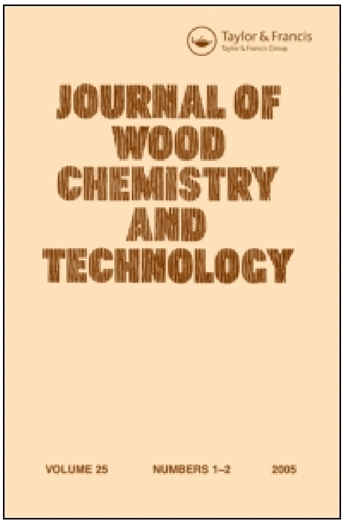

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Do Hexenuronic Acid Groups Represent the Majority of the Carboxyl Groups in Kraft Pulps?

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NOTE

Do Hexenuronic Acid Groups Represent the Majority of the Carboxyl Groups in Kraft Pulps?

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Abstract: The formation of hexenuronic acid groups during kraft pulping via demethylation of the 4-*O*-methylglucuronic acid groups attached to the wood xylan backbone was discovered a long time ago. In recent years, the formation of hexenuronic acid groups has attracted new interest and it has been stated that they represent the majority of the uronic acid groups in kraft pulps. However, the values reported in the literature are scattered. Furthermore, the data reported recently are partly in conflict with the earlier observations, which are based on analytical methods of a different type. It is obvious that more reliable and quantitative methods are needed for the determination of hexenuronic acids in pulps in order to assess their influence on factors associated with the bleaching process and pulp quality.

Keywords: Kraft pulps, xylan, carboxyl groups, hexenuronic acid, 4-*O*-methylglucuronic acid, methoxyl groups

INTRODUCTION

Wood polysaccharides contain 4-*O*-methylglucuronic acid groups attached to the backbone of their xylans. In addition to these uronic acid groups, other carboxyl groups are present in wood, mainly as constituents of the pectic substances. A part of the carboxyl groups in wood are present as esters and lactones, but during kraft pulping the carboxyl groups are liberated through hydrolysis.[1] Because most of the pectic substances are removed during pulping and with proper pulping conditions only a few new carboxyl groups

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are generated, the majority of the carboxyl groups in kraft pulp polysaccharides are the xylan-bound uronic acids.[2] However, the original 4-*O*-methylglucuronic acid groups are partly converted to unsaturated hexenuronic acid groups as shown already in an early work by Clayton [3]. Afterward, Johansson and Samuelson [4,5] confirmed Clayton's results, including the reaction path he had postulated. Finally, much later new interest was directed to this question when a group of researchers succeeded to isolate acid-sensitive xylan-hexenuronic acid fragments from kraft pulps with the aid of specific enzymes (see Tenkanen et al. [6] and the earlier publications cited in that article).

In recent years, additional attention has been directed to formation of the hexenuronic acid groups. Since 1995 more than one hundred papers related to kraft pulping and hexenuronic acids have been referenced in Chemical Abstracts. The key analytical methods are based either on a partial enzymatic hydrolysis of the pulp followed by chromatographic separation of the oligosaccharides liberated or on a mild acid hydrolysis followed by determination of the product by UV-spectrophotometry or colorimetry (Tenkanen et al.[6]). Discrepancies between various results, especially when compared with earlier observations, was the impetus for preparing this manuscript.

EARLY STUDIES

Clayton[3] isolated glucuronoxylan from hardwood species (white birch, white elm, and poplar) and heated it in alkaline solution at 170°C. After treatment the decarboxylation method was used to determine the uronic acid groups. The methoxyl content was calculated from analysis of the methanol liberated in the reaction. Although the accuracy of these determinations was not very good, especially because of the decarboxylation method, the analyses showed that there was a preference for removal of methoxyl groups compared with the removal of carboxyl groups. In addition, unchanged 4-*O*-methyl-glucuronic acid groups were still detected by paper chromatography after 30 min reaction time.

Johansson and Samuelson[4,5] used 2-*O*-(4-*O*-methyl-α-D-glucopyranosyluronic acid)-D-xylitol as a model substance and treated it with 1 M sodium hydroxide at 150°C. They concluded that the hexenuronic acid groups formed were successively degraded upon prolonged treatment, but the reaction rate for their formation was significantly higher than that for their decomposition. This was taken as an indication that an appreciable number of 4-deoxy-β-L-*threo*-hex-4-eno-pyranosyluronic acid moieties were present in kraft pulps. They also pointed out that the instability of the hexenuronic acid groups against acids is the reason why it had not been isolated and thus directly observed in kraft pulp after acid hydrolysis

Prior to Clayton's article[3] Croon and Enström[7] analyzed the 4-*O*-methylglucuronic acid groups in silver birch (hardwood) kraft pulps. These pulps were cooked at 170°C (T_{max}) using two different alkali charges. After delignification the hemicellulose components were fractionated from the pulps by extractions with dimethyl sulfoxide and aqueous alkali. The uronic acid content of the xylan varied between 3.0 and 6.7%, the lower value being for the xylan of pulp cooked with the higher alkali charge. Paper chromatographic analysis showed the presence of 4-*O*-methylglucuronic acid groups. Later, Croon and Enström[8] subjected Scots pine (softwood) kraft pulp to a similar study. The uronic acid content varied between 5.5 and 8.1% of the xylan (decarboxylation method). Calculation of the 4-*O*-methylglucuronic acid content from analyses of the methoxyl group content agreed reasonably well with the results based on decarboxylation.

Aurell and Karlsson[9] prepared kraft pulps from silver birch (hardwood) at 170°C. The decarboxylation method and calculation of the carboxyl content from methoxyl analyses gave nearly identical values and the authors concluded that no selective loss of methoxyl groups occurred during pulping. However, a probable loss of hexenuronic acid groups during their chlorite treatment prior to fractionation of xylan, was not taken into consideration. In any case, considerable amounts of 4-*O*-methylglucuronic acid groups were detected, corresponding to 10–30% of the native birchwood xylan. Aurell and Hartler[10] continued the study with Scots pine (softwood) kraft pulp In this case, the pulp xylan contained 2–6% uronic acid. Again, the decarboxylation method and calculations based on the methoxyl analyses gave similar results.

Methods based on ion exchange offer a possibility for quantitative determination of the carboxyl groups in pulps. Indeed, the ion exchange capacity is a fairly good measure for the uronic acid content in pulps. This method, developed by Sjöström and Haglund,[11] was used by Sjöström and Enström[12] for determination of the uronic acid content of commercial bleached kraft pulps of both softwood (Scots pine) and hardwood (silver birch). Because chlorine dioxide was included in the bleaching scheme of these pulps, they were obviously essentially free of hexenuronic acid. According to the ion exchange measurements the pine kraft pulp contained 3.4 mEq. and the birch kraft pulp 9.4 mEq carboxyl groups per 100 g dry pulp. Additional results obtained after titration of the isolated xylan fractions as well as calculation of the 4-*O*-methylglucuronic acid content from methoxyl analyses agreed reasonably well with the values obtained by ion exchange. The corresponding average content of uronic acid in the pulp xylan determined by the latter methods were 5.0% (pine pulp) and 5.4% (birch pulp).

LATER STUDIES

Tenkanen et al.[6] compared three different analytical methods for the determination of uronic acid groups in softwood kraft pulps. Only one of these methods (VTT), combined with an enzymatic treatment, can be used for determination of 4-*O*-methylglucuronic acid groups. The other two methods (HUT and KTH) are based on reactions of the double bond after certain treatments and the final measurements are made either by UV-spectrophotometry (HUT) or by colorimetry (KTH). According to Table III in Tenkanen et al.[6] the total content of uronic acid groups is surprisingly low for some samples and the results are striking when compared with values reported earlier. Moreover, it is difficult to understand why the total uronic acid contents being reported varies so greatly (cf., e.g., Table III in Tenkanen et al.[6] with Table I in Buchert et al.[13]). It also surprising that in the HPAEC-PAD chromatogram of the enzymatic pulp hydrolyzate (Figure 1 in Tenkanen et al.[6]) no oligomers of the $\mathrm{MeGlcAXyl}_n$ type are present. Finally, it should be mentioned that these samples are not representative of commercial softwood kraft pulps because the maximum cooking temperatures (163°C and 160°C) were lower than that normally used for softwood kraft pulping in mill practice.

Jiang et al.[14] reported considerable variation in the uronic acid values for softwood kraft pulps without commenting on the reasons for these variations. According to some of their data, the hexenuronic acid in softwood contributed about 80% to the total uronic acid content, whereas in hardwood the contribution was about 60%.

Daniel et al.[15] studied the influence of pulping conditions on the formation of hexenuronic acids in hardwood (eucalypt) pulps and their ECF bleachability. Determinations of hexenuronic acid were based on acid hydrolysis followed by UV-spectrophotometry at 245 nm (cf. Tenkanen et al.[6]). In addition, the hexenuronic acid was quantified after dissolving the sample in cadoxen and measuring the content from the UV spectrum (cf. Evtuguin et al.[16]). The results showed that, in the cooks of eucalypt, the hexenuronic acid content in the pulp increased during cooking in contrast to what was the case for softwood pulping. Another surprising observation was that no correlation could be seen between the bleachability and the hexenuronic acid content of the unbleached pulp. A surprising finding was also that in the bleaching of the pulps by a DEDED sequence, chlorine dioxide consumption increased when the hexuronic acid content of the unbleached pulp decreased.

Evtuguin et al.[16] suggested a method for the simultaneous determination of both hexenuronic acid and residual lignin. The method is based on the dissolution of the pulp samples in cadoxen and measuring the UV absorbance at 231 and 280 nm. However, the background absorption of the solvent (cadoxen) is very high at 231 nm, the absorption maximum of the hexenuronic acid appears diffuse, and the absorption of lignin must be subtracted from the total absorption value (cf. also Reference 17).

CONCLUDING REMARKS

It is clear that the 4-*O*-methylglucuronic acid groups are partly converted to hexenuronic acid groups, but the degree of this conversion after different pulping conditions is still an open question.

The influence of the hexenuronic acid groups is obviously most harmful for the bleaching process because they consume bleaching chemicals. As suggested[18] removing them from the unbleached pulp is a rather simple procedure although it means an additional stage and some yield loss.

If bleaching chemicals such as chlorine dioxide are used, most of the hexenuronic acid groups are obviously removed from the pulp but the 4-*O*-methylglucuronic acid groups will remain. It is known that carboxylic acids strongly affect the brightness stability of the pulp[19] but the additional influence of the double bond[13] of the hexenuronic acid is not clear.

The role of hexenuronic acid groups and the benefit of their removal from the unbleached pulp depend on their content in the pulp as well as on the bleaching sequence and the chemicals used for bleaching. Reliable and reasonably simple methods for the determination of the hexenuronic acid groups in kraft pulps are needed.

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