Xylans were selectively removed from paper grade pulps by nitren extraction in order to produce dissolving pulps. The impact of nitren charge on the removal of hemicelluloses was demonstrated for a birch and mixed softwood kraft pulp. The 95% purity level could easily be reached for the birch kraft pulp. Softwood glucomannans were almost insoluble under the investigated extraction conditions applying nitren. Accordingly softwood pulps seem to be less suited for the nitren process.

Furthermore, the selectivity of nitren extraction was compared with cuen. Nitren turned out to be much more selective in xylan removal, whereas cuen also dissolved part of the cellulose, when this solvent was applied at concentrations, which were needed to reach dissolving pulp purity.

Nitren was also tested in its xylan extraction capability in comparison with sodium and potassium hydroxide. Extraction of a xylan-rich birch kraft pulp with nitren resulted into a pulp of highest purity (96% cellulose content), which could not be obtained applying KOH and NaOH. In the case of a eucalyptus kraft pulp, however, nitren and sodium hydroxide extraction resulted into a product of more or less the same cellulose content (97%). With a beech sulfite pulp as the starting material highest purities with regard to the cellulose content were obtained applying 10% sodium hydroxide (97.5%), whereas the nitren procedure yielded into a pulp of 96.5% cellulose content. This was due to the inability of the nitren procedure to remove 2.7% mannan, which was present in the initial paper pulp from beech.

The residual nickel content in all pulps could be removed by a special washing procedure applying lactic acid.

Keywords: carbohydrate composition, cuen, dissolving pulp, extraction, glucomannan, nitren, paper grade pulp, xylan

Introduction

Dissolving-grade pulps are high-value, intensively bleached pulps with special quality requirements. Cellulose contents of 90-99% are necessary to produce regenerated cellulose fibres and cellulose derivatives. Accordingly, the hemicellulose content in dissolving pulps is low (0.5-10%), as well as the residual lignin and extractives content (below 0.2%) [1]. With a view on the worldwide pulp production capacity of about 150×10⁶ tons per year, the production of dissolving
pulps represents only a niche market of totally 2.5% of the global chemical pulp production. This market situation and the high price difference between both pulp categories rises the question, why paper grade pulps cannot be converted into dissolving pulps in an economically feasible process by selective removal of the hemicelluloses.

In this context, enzymatic hydrolysis of hemicelluloses from paper grade pulps with xylanases and mannanases was investigated by Puls et al. [2] and Christov and Prior [3], but the obtained purity levels were not satisfactory. Alkaline extraction could also be a conceivable solution, as this technique is the basis of most analytical procedures for the isolation and characterisation of hemicelluloses [4]. Accordingly dissolving pulps are frequently purified by hot or cold caustic extractions [5]. It is well known that the extraction potential of 10% sodium hydroxide towards pulps is often higher than applying 18% sodium hydroxide, whereas potassium hydroxide is usually used as extraction medium in 18% concentration. NaOH, LiOH, and KOH are equally powerful extractants for xylans. For the extraction of mannans however, KOH is less effective, whereas NaOH and LiOH have a similar potential [6].

Stimulated by investigations of Burger et al. [7], Kettenbach et al. [8], and Saalwächter et al. [9] a new process for the upgrading of paper pulp into dissolving pulp was recently patented by Rhodia Acetow GmbH [10]. The inventors claimed that nitren, a metal complex of tris(2-aminoethyl)amine and nickel(II)-hydroxide (Figure 1), selectively removes hemicelluloses from paper grade pulps. The cellulose content of a eucalyptus kraft pulp could be improved from 81% to 96% by a two-stage extraction with a 3% nitren solution. Moreover, xylans of high purity could be precipitated by lowering the pH value to 4.

Another metal complex, cuen, has been known as a potential cellulose solvent for a long time [11,12,13]. It would be interesting to know about the performance of cuen for hemicellulose extraction in comparison with nitren, when being used at the same concentration level.

In the present study the extraction performance of nitren should be explored for a set of paper pulp samples, namely a high-xylan and a low-xylan hardwood kraft pulp in comparison to a softwood kraft pulp and a sulfite beech pulp. This performance should be compared with the extraction result, when Cuen is being used. In addition selected pulps should also be extracted with NaOH and KOH and the results with regard to purity should be compared with those after nitren extraction.

An important issue is also the question on the residual nickel content of the obtained pulps.

Figure 1. Constitution of nitren and its complexation with xylan in aqueous solution [10].
Experimental

Paper pulp samples
The starting pulp samples were a eucalyptus kraft pulp (SAPPI, Enstra mill), beech sulfite pulp (M-REAL, Stockstadt), mixed softwood kraft pulp (ZPR, Blankenstein), and birch kraft pulp (M-REAL, Örnsköldsvik). Prior to extraction the four starting pulps had the following carbohydrate compositions (cellulose, xylan and mannan): eucalyptus kraft pulp (84.7%, 14.3%, and 0.5%), beech sulfite pulp (87.0%, 10.3%, and 2.7%), softwood kraft pulp (84.1%, 6.3%, and 8.2%), and birch kraft pulp (75.4%, 24.1%, and 0.4%).

Extraction of the pulps
The preparation of the nitren solution and further characteristics of the starting pulps have been described in a previous study [14]. Prior to the extraction procedure pulp sheets were disintegrated in water, centrifuged and climatised to approximately 93% dry content. All extractions were carried out in 20 g-scale in polyethylene bottles for 1h at 30°C on a temperature-controlled roller mixer. The nitren extractions were conducted with 3%, 5%, or 7% nitren solutions whereas for alkaline extractions 10% NaOH and 14% KOH concentrations were used. The liquor to pulp ratio (L/P ratio) was varied between 10:1 and 20:1. Extracts were separated from the pulps by vacuum filtration over a sintered glass crucible (G1). Then the pulp was washed in three steps with 2% sodium hydroxide, 5% lactic acid (nitren extraction), or 20% acetic acid (alkaline extraction), and hot water. Finally the pulp was air dried at 20°C and 65% humidity and the yield was determined gravimetrically.

Pulp analysis
The carbohydrate composition of the pulps was determined according to [15] and [16], applying a 2-step hydrolysis with H₂SO₄. Subsequently the monosaccharides were detected by borate complex anion exchange chromatography. The results were not corrected for sugar losses and water addition during hydrolysis. The residual nickel content of the extracted pulps was measured by ICP-analysis after hydrolysis with 65% nitric acid in a microwave oven.

Results and discussion

Comparison of extraction behaviour of different pulps applying nitren
As a first step nitren was tested for its extraction efficiency for the four selected pulps, applying 3%, 5% and 7% nitren at a liquor to pulp ratio (L/P) of 10:1 at 30°C and a residence time of 60 min. In an earlier study [14] using a hardwood kraft pulp it had been concluded that time and temperature were rather insensitive for the process. After 5 min the mobilisation of the xylan was more or less completed. A prolongation of the extraction to 120 min resulted in only a minor further reduction of the xylose content in the extracted pulp. The differences in xylan content at various temperatures between 20 and 40°C were only marginal, but the effect was significant in favour of lower temperatures. For an industrial application cooling is very costly, and consequently, nitren extraction should be conducted at ambient temperatures. Under industrial conditions, it also seems unrealistic, that short extraction times of dried pulp sheets can be done in a reproducible way. Thus, all following investigations were performed at a reaction time of 1 h. The total nitren charge can be varied by the L:P ratio as well as by the nitren concentration in solution. The nitren charge was a decisive factor regarding xylan removal and pulp purity. The combination of a high nitren concentration and a low liquor to pulp ratio was most effective for xylan removal. However, a high liquor to pulp ratio with a lower
nitren concentration proved to be more selective and minimised cellulose degradation as well [14].

Figure 2 illustrates the carbohydrate composition of birch kraft pulp applying 3%, 5%, and 7% nitren at a liquor to pulp ratio of 10:1. The purity of the pulp was increased from 93.9% glucose for 5% nitren up to 95.9% glucose for 7% nitren. Accordingly the purity level of viscose grade pulps could be reached with 5% nitren, while 7% nitren charge was needed to obtain high quality grades, which might be suitable e.g. for production of cellulose acetate.

Figure 2. Influence of extraction with 3%, 5%, and 7% nitren on the carbohydrate composition of birch kraft pulp (L/P=10:1, T=30°C, t=60min).

In comparison with nitren extraction of the softwood kraft pulp the most important observation is that nitren hardly solubilised mannan in the examined concentration range (Figure 3). The mannan content of the softwood pulp decreased only slightly from 6.3% (initial paper pulp) to 5.6% after extraction with 7% nitren. This observation can be explained by the differences in the configuration of the hydroxyl groups, which are in trans configuration for β-D-glucans and β-D-xylans, while they are in cis configuration for β-D-mannans. It is most likely that for the dissolution of polysaccharides with nitren a trans configuration of the involved hydroxyl groups is required. The xylan content of extracted softwood pulps continuously decreased with increased nitren concentrations analogously to the experiments with hardwood kraft pulps. After extraction with 7% nitren, a cellulose content of 91.4% (softwood pulps) could be achieved for the softwood kraft pulp. This calculation takes into account the glucose content belonging to galactoglucomannans.

Comparison of nitren and cuen extractions
In this comparison the advantage of nitren compared to cuen for selective xylan removal from birch kraft pulp should be verified. Cuen (copper ethylendiamine complex) is a well known cellulose solvent for its viscosimetrical determination of the degree of polymerization [11-13]. 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 seemed to be 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%.

Comparison of nitren, sodium hydroxide, and potassium hydroxide extractions

In the final investigations on the potential of nitren extraction of hemicelluloses from paper pulps in comparison to the potential of NaOH and KOH (Figures 5-7) only hardwood paper pulps were included due to the inability of nitren for glucomannan mobilisation. A comparatively high liquor to pulp ratio of 20:1 was chosen for the alkaline media in order to take advantage of the full potential of the extractants. The nitren extraction was performed with 5% and 7% nitren concentration. From reasons of comparison with earlier results (Figures 2-4) liquor to pulps ratios of 10:1 and 20:1 were applied. NaOH was applied at 10% concentration, whereas KOH was applied at 14% concentration.
Figure 5 illustrates the carbohydrate composition of the extracted birch kraft pulp in comparison to the starting material. The cellulose content of 75.4% in the initial pulp was raised to 96% after 5% nitren extraction (20:1). This purity could not be obtained using NaOH or KOH. The cellulose content of the pulp after 14% KOH extraction was increased to 95.4%, whereas extraction with 10% NaOH resulted in 95% purity. The cellulose content of the eucalyptus sulfate pulp (84.7% cellulose, 14.3% xylan) could be raised to 97% by nitren extraction at a nitren charge of 5% and a liquor to pulp ratio of 20:1 (Figure 6). This grade in purity could also be achieved with 10% NaOH (96.1% cellulose) and 14% KOH (96.3%).

Comparing the efficiency of nitren and alkali extraction of the beech sulfite pulp (88% cellulose, 10% xylan, 2% mannan) it becomes clear that alkaline extraction resulted in a slightly higher purity (97.5%) compared to nitren extraction (best result 96.5% cellulose, see Figure 7). The comparatively high amount of mannan (2.7%) in the starting material was unfavourable, since this hemicellulose component could not be removed by nitren extraction, whereas sodium hydroxide was most efficient to mobilize mannan besides of xylan. The early results of Hamilton and Quimby [7] and Scott and Pinchot [17] on the better performance of sodium hydroxide for mannan extraction compared to potassium hydroxide could be confirmed.

Reflecting the results from the comparative extraction experiments it can be concluded carefully that nitren is a favourable extraction agent for paper pulps with a high xylan content. As a rule these are kraft paper pulps containing xylans, which have been stabilized under alkaline pulping conditions [18], hindering their complete mobilisation by applying alkali. Nitren, however is capable remove more than 90% of the initial xylan content. These polysaccharides can be utilized elsewhere [19]. Surprisingly by alkaline extraction the eucalyptus kraft pulp could also be upgraded to the required purity of 97.1% cellulose content. The starting material had a lower xylan content. This could be due to the normally lower xylan content in eucalyptus wood chips, compared to beech and birch. Eventually the eucalyptus kraft pulp had been produced according to a modified kraft process, in order prevent a reprecipitation of the initially dissolved lignin and xylan proportion onto the fiber surface [20, 21]. Due to the acid pulping conditions sulfate pulps excel by their lower hemicellulose content [22]. The xylan proportion (10.3%) in the beech sulfite pulp could be removed by nitren as well as by alkali. Highest grades in purity were obtained applying sodium hydroxide. This was due to the fact that sodium hydroxide could mobilize both, xylan and mannan, whereas nitren was rather selective in xylan removal (Figure 7).

**Conclusions**

Nitren is a very selective solvent for xylans. This could be demonstrated, when nitren was used in the same concentration range as cuen and when softwood pulps were the starting materials. Cuen also dissolved considerable proportions of cellulose at concentrations, which were necessary to reach a cellulose content >95% whereas nitren was rather selective. Glucomannans were almost insoluble in the investigated concentration range, when nitren was used. Thus pulps with a high glucomannan content, e.g. softwood pulps, are not suitable raw materials for the nitren process, particularly not if the production of high purity dissolving pulp is envisaged. The extraction of hardwood pulps from both the kraft and the sulfite processes is well suited for the production of high purity dissolving pulps.
The total amount of nitren applied was the primary factor for adjusting the degree of xylan removal. Applying the most economic liquor to pulp ratio of 10:1 and 5% nitren, the cellulose content of hardwood kraft pulps could be raised up to 94-96%. Cellulose contents of 96-97% could be achieved by extracting with 7% nitren solutions. Hardwood sulfite pulps could be upgraded to 96% cellulose content, even at lower nitren charges of 5%. Provided the case that a high value application can be found for the extracted xylan, kraft pulps might be preferable due to their higher xylan content. If dissolving pulp is the product of higher value, sulfite pulps seem to be superior, because higher pulp yields can be obtained with lower nitren concentrations. However a slightly higher purity could be obtained, when sodium hydroxide was applied as extraction agent. This was due to the fact that nitren was unable to mobilize the residual mannan content in the beech sulfite pulp.

Acknowledgements

SAPPI, M-REAL, and ZPR are thanked for the provision of paper pulp samples. The skilful technical assistance of Mrs. Nicole Erasmy, Mr. Jan Benthien, Mr. Eugen Pauls, and Mr. Thomas Schwarz is gratefully acknowledged. The authors are indebted to Dr. Armin Stein of Rhodia Acetow for helpful discussions. Financial support for this research was provided by AiF (German Federation of Industrial Research Associates "Otto von Guericke" e.V., AiF project 13892N).

References

möglichkeiten von EWNN und Cadoxen in der Cellulosechemie. Das Papier 28, 12, 528-533.


