Polymer Bulletin 6, 547–552 (1982)

Polymer Bulletin

Formation of Aldonic Acid End Groups During NO_2/O_2 Treatment and Alkali Cooking of Wood Meal

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Summary

The increased carbohydrate yield after NaOH cooking of wood resulting from NO_2/O_2 pretreatment is related to the oxidation of reducing sugar end groups to aldonic acid groups during both the pretreatment and the subsequent alkali cook. This leads to a suppressed end-wise degradation during the alkali cook, reflected in a lowered formation of 3-deoxyaldonic and 2-C-methylglyceric acid end groups in competing reactions.

Introduction

Pretreatment of wood with nitrogen dioxide in the presence of oxygen results in an enhanced delignification rate and a slower dissolution of carbohydrates during a subsequent cooking with sodium hydroxide ("soda cooking") compared to those of a blank without pretreatment. The purpose of the present work is to elucidate the carbohydrate stabilization by the determination of aldonic and deoxyaldonic acid end groups after NO_2/O_2 pretreatment of wood meal and after a subsequent NaOH cook at 170°C. Model experiments with hydrocellulose are also reported.

Experimental

The hydrocellulose was prepared from extracted and kier boiled cotton by hydrolysis with boiling dilute sulfuric acid. The intrinsic viscosity was 174 dm^3/kg. The NO_2/O_2 pretreatment was carried out at 29% consistency as described by ÅBRAHAMSSON et al. (1981).

The pretreated wood meal (*Picea abies*) and the alkali-cooked pulps were from an investigation by BIHANI and SAMUELSON, which will be reported separately. The wood meal had been extracted with acetone, air dried and then conditioned with water so that the wet material contained 54% solids. The reactor containing the wood meal was evacuated and heated to 50°C. The NO_2, which was added during 5 min, corresponded to 5% calculated on dry wood. Oxygen was then introduced so that atmospheric pressure was reached. The temperature was maintained for 30 min. The pretreatment was then terminated by washing with cold water. The loss of material was negligible.

The cooking was made at 170°C for 120 min with an addition of 32% NaOH calculated on dry, untreated wood. The ratio of wood to liquor was 1:7. The yields and analyses of the pulps are shown in Table 1. The analyses were made by SCAN methods and the lignin content calculated as 0.15 x kappa number.

0170-0839/82/0006/0547/$ 01.20

TABLE 1

Yields and analysis of NaOH cooked pulps prepared from extracted spruce meal with and without NO_2/O_2 pretreatment

	Pretreatment 5% NO_2	 No
Kappa number	38.8	62.3
Lignin content, %	5.8	9.3
Yield, % (dry basis)	51.5	49.7
Carbohydrate yield, %	48.5	45.1
Intrinsic viscosity dm^3/kg	655	612

The aldonic acids were determined as described by LÖWENDAHL and SAMUELSON (1977). Ion exchange chromatography in 0.15 M potassium tetraborate was used to resolve the fractions containing erythronic, threonic and lyxonic acids.

Results and discussion

Hydrocellulose. A simple way to study the oxidation of reducing sugar end groups in polysaccharides to aldonic acid end groups is to treat hydrocellulose with the oxidant. The hydrocellulose sample used contained approximately 3 mmol of reducing glucose end groups per 100 g. The loss in viscosity during the NO_2/O_2 treatments was 3%, *i.e.*, hardly significant. The aldonic acids found after acid hydrolysis are given in Table 2.

TABLE 2

Carboxylic acid end groups in hydrocellulose before and after NO_2/O_2 treatment

	No treatment mmol/100 g	7.5% NO_2 25°; 10 min mmol/100 g	5.0% NO_2 50°; 30 min mmol/100 g
Gluconic	0.033	0.054	0.055
Arabinonic	0.022	0.035	0.027
Tetronic [a)]	0.070	0.055	0.060
Glyceric	0.085	0.075	0.070
Total	0.210	0.219	0.212

a) About equal amounts of erythronic and threonic acids

In agreement with observations by LARSSON and SAMUELSON (1969), a small proportion of aldonic acid groups was present in the hydrocellulose. A slight increase in the number of gluconic and arabinonic acid end groups was observed after the NO_2/O_2 treatment, while the proportions of tetronic and glyceric acids were slightly lowered by the treatment. This may be explained by a dissolution of xylan present as an impurity.

To find out if the glyceric acid was possibly an artefact formed during the acid hydrolysis from material containing a keto group, experiments were made in which the treated hydrocellulose was reduced with potassium hydridoborate before the total acid hydrolysis preceding the chromatographic analysis. The last column in the table refers to a sample subjected to this treatment. The results suggest that like the other aldonic acids the glyceric acid was derived from terminal groups.

Pretreatment of wood meal. No appreciable amounts of the carboxylic acid end groups listed in Table 3 are present in untreated wood. As may be seen from the table, the NO_2/O_2 pretreatment resulted in the formation of gluconic and mannonic acid end groups. Evidently, these are formed by oxidation of reducing sugar groups in glucomannan and cellulose. Analogously, xylonic acid groups were formed in the xylan. The comparatively large amount of arabinonic acid is ascribed to an oxidation of terminal reducing glucose and mannose end groups with a loss of C-1. The formation of threonic acid is explained by an analogous xylan reaction.

Erythronic acid end groups can be formed from reducing glucose and mannose end groups by a loss of both C-1 and C-2. By treatment with some oxidants, they can also be formed by an oxidative cleavage of the hexose groups in the chain molecule. In the latter case a carboxylic acid end group which upon acid hydrolysis gives rise to glyoxylic acid should be obtained. Glyceric acid, which was the most abundant aldonic acid, must be derived from the xylan. Its formation should be analogous to that of erythronic acid in glucomannan and cellulose. No glyoxylic acid was present after hydrolysis in 43% hydrochloric acid under conditions suitable for the determination of aldonic acid groups. Likewise, hydrolyzates obtained by partial hydrolysis in 0.5 M sulfuric acid for 20 hours at 100°C contained no detectable amount of glyoxylic acid. The results suggest that the erythronic and glyceric acid end groups were formed from reducing sugar end groups, present in the wood or produced as intermediates.

Approximately 30% of the reducing hexose groups present in the spruce meal were converted to hexonic, arabinonic and erythronic acid end groups during the NO_2/O_2 pretreatment, while a hardly significant proportion (about 1%) of the reducing glucose end groups in hydrocellulose gave rise to aldonic acid end groups. No cellobionic acid was formed when an aqueous solution of cellobiose was subjected to the same treatment. The results suggest that NO_2 (including N_2O_4 and species formed during the treatment of the hydrocellulose or cellobiose) has little ability to oxidize the reducing sugar end groups, while some active intermediate with this ability is formed with the lignin in wood.

TABLE 3

Aldonic, deoxyaldonic and 2-C-methylglyceric acid end groups

Acid	NO_2/O_2 pretreatment mmol/100 g	NO_2/O_2 followed by NaOH cook mmol/100 g	NaOH cook without pretreatment mmol/100 g
Gluconic	0.039	0.105 (0.054)	0.026
Mannonic	0.017	0.090 (0.046)	0.022
Arabinonic	0.048		
Erythronic	0.044	0.104 (0.053)	0.040
Threonic	0.068	0.085 (0.043)	0.026
Lyxonic		0.078 (0.040)	0.025
Xylonic	0.022	0.038 (0.020)	0.027
Glyceric	0.346	0.468 (0.24)	0.079
3-Deoxy-*ribo*-hexonic		0.076	0.101
3-Deoxy-*arabino*-hexonic		0.079	0.106
2-C-Methylglyceric		0.063	0.088
2-Deoxy-hexonic	0.017	0.099	
3-Deoxy-*erythro*-pentonic		0.013	0.010
3-Deoxy-*threo*-pentonic		0.030	0.007
Total	0.601	1.328	0.557

Values within parenthesis refer to the number (mmol) of carboyxlic acid groups calculated per 100 g extracted wood

NaOH cooking of wood meal. Table 3 shows that, calculated on the same weight of material, the number of hexonic acid groups was much larger in the pulp prepared from the pretreated wood than in the pretreated wood meal. The recalculation on a wood basis shows that a formation of hexonic acid end groups occurred also during the NaOH cook. The proportion between the two isomers changed, which can be explained by an epimerization at high temperature. The corresponding reactions in xylan resulting in an increased number of 1,4-linked pentonic (lyxonic and xylonic) acid groups were reflected in a large increase in the number of lyxonic acid groups.

The loss of arabinonic acid end groups, which are 1,3-linked, confirms the finding by MALINEN et al. (1973) that these end groups are unstable in alkaline media at high temperature. The same reaction in xylan would lead to a loss of the 1,3-linked threonic acid groups. The observed decrease was comparatively small. A probable explanation is that after the alkali cook a large proportion of the threonic acid groups were 1,2-linked and formed during the treatment at 170°C in cellulose and glucomannan.

The number of glyceric acid end groups calculated per 100 g wood was much lower after the NaOH cook of the pretreated meal than after the pretreatment. This can be ascribed to the loss of a large proportion of the xylan during the NaOH cook. The observation is consistent with the fairly low proportion of anhydroxylose (4.4%) determined chromatographically after acid hydrolysis of the pretreated and alkali-cooked wood meal without any correction for the destruction during the hydrolysis.

All aldonic acid groups found in the pulp prepared by NaOH cooking of the pretreated wood were formed also during the cooking of untreated wood, although in much smaller numbers. The results are consistent with the theory that redox reactions are of importance during alkaline pulping also when no redox catalysts are used as additives.

The conversion of reducing hexose end groups to 3-deoxyhexonic and 2-C-methylglyceric acid end groups in cellulose and glucomannan during alkali cooking is extremely important since these end groups result in a stopping of the alkaline peeling responsible for the loss of cellulose and glucomannan. Since a large proportion of the reducing end groups were converted to aldonic acid end groups during the pretreatment, it can be predicted that the proportion of these "stopping acids" should be lower after cooking of the pretreated wood than after cooking of the untreated wood under identical conditions. This was confirmed by the results shown in Table 3.

For xylan the situation is complicated by the fact that the molecule contains uronic acid units linked glycosidically at C-2. These groups retard the alkaline attack and give rise to end groups which are unstable in acid and cannot be determined by existing methods. The low proportion of 3-deoxypentonic acids, formed from 1,4-linked xylose groups by β-hydroxyelimination and benzilic acid rearrangement, was therefore expected (JOHANSSON and SAMUELSON, 1977). The large proportion of aldonic acid groups in the final pulp and the suppressed formation of 3-deoxyhexonic and 2-C-methylglyceric acid end groups as a result of the NO_2/O_2 pretreatment show that the dramatic increase in carbohydrate yield after a given duration of the cooking can mainly be ascribed to a stabilization of the carbohydrates due to the formation of aldonic acid end groups. In addition, the pretreatment leads to an improved delignification. The higher yield compared at the same lignin content in the pulp, is a combined effect of the carbohydrate stabilization and the shorter cooking time.

Acknowledgements

The financial support from the Swedish Board for Technical Development and the 1959 Ars Fond för Teknisk och Skoglig Forskning samt Utbildning is gratefully acknowledged.

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Received February 3, accepted February 5, 1982

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