

Xylans from Oat Spelts and Birch Kraft Pulp

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Summary: Two different approaches for the isolation of xylan from hemicellulose-rich sources have been investigated: Alkaline extraction from roller-mill pretreated oat spelts and Nitren extraction of birch kraft pulp. For xylan recovery from oat spelts the experiments included extraction with 5% NaOH at 90 °C, followed by precipitation in methanol or 2-propanol without neutralisation in order to facilitate NaOH recovery. A subsequent peroxide bleaching yielded a product of approximately 90% ISO brightness. The work on Nitren extraction of birch kraft pulp included the optimisation of the extraction process with regard to the Nitren charge. Nitren was much more specific in xylan extraction compared to Cuen, and up to 90% of the xylan content of the birch kraft pulp could be removed. It turned out that dried pulps were superior for this process compared to never-dried pulps, since substantial cellulose proportions in never-dried pulps were also mobilised by Nitren treatment. The properties of the recovered xylans from both processes were compared with regard to molar mass and substitution. It could be demonstrated that more or less intact arabinoxylans with molar masses of 30,000 g/mol could be obtained from oat spelts. The arabinoxylans contained 8–10 mol-% arabinofuranose and 2 mol-% 4-O-methylglucuronic acid substituents. Nitren extraction of a birch kraft pulp yielded xylans of 9,400 and 11,200 g/mol. Only traces of 4-O-methylglucuronic- and hexenuronic acid substituents could be found.

Keywords: birch kraft pulp; extraction; Nitren; oat spelts; xylan

Introduction

Hemicelluloses, particularly xylans are unwanted wood components in dissolving pulp production. In paper-grade pulp production, however, they play a positive role with regard to yield and the strength properties of the resulting paper. In spite of the huge amount of hemicelluloses produced by nature, they are lacking the importance, which cellulose, starch, or pectins have. One of the reasons may be the lack of availability, which hinders their use in spite of their positive impact on products derived from agricultural and

forest products. Due to the European legislation it becomes more and more difficult for the cereal industry to market by-products from grain production, e.g. oat spelts, as animal feed. Alternative thermal or material uses are rather difficult to set into operation. This situation and the high xylan content in oat spelts (>30%) caused the authors to initiate a research programme on the recovery of polymeric xylan from oat spelts. Xylans from straw, grasses and agricultural residues including oat spelts generally have a backbone of β -1,4-linked xylose units and have mostly single arabinose units attached to some C-3 positions of the main xylan chain as the principal substituent. In addition they carry minor amounts of 4-O-methylglucuronic acid residues, mainly linked to the C-2 position.^[1]

Another source for xylan recovery may be created by a novel approach for the production of dissolving pulp from paper

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pulp by subsequent hemicellulose removal applying Nitren extraction. Generally dissolving pulps are nearly free of lignin. In addition they distinguish themselves by comparatively low hemicellulose proportions compared to paper-grade pulps. Due to the high costs of traditional dissolving pulp production they are more expensive compared to paper-grade pulps. This price difference in addition to the prospect for an additional income by selling polymeric xylan had initiated many research efforts to explore the conversion of paper pulp into dissolving pulp by applying hydrolytic, oxidative, extractive and enzymatic methods.^[2] However none of these methods have been successful, specially with regard to the selectivity in hemicellulose removal.

Aqueous solutions of a number of metal complexes are known as cellulose solvents for a long time. Recently, a number of new metal complexes have been developed by Klüfers and his group for complete dissolution of cellulose.^[3] One of these new systems has been Nitren, and the abbreviation tren stands for tris(2-aminoethyl)amine. Nitren not only functions with cellulose but also with xylan by de-protonating and coordinative binding of the OH groups in the C2 and C3 position of the anhydro xylose units. The most favourite concentration range for the xylan-Nitren complex is in the range of 3% Nitren.^[4] Concentrations beyond 7% Nitren lead to a dissolution of cellulose,^[5] lower concentrations are ineffective towards xylan extraction, which can be completed within 30–60 min.^[4] The dissolved xylan can be precipitated by dropping the pH with glacial acetic acid. The precipitation starts at pH 10 and is completed at pH 4. Nickel removal can be achieved by subsequent washing steps with 3% lactic acid. Using this procedure a nearly colourless powder, consisting of polymeric xylan can be obtained.^[4]

Results and Discussion

Arabinoxylan Extraction from Oat Spelts

Prior to the extraction process the oat spelts have been roller-mill pretreated in order to

facilitate the penetration of the extraction medium (NaOH). At the same time this treatment enabled the separation of the residual starch granules from the spelts. Insofar the pretreatment was also important with respect to the purity of the extracted xylan. Pretreated and sifted oat spelts were characterised regarding their monosaccharide composition after acid hydrolysis: Glucose (31.9%) was completely derived from cellulose. No starch could be detected. Xylose (28.1%) and arabinose (3.5%) were the arabinoxylan components. Galactose and rhamnose were present in small quantities adding up to less than 2%. Due to the presence of 21.3% lignin in the oat spelts an effective extraction of xylan required the application of elevated temperatures. In an earlier study it was found that extraction with 5% (w/v) NaOH at 90 °C for 60 min. was optimal for xylan recovery.^[6] The further refining of the arabinoxylan consisted of a precipitation step followed by peroxide bleaching. These additional treatments were necessary for the degradation of the particular lignin proportion, which had been co-extracted with the arabinoxylan. The arabinoxylan precipitation was optimised using methanol and 2-propanol. In order to facilitate the NaOH-recovery a neutralisation step prior to alcohol addition was avoided in any case. The alcohol:water ratio in the precipitation bath had a tremendous impact on the consistency and purity of the recovered xylan. A proportion of 60% methanol yielded a light fluffy arabinoxylan powder, whereas 75% and 45% methanol proportions in the precipitation bath were sub-optimal with regard to consistency and brightness. Most of the lignin was removed by precipitation. The residual lignin had to be degraded by peroxide (P) bleaching and a subsequent washing step. 4% hydrogen peroxide in 6% NaOH at 90 °C for 2 hours at 10% consistency were the favourite bleaching conditions.^[6] The washing step turned out to be rather critical, since a pure water wash was rather detrimental with regard to yield, whereas a 100% methanol wash was ineffective with regard to removal

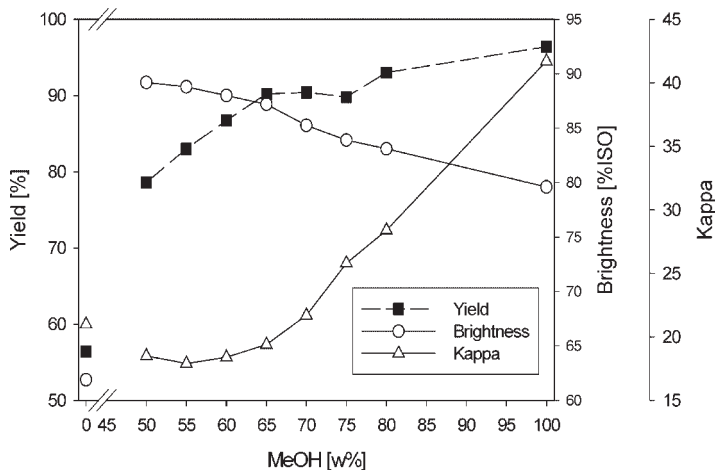


Figure 1.

Effect of the methanol:water ratio in xylan washing after peroxide bleaching. The particular arabinoxylan had been precipitated in 100% methanol after neutralisation and subsequently being bleached with 4% H_2O_2 in 6% NaOH, 2 h, 90 °C at 10% consistency.

of degraded lignin fragments (Figure 1). A washing step with 60% aqueous methanol was favourite with regard to yield and brightness. Lower methanol proportions led to an increase in brightness of the arabinoxylan, however, at the same time the yield of the recovered xylan was reduced. The lignin content in the arabinoxylan increased significantly, accompanied by reduced brightness, when the methanol proportion in the washing medium was increased.

Due to favourite engineering aspects in the recovery the use of 2-propanol as an alternative precipitation medium was also investigated. In this context the precipitation of the alkaline arabinoxylan extract into 45% 2-propanol turned out to be favourite (Figure 2). It yielded a brightness of 50% ISO, which was comparatively low in comparison to methanol as precipitation agent (85% ISO brightness, Figure 1).

Arabinoxylans obtained at higher 2-propanol proportions in the precipitation

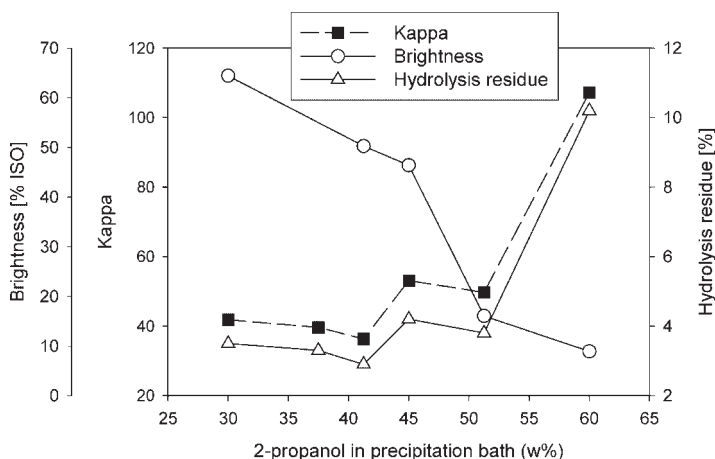


Figure 2.

Precipitation of NaOH-extracted xylan in 2-propanol without neutralization.

bath than 45% contained considerable amounts of NaOH (data not shown). Accordingly 2-propanol was inferior with regard to NaOH exclusion compared to methanol as precipitation agent.

Some advantage could be taken from the presence of NaOH in the precipitated xylan in the succeeding peroxide bleaching stage. However precautions had to be taken in order to avoid surpluses of NaOH resulting into brightness reductions of the final product due to alkaline yellowing. Accordingly 6–8% of the NaOH had to be neutralised prior to bleaching with 6% H_2O_2 in order to achieve optimal conditions with regard to residual lignin and brightness of the final product. Indeed xylenes of 90% ISO brightness could be obtained, using this procedure (Figure 3).

Xylan Extraction from Paper-Grade Pulps

As a basis for the design of a process for the conversion of paper-grade pulps into dissolving pulps based on Nitren, some relevant basic parameters have been studied. It was the first goal to verify the advantage of Nitren in comparison to the well-known cellulose solvent Cuen for selective xylan removal from birch kraft pulp, consisting of approximately 75% cellulose and 25% xylan. Increasing charges

of Nitren and Cuen between 20% and 100%, based on pulp, were used at a liquor to pulp ratio of 20:1 at 30 °C for 1 hour (Figure 4). Both solvent systems were equally well suited for xylan extraction. About 90% of the xylan present in the birch kraft pulp could be removed using both systems at extraction charges of 90%, based on pulp. However Nitren turned out to be much more selective from a charge of 60% on. As can be visualized from Figure 4 substantial quantities of cellulose (>20%) were dissolved at those Cuen charges, which were necessary for xylan removal in order to obtain dissolving pulp qualities, whereas cellulose dissolution, initiated by Nitren, was always <5%.

Another aspect was related to the question, whether never-dried or dried pulp would be more favourable for the extraction process. Accordingly differently treated birch pulps were extracted with a total Nitren charge between 20% and 60%, based on pulp (Figure 5).

A slightly higher xylan proportion could be extracted from the never-dried pulp sample. Also cellulose from the same pulp was clearly more accessible. Specially at higher Nitren charges the difference in cellulose dissolution between the two pulps amounted up to 4%. This cellulose loss

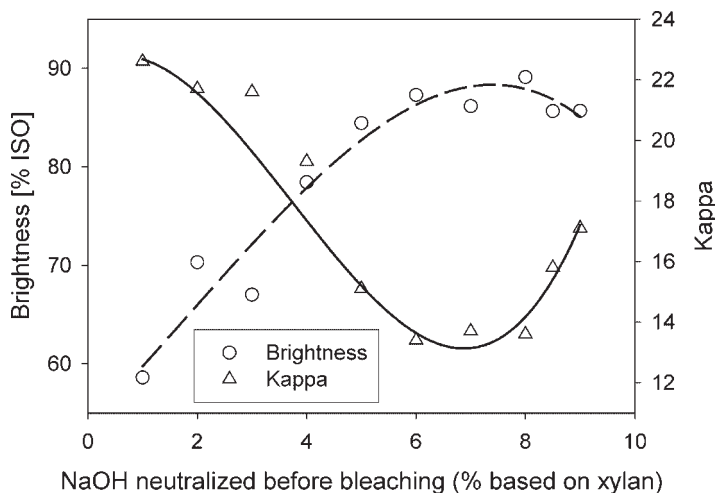


Figure 3.

Effect of partial neutralisation of residual NaOH before peroxide bleaching (6% H_2O_2). NaOH-extracted arabinoxylan has been precipitated before from 45% 2-propanol.

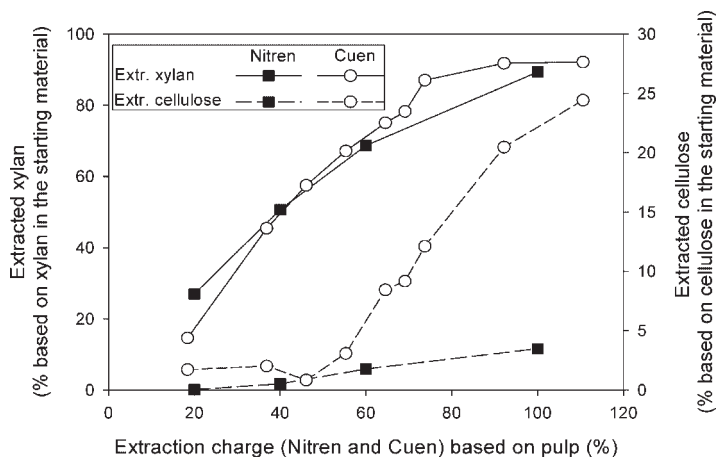


Figure 4.

Impact of Nitren and Cuen amount on dissolved xylan and cellulose from a birch kraft pulp (liquor:pulp ratio = 20:1, 1h, 30 °C).

could not be accepted. Consequently dried pulp samples were used in the following optimisation work.

Based on the results obtained so far not more than 90% of the total xylan could be extracted. Possibly the extraction effectiveness could be improved in case the total Nitren charge would be divided into two extraction steps. Actually it came out that single extractions, applying the complete Nitren charge, resulted into a more inten-

sive xylan removal than two extractions with 50% of the total Nitren charge in each step (Figure 6). This was not only true for the extracted xylan, but also for cellulose.

Dissolving pulps are being used for a variety of applications with different needs with respect to the residual hemicellulose content. Results obtained so far have verified that a total Nitren charge of ca. 60%, based on pulp would be needed in order to mobilise around 90% of the xylan.

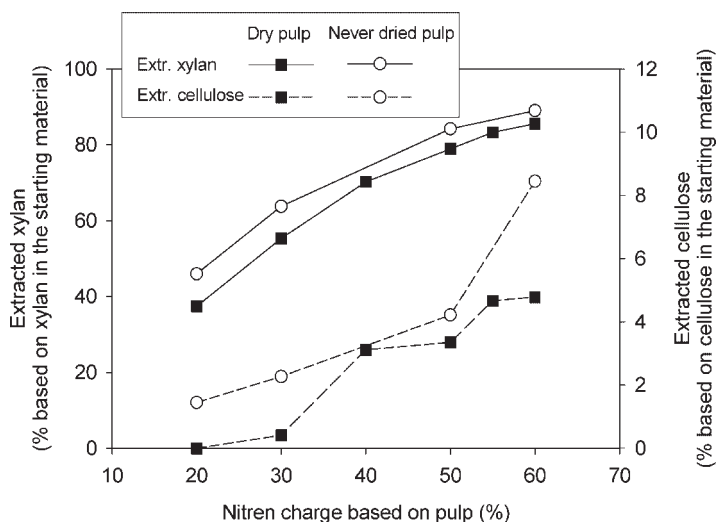


Figure 5.

Nitren initiated dissolution of cellulose and xylan from dry and never-dried birch kraft pulp (liquor:pulp ratio = 10:1, 1h, 30 °C).

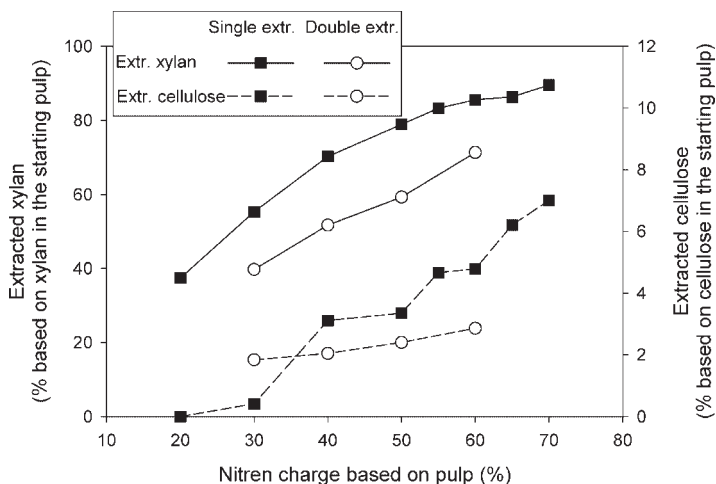


Figure 6.

Extracted xylan and cellulose from birch kraft pulp after single and double extraction (liquor:pulp ratio = 10:1, 1 h, 30 °C).

However there also exist applications with the need for less pure dissolving pulps. Accordingly mass balances have been established for a total Nitren charge of 20% (Figure 7A) and 60% (Figure 7B).

Up to now only liquor to pulp ratios of 10:1 have been used in this study. Now higher liquor to pulps ratios of 15:1 and 20:1 have been investigated as well. At an overall Nitren charge of 20%, between 6.6% and 9.2% from the total 24.1% xylan in the initial pulp could be extracted. At this

Nitren charge the highest extraction yield was obtained at the lowest liquor to pulp ratio (10:1).

Also from the experiments applying 60% Nitren charge it came out that lower liquor: pulp ratios favoured the mobilisation of xylan, since Nitren was present at a higher concentration. This result could be anticipated from earlier experiments, where single extractions at higher Nitren concentrations were more beneficial than double extractions at lower actual Nitren

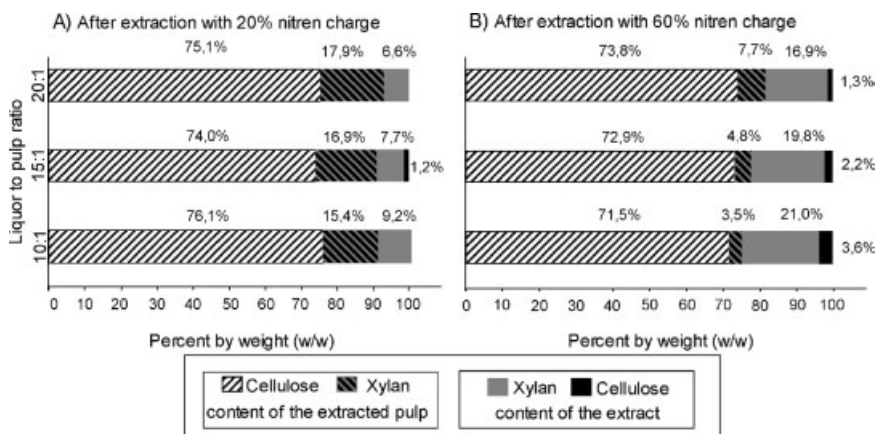


Figure 7.

Mass balances of birch kraft pulp after extraction with 20% (A) and 60% (B) Nitren charge, based on pulp (extraction for 1 h at 30 °C).

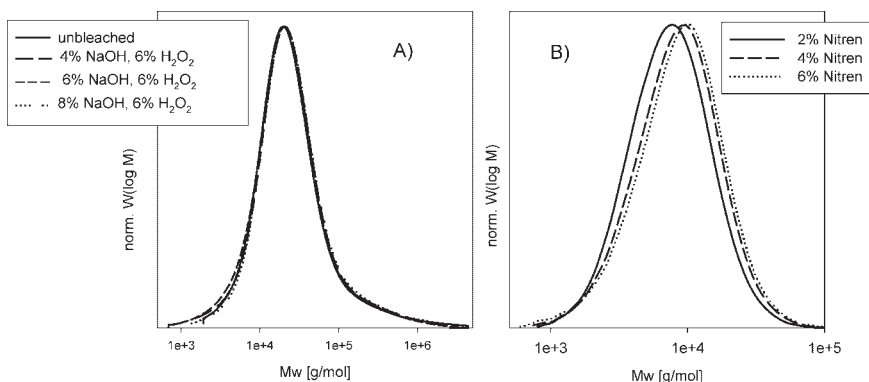


Figure 8.

Differential molecular weight distribution of unbleached arabinoxylans from oat spelts and after bleaching with 2%, 3%, and 4% H₂O₂ (A) and of birch xylans (B) after 2%, 4% and 6% nitren extraction (liquor:pulp ratio = 10:1, 1h, 30 °C). SEC using DMSO:water = 90:10 with addition of 0.05 M LiBr as mobile phase.^[9]

concentrations. At 20% Nitren charge α -cellulose contents of pulps between 80.8%, 81.4%, and 83.2% have been obtained for 20:1, 15:1, and 10:1 liquor to pulps ratios. No cellulose could be identified in the extracts with the exception of the 15:1 liquor to pulp ratio, where 1.2% cellulose (based on pulp) was co-extracted with the xylan. At 60% Nitren charge between 16.9% xylan (20:1) and 21.0% xylan (10:1) have been extracted (figures based on pulp). Besides of the effective xylan extraction at higher Nitren concentrations these conditions also led to certain cellulose losses into the extract, which amounted between 1.3% and 3.6%. At 60% Nitren charge pulps with α -cellulose contents of 90.6% (20:1), 93.8% (15:1) and 95.3% (10:1) were obtained.

It is clear that the viscosity values of Nitren extracted pulps were also improved with increasing α -cellulose content due to intensified extraction of comparatively low molecular weight xylan: The initial birch kraft pulp had a viscosity of 730 ml/g⁻¹. This value was increased steadily with increased Nitren charge and Nitren concentration. However under conditions of pronounced cellulose losses applying (80% Nitren charge, the viscosity values dropped again. Maximum viscosity values ranged between 815 and 840 ml/g (40% Nitren charge) and 890 and 850 ml/g⁻¹ (60% Nitren charge).

Properties of Arabinoxylan from Oat Spelts and Xylan from Birch Kraft Pulp

After extraction and bleaching the arabinoxylans from oat spelts had a molar mass of about 30,000 g/mol, corresponding to a DP_w of 194, independent of the peroxide charge during bleaching (Figure 8A).

¹H-NMR-spectroscopic studies indicated that the bleached arabinoxylan still carried 8–10 mol-% arabinofuranose and 2 mol-% 4-O-methylglucuronic acid substituents, which is an important prerequisite for the water-solubility of this polymer. Higher molar mass values between 38,500 and 41,000 g/mol have been reported for an arabinoxylan, which has obtained by alkaline peroxide extraction from barley straw.^[7] Hemicellulose preparations, which have been isolated from barley straw in the absence of hydrogen peroxide had molar masses between 28,000–29,000 g/mol.^[8]

For the Nitren extracted xylan from birch kraft pulp (Figure 8B) the molar masses ranged between 9,400 and 11,200 g/mol with a trend to higher values, when higher Nitren concentrations were applied during extraction. The xylan of molar mass 11,200 g/mol was obtained at an actual Nitren concentration of 6%, whereas 2% Nitren led to a molar mass of 9,400 g/mol. From the monosaccharide composition of these xylans after acid hydrolysis no indications on the presence of 4-O-methyl-

glucuronic acid substituents were obtained. Additional ^1H -NMR-spectroscopic studies indicated the presence of only traces of 4-O-methylglucuronic acid and hexenuronic acid substituents. The drastic reduction in molar mass of xylan and its minor number of substituents reflects the history of the pulp including strongly alkaline conditions during kraft pulping and acid conditions during bleaching. Similar data with respect to molar mass and substitution have been reported for a xylan, which had been alkaline extracted from a birch kraft pulp.^[10] Conditions during kraft pulping and bleaching of the birch pulp are by far more severe compared to the extraction of the oat spelts with 5% NaOH at 90 °C. Correspondingly the xylans obtained by both processes are very different, which certainly will also have an impact on their use.

Conclusion

Some basic parameters for the isolation of xylans from a lignified agricultural residue like oat spelts and a lignin-free paper-grade pulp have been developed as a basis for a process design. NaOH extraction of xylan from oat spelts resulted into a polymeric product, which needed an additional bleaching and washing procedure in order to receive a bright final material. Xylans obtained by Nitren extraction of paper-grade pulps needed an additional washing operation to eliminate the residual nickel content. The xylans differed considerably with respect to molar mass and number of substituents due to differences in their

origin. Whereas the arabinoxylans from oat spelts had more or less preserved their initial molar mass and the number of their arabinofuranose substituents the xylans from birch kraft pulp were reduced in molar mass and had lost most of their original 4-O-methylglucuronic acid side chains. Certainly these differences will have consequences on the final use of both xylans.

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