) and 142 °C for 31% EA (as NaOH). After cooking, the autoclaves were placed in a cold-water bath, the black liquor was withdrawn, and the pulp was washed for at least 12 h in running deionized water. Thereafter, the pulps were disintegrated in a water-jet disperser (Nordiska Armaturfabriken, Sweden) at a pressure of 2.0 bar(g) and centrifuged before analysis and further oxygen delignification.

## Xylanase Treatment

Xylanase treatment was carried out in polyethylene bags containing 25 g of o.d. pulp in a 20 mmol $L^{-1}$ phosphate solution buffered to pH 7. The consistency was 4% and the treatment was performed for 2 h in a 60 °C water bath. The xylanase charge was varied in the 0.1–100 XU $g^{-1}$ interval. After treatment, the pulp suspension was filtered off on a wire-coated Büchner funnel and the pulp was put in bags with water of 90 °C and immersed in a 90 °C water bath for 10 min to deactivate the enzyme.

## Oxygen Delignification

The prehydrolyzed kraft pulp was oxygen delignified in a 2.5-L stainless steel autoclave containing 20 g of o.d. pulp. The operating conditions were as follows: temperature of 105 °C, 20 kg of sodium hydroxide per o.d. tonne of pulp, 5 bar(g) oxygen pressure, retention time of 90 min (including heating-up time), and 12% pulp consistency. The pulp and sodium hydroxide solution were mixed using a kitchen hand blender (Carlton Basicline, CAR200, China). Xylanase-treated pulp was oxygen delignified in 2-L PTFE-coated stainless steel autoclaves containing 40 g of o.d. pulp. The operating conditions were as follows: temperature of 105 °C, 20 kg of sodium hydroxide per o.d. tonne of pulp, 5 bar(g) oxygen pressure, retention time of 90 min (including heating-up time), and 10% pulp consistency. The sodium hydroxide solution was mixed with the pulp using the kitchen blender. After oxygen delignification, the free liquor was collected for determination of the final pH of the spent liquor. The pulp was then carefully washed with deionized water before analysis.

## Analyses

The residual hydroxide ion concentration (SCAN N 33:1994), kappa number (ISO 302:2004), and limiting viscosity number (ISO 5351:2004) were analyzed according to the applicable SCAN and ISO standards. The cellulose limiting viscosity number was calculated by subtracting the hemicellulose portion (as weight fraction) of the pulp, assuming an estimated viscosity of 70 mL $g^{-1}$, from the limiting viscosity number according to:

$$[n]_{cellulose} = \frac{[n]_{pulp} - x_{hemicellulose} \cdot 70}{x_{cellulose}} \qquad (1)$$

The neutral sugar units in the pulps were analyzed after acid hydrolysis according to SCAN-CM 71:09 using a high-performance anion-exchange chromatograph equipped with a pulsed amperometric detector (HPAEC-PAD) and a CarboPac PA1 column

supplied by Dionex (Sunnyvale, CA, USA). The amount of Klason lignin was filtered and gravimetrically determined after acid hydrolysis according to SCAN-CM 71:09 and oven drying at 105 °C. The amount of pulp used for the Klason lignin analysis was 300 to 500 mg for the unbleached and approximately 1 g for the oxygen-delignified pulps. The coefficient of variation of Klason lignin data varied by 1 to 20% for the unbleached and 3 to 45% for the oxygen delignified pulps. The standard deviation, $\sigma_y$, of the degree of delignification was estimated using formula 2 and 3 as described by Miller and Miller (1993). Triple samples were used of each pulp sample for the Klason lignin analysis and standard deviation was determined for each pulp sample, respectively.

$$y = \frac{a}{b} \tag{2}$$

$$\sigma_y = \frac{a}{b} \cdot \sqrt{\left(\frac{\sigma_a}{a}\right)^2 + \left(\frac{\sigma_b}{b}\right)^2} \tag{3}$$

$$a = m_{Klasonunbleached}(\%) - m_{KlasonO\ delignified}(\%) \tag{4}$$

$$b = m_{Klasonunbleached}(\%) \tag{5}$$

$$\sigma_a = \sqrt{\sigma^2_{Klasonunbleached} + \sigma^2_{KlasonO\ delignified}} \tag{6}$$

The standard deviation, $\sigma_y$, of the degree of delignification was then adjusted for a 95% confidence interval. Formulas 2 to 6 were also used to calculate the standard deviation of the degree of delignification expressed as kappa number and HexA-corrected kappa number with the modification that Klason lignin was replaced by either kappa number or HexA-corrected kappa number. The same formulas were also used for the standard deviation of the selectivity (Δcellulose viscosity/ΔHexA corrected kappa number) with the modification that formula 5 was similar to formula 4. Double samples were used for each pulp sample for the kappa number, HexA, and carbohydrate analyses, and the standard deviation was determined for each pulp sample. All error bars were adjusted to a 95% confidence level.

The hexenuronic acid (HexA) content was determined according to Gellerstedt and Li (1996). A mercury acetate solution was charged into the pulp, and after 1 h of reaction, the HexA in the hydrolyzate was quantified on a reversed-phase HPLC device equipped with an Ascentis C18 column (250 mm × 4.6 mm × 5 μm; Sigma-Aldrich, St. Louis, MI, USA) and a photodiode array detector. The mobile phases were: A) 1% trifluoroacetic acid in water, and B) acetonitrile. The flow was set to 1 mL min$^{-1}$ and started with isocratic conditions using 10% of solvent B for 2 minutes. Thereafter, the proportions were linearly increased to 100% of solvent B for 5 minutes. After 12 min at 100% of solvent B, the proportions were changed linearly to 10% for 1 min followed by 10 min of isocratic conditions of 10% of solvent B. The total cycle time was 23 minutes. A benzoic acid solution with a concentration of 4 mmol L$^{-1}$ was used as a monitor standard and mixed with the sample in a ratio of 1:1 before injection. The column effluent was monitored using a detector wavelength of 236 nm. An oxygen-delignified

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birch kraft pulp containing a known amount of HexA was used as a reference. Coefficient of variation of the amount of HexA varied by 5% expressed as $\mu$mol g$^{-1}$ pulp. The contribution of HexA to the kappa number was calculated according to the relationship: 1 kappa number unit = 11.6 $\mu$mol g$^{-1}$ of o.d. pulp (Li and Gellerstedt 2002).

## RESULTS

This study aimed to manufacture pulps with a large xylan content range, the same final lignin content, and small variation in cellulose content and cellulose depolymerization. Two methods were chosen for varying the xylan content: enzymatic treatment using xylanase (Pulpzyme HC) and prehydrolysis kraft cooking. These pulps were then oxygen delignified under similar conditions to investigate the effects of xylan content on the degree of delignification in the oxygen delignification. Note that each series should be studied individually, since the raw material, cooking conditions, and oxygen delignification conditions differed between the series.

### Variation in Xylan Content

Table 1 shows the results of the xylanase treatment.

**Table 1.** Xylan Content Varied Using Xylanase and the Effect on Pulp Properties

| Unbleached | Xylan (Rel%) | Kappa no. | Klason (% on pulp) | HexA ($\mu$mol g$^{-1}$) | Lim. visc. no. (mL g$^{-1}$) | Cellul. lim. visc. no. (mL g$^{-1}$)* |
|---|---|---|---|---|---|---|
| Xylanase (XU g$^{-1}$) | | | | | | |
| 0 | 17.4 | 17.0 | 1.6 | 74.4 | 1390 | 1680 |
| 0.1 | 16.7 | 16.5 | 1.8 | 68.5 | 1400 | 1680 |
| 1 | 14.9 | 14.9 | 1.8 | 57.9 | 1430 | 1680 |
| 10 | 13.6 | 13.8 | 1.4 | 51.0 | 1450 | 1680 |
| 100 | 12.3 | 13.1 | 1.4 | 44.1 | 1460 | 1660 |
| * The cellulose viscosity number is corrected for the hemicellulose content by subtracting the hemicellulose part, assuming an estimated viscosity of 70 mL g$^{-1}$. | | | | | | |

The xylanase treatments managed to reduce the xylan content of the unbleached mill *E. urograndis* kraft pulp from 17% to 12%. The cellulose depolymerization, reported as cellulose viscosity number, which is the limited viscosity number corrected for the hemicellulose contribution, was unaffected. The lignin content measured as Klason lignin was also essentially unaffected by the xylanase treatments.

Table 2 shows the results of the prehydrolysis kraft cooking. Variation in xylan content with prehydrolysis kraft cooking was achieved using various prehydrolysis times ranging from 60 to 200 min at two alkali charges in the kraft cook, one moderate alkali charge at 18% EA (as NaOH) and one high charge at 31% EA (as NaOH). To enable a constant cooking time for all the pulps, the temperature was also adjusted, being 150 °C for the moderate alkali charge cook and 142 °C for the high alkali charge cook. Note that the prehydrolysis kraft cooks at 0 min were kraft cooks without any prehydrolysis treatment.

**Table 2.** Xylan Content Varied Using Prehydrolysis-kraft Cooking and the Effect on Pulp Properties

| Unbl. | Xylan (Rel%) | Kappa no. | Klason (% of pulp) | Yield (% of wood) | Residual cooking alkali (g L$^{-1}$) | HexA ($\mu$mol g$^{-1}$) | Lim. visc. no. (mL g$^{-1}$) | Cellul. visc. no. (mL g$^{-1}$)* | Cellul. content (% of wood) |
|---|---|---|---|---|---|---|---|---|---|
| **PH kraft cook, 18% EA, 150°C** | | | | | | | | | |
| 0 min | 15.6 | 16.8 | 1.8 | 52.5 | 7.8 | 71.0 | 1330 | 1566 | 43.3 |
| 0 min | 14.5 | 15.7 | 1.6 | 51.5 | 7.1 | 60.3 | 1300 | 1514 | 43.0 |
| 80 min | 13.6 | 16.3 | 1.5 | 51.3 | 6.5 | 56.3 | 1300 | 1502 | 43.3 |
| 120 min | 12.2 | 15.2 | 1.5 | 50.8 | 4.7 | 50.1 | 1300 | 1479 | 43.5 |
| 200 min | 10.1 | 15.3 | 1.7 | 48.3 | 9.2 | 38.1 | 1400 | 1554 | 42.4 |
| **PH kraft cook, 31% EA, 142°C** | | | | | | | | | |
| 0 min | 11.2 | 13.0 | 2.3 | 49.5 | 34.1 | 42.4 | 1170 | 1314 | 42.6 |
| 60 min | 10.2 | 12.4 | 2.3 | 49.1 | 34.4 | 37.5 | 1130 | 1256 | 42.8 |
| 80 min | 9.6 | 12.4 | 2.2 | 48.1 | 34.6 | 32.5 | 1170 | 1292 | 42.2 |
| 120 min | 9.2 | 11.8 | 2.1 | 47.2 | 34.1 | 31.4 | 1150 | 1265 | 41.6 |
| 200 min | 8.2 | 11.6 | 2.2 | 46.3 | 32.4 | 27.7 | 1140 | 1239 | 41.3 |

* The cellulose viscosity number is corrected for the hemicellulose content by subtracting the hemicellulose part, assuming an estimated viscosity of 70 mL g$^{-1}$.

The preliminary idea of using lower cooking temperature at high alkali charge of 31% EA was to slow down the rate of cellulose depolymerisation. Because the cleavage of the glycosidic bond within the cellulose chain has a higher activation energy than the activation energies for all the delignification rates, the pulp selectivity (pulp viscosity versus kappa number) is always improved by a decrease in temperature (Lindgren 1997). Previous research studies have demonstrated using constant composition cook that the viscosity number in the temperature range of 150 to 180 °C (Lindgren 1997) and the cellulose viscosity number in the range of 140 to 170 °C (Johansson and Germgård (2008) are negatively affected by an increase in cooking temperature. The purpose of using a lower cooking temperature at high alkali in the present study was to slow down the cellulose degradation rate to obtain small variation in cellulose depolymerization and cellulose content between the samples points within the 31% EA series.

The prehydrolyzed kraft pulps at the moderate alkali charge cook of 18% EA resulted in a xylan content of 10 to 16% of pulp (or 5 to 8% of wood), while the prehydrolyzed kraft cook at the higher alkali charge cook of 31% EA resulted in a xylan content of 8 to 11% of pulp (or 4 to 5% of wood).

The cellulose depolymerization in the prehydrolysis kraft-cooked pulps was evaluated as cellulose loss units and cellulose viscosity number. The cellulose loss units were calculated based on following expressions (7 to 9),

$$Cellulose \; loss \; unit \left[ \% \; of \; wood \right] = cellulose \; in \; wood - cellulose \; in \; pulp \quad (7)$$

$$Cellulose \; in \; wood = (m_{glucanin\,wood} - m_{mannanin\,wood}) \quad (8)$$

$$Cellulose \; in \; pulp = Yield_{reject\,and\,Klasonlignin\,free} \cdot (x_{glucanin\,pulp-mannanin\,pulp}) \quad (9)$$

where $m$ is the mass and $x$ is relative percentage of the total anhydrosugar content.

Figure 1 shows the cellulose loss in the prehydrolyzed kraft pulps pulped for various prehydrolysis times. Higher alkali concentration and higher cooking temperature during kraft cooking affect the cellulose content negatively (Gustavsson and Al-Dajani 2000). The cellulose loss presented in Fig. 1 is to the most extent the combined contribution from the alkali and temperature, respectively.
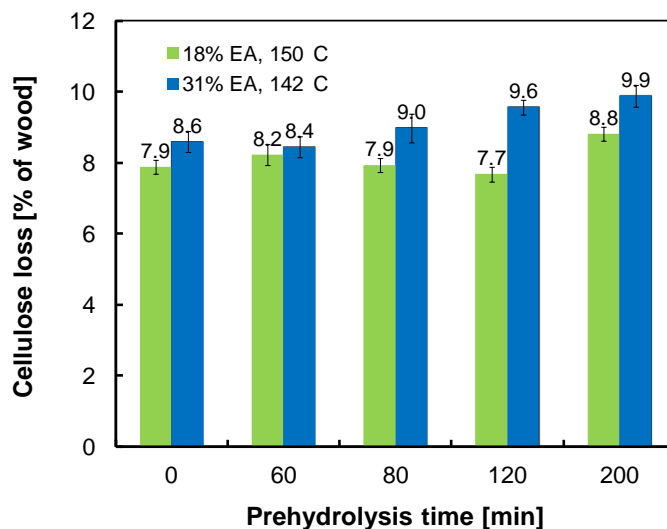


**Fig. 1.** Influence of prehydrolysis pretreatment duration on cellulose loss (% of wood); prehydrolyzed lab-cooked eucalypt kraft pulps were cooked at effective alkali of 18% (150 °C) and 31% (142 °C).

After 120 min of prehydrolysis treatment, the 18% EA prehydrolyzed kraft pulps kraft cooked at 150°C started to lose cellulose, and at 200 min, the loss was 0.9 percentage points of wood greater than that of pulp without prehydrolysis treatment (0 min). For the 31% EA prehydrolyzed kraft pulp at 142 °C kraft cooking temperature, the loss appeared after only 80 min of prehydrolysis treatment, and after 200 min, the loss was 1.3 percentage points of wood greater than that of the kraft pulp without prehydrolysis treatment. The cellulose loss could also be expressed in percent of initial cellulose content, and was 1.8 and 2.5 percentage points greater at 200 min of prehydrolysis treatment for the 18% and 31% EA pulp series, respectively, than for the kraft pulps without prehydrolysis treatment in the respective series.

Furthermore, the drop in cellulose viscosity number with increased prehydrolysis time was determined using simple second-polynomial regression, and it was found to decrease as much as 70 mL $g^{-1}$ (Table 2). The lignin content was essentially unaffected by the prehydrolysis time (Table 2).

## Effect of Oxygen Delignification on Pulps

Oxygen delignification was performed at 20 kg sodium hydroxide charge per o.d.t. for all investigated pulps. The residual pH of the filtrate after oxygen delignification affects bleachability if it is below pH 10.4 (Ragnar and Backa 2005). In the present study, the final pH of all the pulps to be investigated was above 10.4. The characteristics of the pulps after oxygen delignification are shown in Table 3.

**Table 3.** Characteristics of Oxygen-delignified Pulps Produced by Xylanase Treatment and Prehydrolyzed Kraft Cooking

| O delig. | Kappa no. | Klason (% of pulp) | HexA ($\mu$mol g$^{-1}$) | Lim. visc. no. (mL g$^{-1}$) | Cellul. visc. no.[1] (mL g$^{-1}$) |
|---|---|---|---|---|---|
| **Xylanase (XU g$^{-1}$)** | | | | | |
| 0 | 11.1 | 0.8 | 72.1 | 1140 | 1375 |
| 0.1 | 10.7 | 1.1 | 67.3 | 1150 | 1376 |
| 1 | 9.1 | 0.9 | 54.1 | 1130 | 1323 |
| 10 | 8.2 | 0.6 | 48.5 | 1140 | 1316 |
| 100 | 7.8 | 0.9 | 43.3 | 1150 | 1307 |
| **PH kraft cook, 18% EA, 150°C** | | | | | |
| 0 min | 9.7 | 1.3 | 68.2 | 1000 | 1175 |
| 60 min | 8.7 | 1.2 | 59.6 | 920 | 1068 |
| 80 min | 8.3 | 1.3 | 53.4 | 960 | 1106 |
| 120 min | 7.5 | 1.1 | 46.0 | 910 | 1032 |
| 200 min | 6.8 | 1.3 | 35.1 | 930 | 1030 |
| **PH kraft cook 31% EA, 142°C** | | | | | |
| 0 min | 6.8 | 1.2 | 43.7 | 860 | 964 |
| 60 min | 6.3 | 1.1 | 40.8 | 810 | 898 |
| 80 min | 6.3 | 1.1 | 36.7 | 790 | 870 |
| 120 min | 5.9 | 1.0 | 37.3 | 790 | 867 |
| 200 min | 5.5 | 1.1 | 31.0 | 740 | 802 |

[1] The cellulose viscosity number is corrected for the hemicellulose content by subtracting the hemicellulose part, assuming an estimated viscosity of 70 mL g$^{-1}$.

The lignin removal efficiency in the oxygen delignification was evaluated as degree of delignification based on uncorrected kappa number, HexA-corrected kappa number, and Klason lignin content. Figure 2 shows the degree of delignification in terms of kappa number.
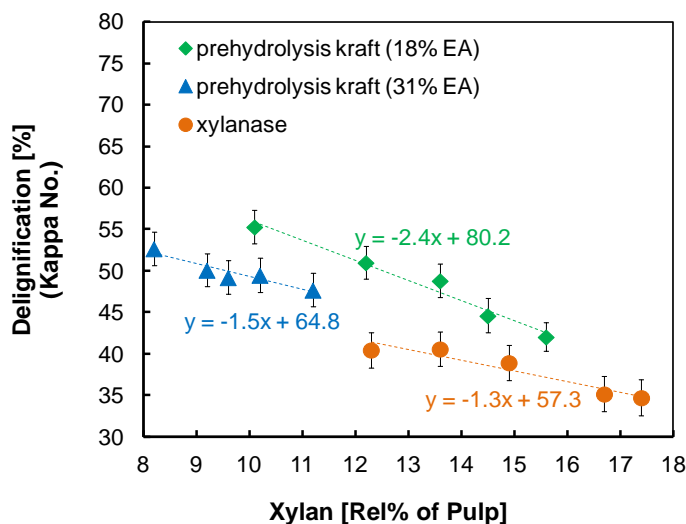


**Fig. 2.** Degree of delignification in the oxygen delignification as kappa number; prehydrolyzed lab-cooked kraft pulps at effective alkali levels of 18% (150 °C) and 31% (142 °C), and xylanase-treated industrial kraft pulp of *E. urograndis*

As can be seen in Fig. 2, the degree of oxygen delignification, defined as uncorrected kappa number reduction, decreased with increased quantity of xylan in the unbleached pulps.

After HexA correcting the kappa number as shown in Fig. 3, no significant trend of the degree of delignification as HexA-corrected kappa number with increasing xylan content, could be seen at the 95% confidence level.
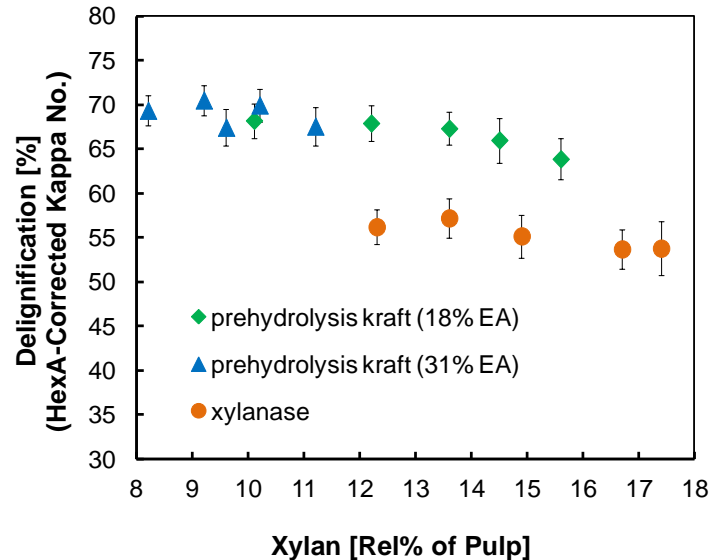


**Fig. 3.** Degree of delignification in the oxygen delignification as HexA-corrected kappa number; prehydrolyzed lab-cooked kraft pulps at effective alkali levels of 18% (150 °C) and 31% (142 °C), and xylanase-treated industrial kraft pulp of *E. urograndis*

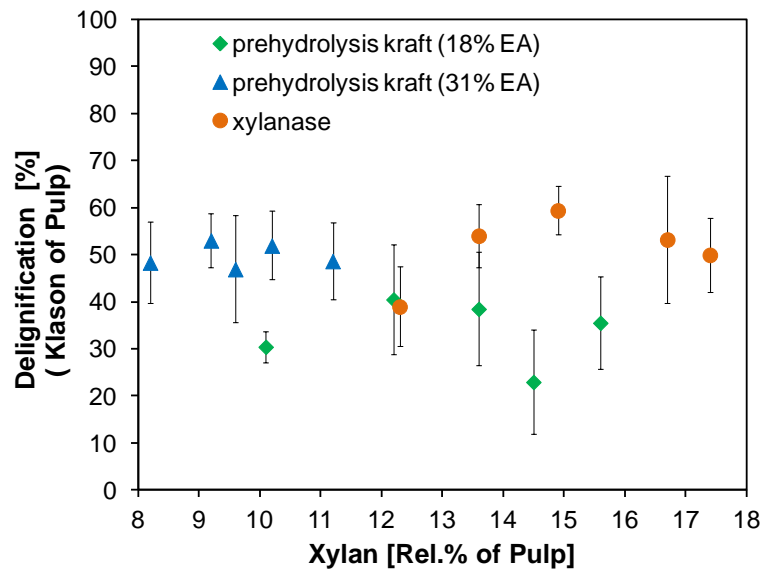Figure 4 shows the degree of delignification as Klason lignin content.



**Fig. 4.** Degree of delignification in the oxygen delignification as Klason lignin content; prehydrolyzed lab-cooked kraft pulps at effective alkali levels of 18% and 31%, and xylanase-treated industrial kraft pulp of *E. urograndis*

Low residual alkali after cooking is reported to positively influence the efficiency of oxygen delignification (Colodette *et al.* 2002). It should be pointed out that the lowest residual alkali among the prehydrolyzed kraft pulps was 5 g $L^{-1}$, which should be sufficiently high not to affect the degree of oxygen delignification based on kappa number or HexA-corrected kappa number.

Since the coefficient of variation of Klason lignin analysis varied by 3 to 45%, the amount of Klason lignin in the oxygen-delignified pulps was approximately 1%. The effect of the degree of delignification as Klason lignin content did not indicate any significant or clear trend, at the 95% confidence level, as shown in Fig. 4.

The limiting viscosity number was determined for the oxygen-delignified pulps and reported as cellulose viscosity number in Table 3. In the oxygen delignification the pulp having the lowest xylan content indicated slightly higher loss in cellulose viscosity number.

# DISCUSSION

To evaluate the effect of xylan content in unbleached pulp on oxygen delignification efficiency, the variation in cellulose degradation and lignin content should be very small between the pulps studied. For the xylanase-treated pulps, this was achieved. The prehydrolysis treatment was also mild enough to affect the cellulose loss only slightly, resulting in similar cellulose viscosity numbers and lignin contents for all pulps subject to the same cooking conditions.

## Klason Lignin

Hardwood kraft pulping intended for manufacturing bleached pulp is normally terminated when there is approximately 1 to 2% of the lignin remaining in the pulp. The small amounts of lignin in the unbleached eucalypt kraft pulps would, after oxygen delignification, be even lower at approximately 0.5 to 1%. As shown in Fig. 4, the standard Klason lignin analysis suffered from high standard deviation, affecting the evaluation of the degree of delignification as Klason lignin content. Since no error bars were reported by Zou *et al.* (2002), who also dealt with a similar lignin content, the question is whether the degree of delignification results, expressed as Klason lignin content, were actually significant.

## HexA and "Other Non-lignin" Structures

Since the kappa number test measures all oxidizable structures in the pulp, not only the lignin, but also HexA and other carbohydrate-related structures, so-called "other non-lignin" or "false" lignin structures contribute to the kappa number. Figure 3 shows the HexA-corrected degree of delignification. It can be seen that no significant trend with an increase in xylan could be seen in the xylan range 8 to 17%. Therefore, after correcting the kappa number for HexA it was found that xylan content in the range 8 to 17% had no significant effect on the efficiency of the oxygen delignification.

The lower efficiency of the xylanase-treated pulp may be due to the mill-operating conditions, but also due to differences between the characteristics of the *E. urograndis* wood species.

Using a HexA-corrected kappa number when calculating the degree of delignification indicates the lignin removal efficiency, but a better value would still be obtained after correcting for the other non-lignin structures as well. The lignin kappa number could be analyzed using oxymercuration and demercuration according to Li and Gellerstedt (2002), which is a treatment that eliminates the effect of the HexA and other non-lignin structures. Though these processes were not used in the present study, it is still possible to estimate the effect of the other non-lignin structures on the kappa number after oxygen delignification by multiplying the hemicellulose content as a percent of the pulp by a factor of approximately 0.08, based on the non-lignin kappa numbers and hemicellulose contents reported by Antonsson *et al.* (2003). Contradictory results concerning the formation or degradation, during oxygen delignification, of other non-lignin structures have been reported in literature. Näsman *et al.* (2007) demonstrated that the non-lignin contribution to the kappa number of eucalypt kraft pulp decreased during oxygen delignification, which is consistent with the results of Wedin *et al.* (2005) regarding lignin-free pulps, whereas Li *et al.* (2002) found an approximately one-kappa-number increase during oxygen delignification due to other non-lignin structures. Irrespective of any increase or decrease in other non-lignin structures during oxygen delignification, the contribution of other non-lignin structures to the degree of delignification would be either negligible or possibly slightly positive. The only way to be sure of this would be to analyze the lignin kappa number. The exact structures of the other non-lignin structures are not completely understood, though double bonds and conjugated carbonyl groups (Li and Gellerstedt 2002) may be present in the hemicellulose (Antonsson *et al.* 2003; Näsman *et al.* 2007).

## Oligolignin Bound via LCC

The findings in Fig. 3, showing no significant effect on the oxygen delignification efficiency with xylan content in the range 8 to 17%, indicates that LCC would not play as large a role, in the studied lignin range, in retarding the oxygen delignification as indicated by the literature (Zou *et al.* 2002; Sixta *et al.* 2006b). This does not contradict the importance of LCC in ultimately limiting the oxygen delignification when extending the oxygen delignification toward very low lignin contents below 1% of pulp (*i.e.*, kappa numbers below 8 to 10 for regular kraft pulps). Toward the end of the cook, most lignin macromolecules would be present as oligolignin bound via LCC structures, whereas toward the end of the oxygen delignification process, the oligolignin would be present primarily as monolignol (one lignin monomer) structures bound to hemicellulose via the LCC (Backa *et al.* 2004). Since the lignin content in the present study was approximately 2% of pulp before oxygen delignification, this lignin was likely mainly present as oligolignin bound to the hemicellulose via LCC. It is possible that xylan does not hinder the oligolignin bound via LCC to be depolymerized to monolignol through the standard oxygen and phenolate ion reaction mechanism.

In practice when producing kraft pulps, the increase in xylan yield for eucalypt would be limited to 1 to 2 percentage points. The present results indicate that such an increase would not be expected to affect the degree of oxygen delignification more than marginally, regardless of correction for the effect of other non-lignin structures on the kappa number. This implicit lignin would still be present as oligolignin bound to hemicellulose via LCC. In other words, high-xylan versus low-xylan pulp containing equal quantities of oligolignin bound via LCC would not necessarily require harsher

oxygen delignification conditions to achieve the same degree of delignification. For high-kappa-number eucalypt kraft pulps, the situation is more complex, since not only could a high amount of xylan be present, but there is also a high amount of lignin and cellulose contents (Näsman *et al.* 2007; Wedin *et al.* 2010). Based on the present results, similar behavior would likely be seen at high kappa numbers, although the oligolignin bound via LCC would probably consist of more linked lignin residues at high kappa numbers than at standard cooking kappa numbers. Factors other than LCC may explain why high-kappa-number pulps lose portions of their retained xylan during extended oxygen delignification. It is therefore difficult, based on the present results, to speculate about the degree of xylan retention during oxygen delignification.

## Selectivity of Oxygen Delignification

Zou *et al.* (2002) demonstrated that an increased amount of hemicellulose, mainly xylan, improves the selectivity of oxygen delignification. It was suggested that hemicellulose polymers would protect the cellulose from, for example, hydroxyl radicals, leading to less depolymerization of the cellulose and thereby reducing the decline in the limiting viscosity number. In the present study, the selectivity was expressed as the drop in cellulose viscosity number versus the drop in the HexA-corrected kappa number. Figure 5 shows the selectivity versus xylan content for the unbleached pulps. The results indicate, for at least two of the pulps, that increased xylan quantity improves the selectivity of oxygen delignification. No obvious explanation could be found for why the prehydrolysis kraft pulp at a moderate initial EA of 18% (as NaOH) did not follow the linear trend.
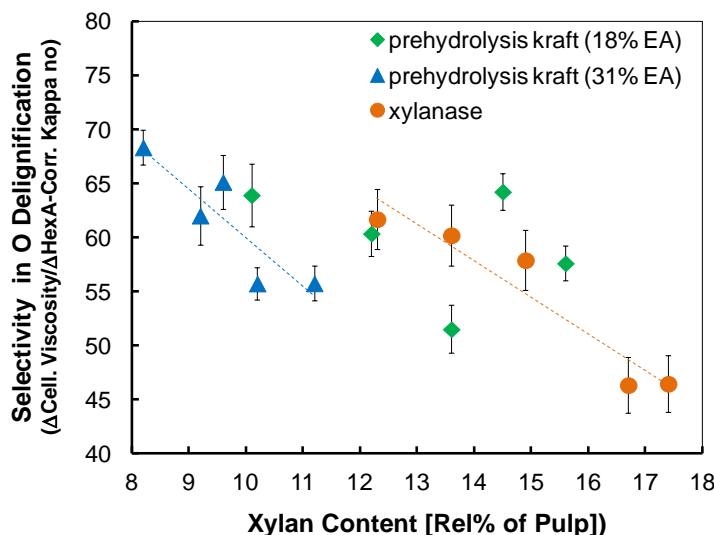


**Fig. 5.** Selectivity of the oxygen delignification (cellulose viscosity drop/HexA-corrected kappa number drop); prehydrolyzed kraft *E. urograndis* pulps cooked at 18% and 31% effective alkali and xylanase-pretreated industrial *E. urograndis* kraft pulp.

The selectivity results partly confirm previous findings for oxygen-delignified AQ kraft pulps (Zou *et al.* 2002) and for polysulfide-kraft pulps of low kappa numbers of 20–5 (Lindström and Teder 1995).

# CONCLUSIONS

1. An increase in xylan content within the range of 8 to 17% in eucalypt kraft pulp indicated no significant impact on the oxygen delignification efficiency after correcting for the hexenuronic acid contribution to the kappa number.

2. The Klason lignin method provided no significant results concerning the effect of xylan content on lignin removal during oxygen delignification. This implies that the Klason lignin method is an uncertain means to study the degree of delignification in hardwood kraft pulp, due to the small amount of lignin remaining after oxygen delignification.

# ACKNOWLEDGEMENTS

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