New Aspects in Cationization of Lignocellulose Materials. V. Modification of Rotten Aspen Wood Meal with Quarternary Ammonium Groups

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Synopsis

Holocelluloses prepared from clear and rotten aspen wood were gradually fractionated with 2.5% NH_4OH, 4.5% NaOH, and 17.5% NaOH, respectively. A higher yield of polysaccharides (24.4%) was obtained from the rotten sample in comparison with clear wood (20.9%). Trimethylammonium-2-hydroxypropyl (TMAHP) derivatives of rotten aspen were prepared by the reaction of wood with 3-chlor-2-hydroxypropyltrimethylammoniumchloride (CHMAC) in alkaline medium. The quantity of TMAHP—hemicelluloses (yield 14.1%) is only slightly lower in comparison with TMAHP–hemicelluloses (yield 15.8%) obtained by modification and subsequent extraction from clear aspen wood meal. The hemicelluloses isolated from the rotten aspen wood meal are contaminated with low molecular cellulose fraction, the degradation products of cellulose attacked by fungi. The lignin component of rotten wood is less intensively attacked by fungi than the polysaccharidic one.

INTRODUCTION

Among forest tree species of Alberta, trembling aspen (Populus tremuloides Michx) is the most widely distributed species. This wood species suffers through decaying by Fomes igniarius var. populinus (Neuman) Campbel, a white rot fungus.[1] There is only a little information about changes of wood components properties caused by fungal attack. After the study of nondecayed beech[2] and aspen[3] wood, the object of the present work was obtain some new information about changes in wood components by the attack of fungus.

EXPERIMENTAL

Materials. Wood meal (0.2–0.4 mm) from aspen (Populus tremuloides Michx) and rotten aspen wood meal (Klason lignin 21.2 and 26.7%, respectively) were used as the lignocellulose materials in alkylation and fractionation. A 50% (vol) aqueous solution of 3-chloro-2-hydroxypropyltrimethylammoniumchloride (CHMAC) was used as alkylating agent. The holocellulose sample was prepared from lignocellulose material (8 g) by the Klauditz method (holocellulose Klason lignins from clear and rotten aspen were 0.62 and 1.94%, respectively). The dioxane lignin was prepared from the sample (5 g) by the action of dioxane (90 mL), water (8 mL), and hydrochloric

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acid (1.8 mL) mixture. The resulting mixture was tempered at 95°C for 8 h under nitrogen atmosphere. The sample was left overnight at room temperature and washed with dioxane (90 mL) and the eluant was dialyzed and freeze-dried. The extraction residue was washed with ethanol and air dried. All yields were related to the oven-dried (o.d.) wood.

Methods. The elemental composition of the modified samples were determined by the Perkin-Elmer elementar analyzer Model 240. Infrared (IR) spectra for samples in KBr pellets were recorded using a Perkin-Elmer spectrometer, Model 457. The quantitative content of quarternary ammonium groups was determined using potentiometric titration or calculated from the nitrogen content. The isolation of individual fractions was done as shown in Figures 1–3. The conditions for the TMAHP–wood meal sample preparation were the same as described previously.[4] The isolated TMAHP–hemicelluloses,

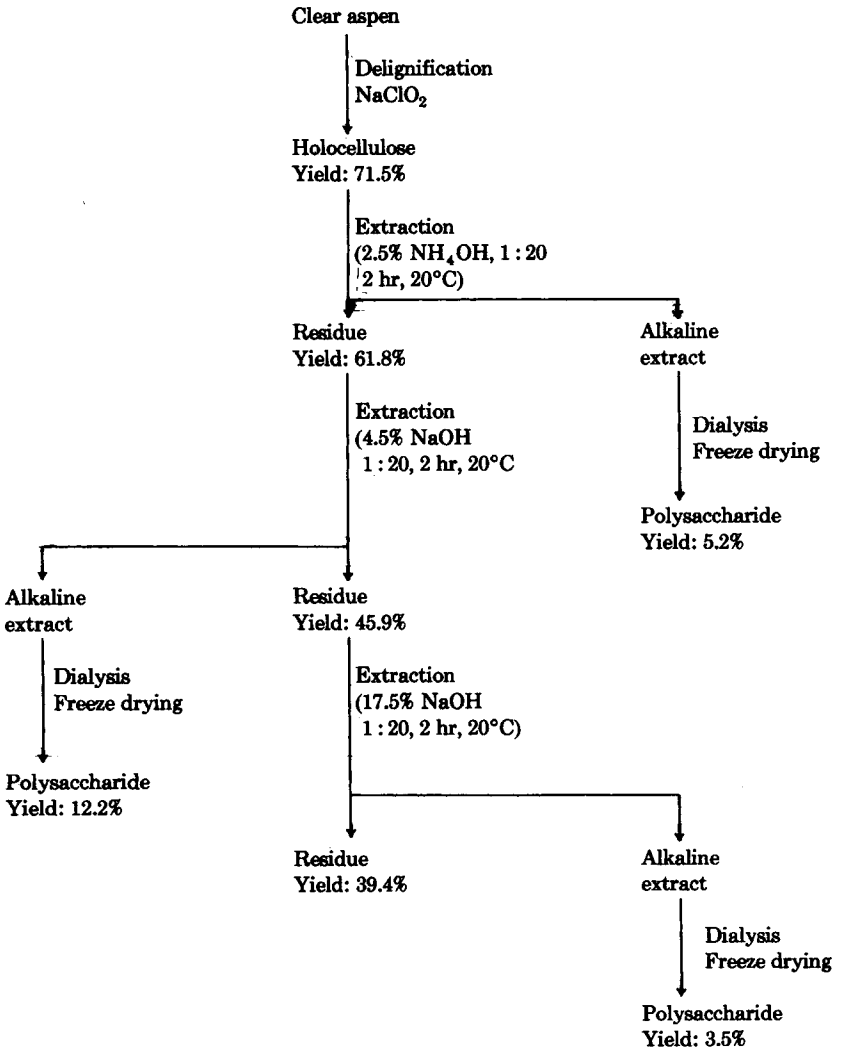

Fig. 1. Fractionation scheme of clear aspen holocellulose.

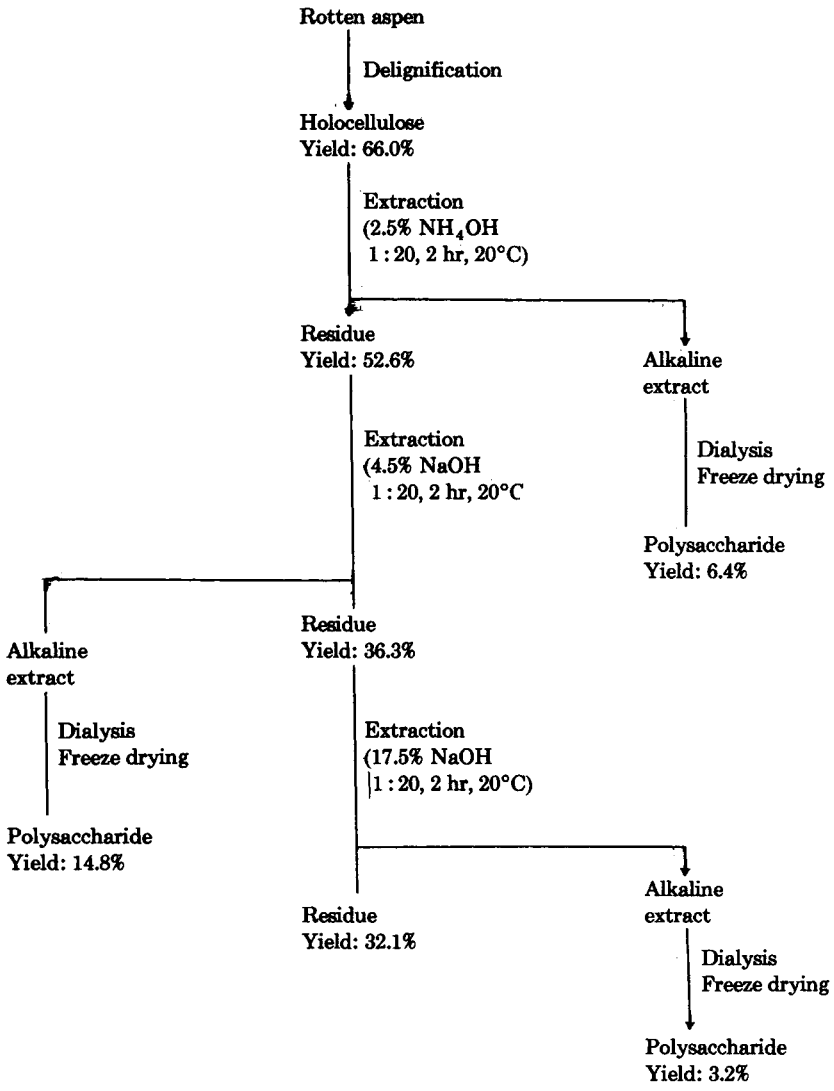

Fig. 2. Fractionation scheme of rotten aspen holocellulose.

as well as, polysaccharides extracted from clear and rotten unmodified aspen wood meal were hydrolyzed with 2*M* F_3C COOH[5] and the sugar composition was determined qualitatively by paper chromatography (PC) on Whatman 1, using the system ethylacetate : pyridine : water = 8 : 2 : 1. The Klason lignin was determined according to Tappi Standard T13 m-54.

RESULTS AND DISCUSSION

To find the differences in the composition of clear and rotten aspen wood meal, we prepared holocellulose samples. In Figure 1 there is the scheme of clear aspen fractionation. The prepared holocellulose (yield 71.5%) was ex-

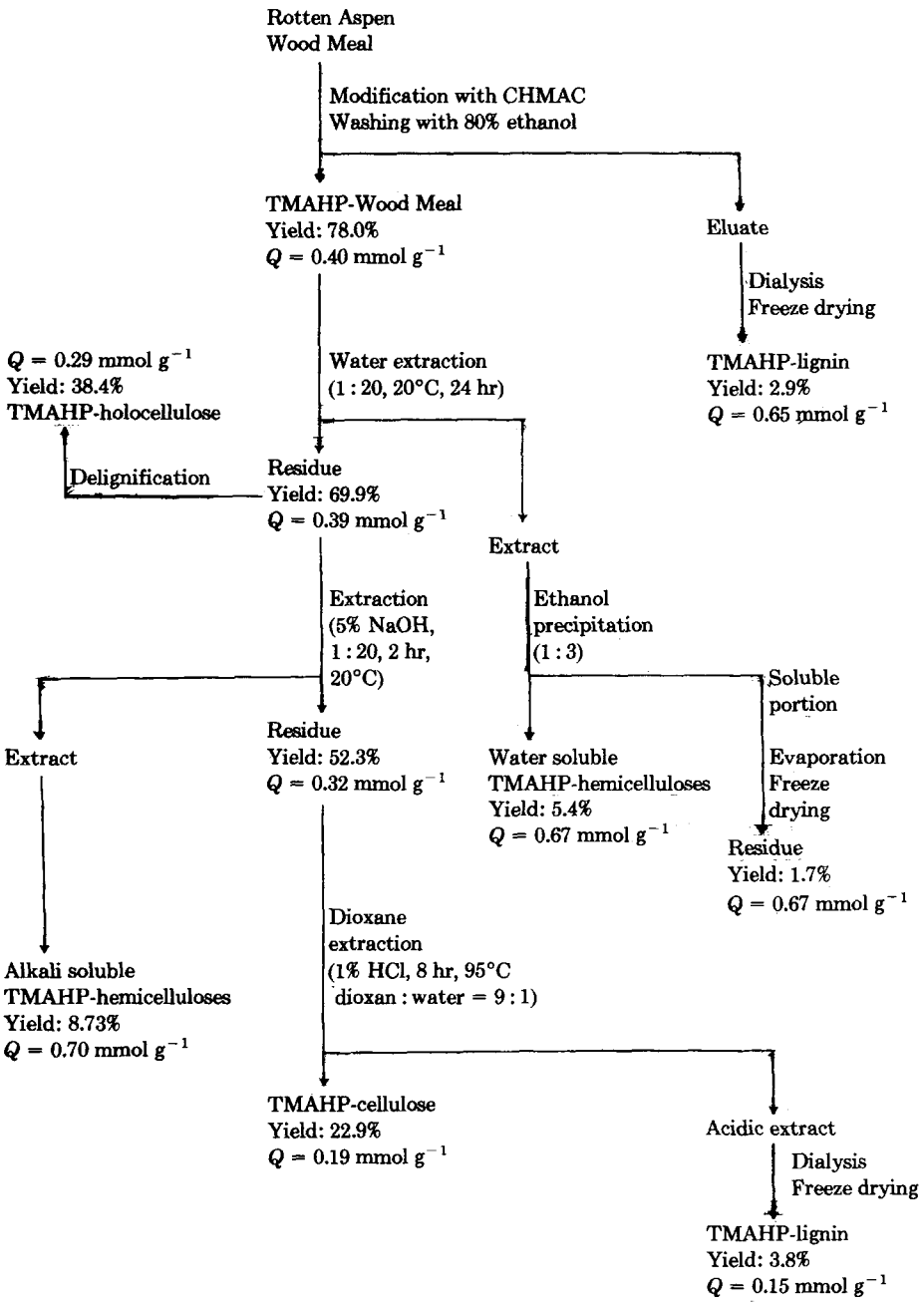

Fig. 3. Fractionation scheme of TMAHP–rotten aspen wood.

tracted with the 2.5% solution of NH_4OH (yield 5.2%), with 4.5% solution of NaOH (yield 12.2%), and with 17.5% solution of NaOH (yield 3.5%). When the rotten aspen wood meal was delignified and extracted in the same way as previously described (Fig. 2), the yield of holocellulose (66.0%) was lower, but the yields of NH_4OH extract (6.4%) and 4.5% NaOH extract (14.8%) were

slightly higher. The yield of extract with 17.5% NaOH (3.2%) was similar as for healthy wood.

The IR spectrum of NH_4OH extract from clear wood showed absorption bonds at 3400 (OH stretching), 2940 (CH_2 asymmetric stretching), 2870 (CH stretching), 1632 (water of hydration), 1580 (COO^- asymmetric stretching salt), 1415 (COO^- symmetric stretching salt), 1250 (OH in plane bending), 1050 (C—O stretching), 900 (C_1 group frequency or ring frequency), 800, and 640 cm^{-1} (OH out-of-plane bending). These bonds were assigned on the basis of known spectral data about (4-O-methyl-D-glucurono)-D-xylan.[6] From the results of qualitative PC of the hydrolystate of NH_4OH extract of clear wood it can be seen that the predominant sugar is D-xylose and D-glucose was present only in traces. That is why we considered this fraction as (4-0-methyl-D-glucurono)-D-xylan. The IR spectrum of NH_4OH extract of rotten aspen exhibited practically the same absorption bonds in the region from 1800 to 1000 cm^{-1}. So we drew the conclusion from the IR spectra that both extracts contained (4-0-methyl-D-glucurono)-D-xylan. The hydrolysate of NH_4OH extract from rotten aspen except D-xylose contained also D-glucose as the second mostly abundant sugar. From these results we concluded that the hemicelluloses isolated from the rotten aspen wood meal were contaminated with low molecular cellulose fraction, the degradation products of cellulose attacked by fungi. The IR spectra of the other extracts did not show absorption bonds at 1600 and 1415 cm^{-1}, respectively, and no significant differences between the spectra were observed. The value of Klason lignin determined in rotten aspen (26.7%) was higher than for clear aspen (21.2%). This could be explained by the hypothesis that lignin portion of wood is less intensively attacked by fungi than the polysaccharidic one. The holocellulose samples contained only small quantities of Klason lignin, and that is why the yields of individual fractions could not be influenced by the presence of lignin.[7]

To influence the yields of hemicelluloses by fractional extraction, the rotten aspen wood meal was modified by quarternary ammonium groups. In Figure 3 there is the scheme according to which the modified rotten aspen wood meal (Klason lignin 22.3%) was extracted after modification with quarternary ammonium groups. The exchange capacity (Q = 0.40 mmol g^{-1}) as well as the yield (78.0%) of modified rotten wood meal are lower than the value for clear aspen.[3] This could be explained by the fact that the most easily accessible parts of wood components were degraded to lower molecular weight products by fungi, which were eluated with 80% ethanol during the isolation of the TMAHP–wood meal from the reaction medium. The TMAHP–lignin fraction was isolated from eluant after dialysis. The IR spectrum of this fraction showed the characteristic lignin absorption bonds: 1715–1705 (C=O stretching nonconjugated to aromatic ring), 1600 and 1500 (aromatic ring vibration), 1460 (asymmetric C—H deformations), 1420 (aromatic ring vibration), and 1125 cm^{-1} (syringyl aromatic ring planar vibration).[8] The exchange capacity was slightly lower in comparison with TMAHP–lignin extracted from eluant of the modified clear aspen with CCl_4^3 and the yield was 2.9%.

The TMAHP–wood meal was extracted with water (Fig. 3). The obtained water soluble TMAHP–hemicelluloses exhibited lower exchange capacity (Q = 0.67 mmol g^{-1}) and three times lower yield (5.4%) as in the case of water soluble TMAHP–hemicelluloses from clear aspen.[3] The yield of water soluble

part, which could not be precipitated, was also lower as in the case of TMAHP–aspen meal. From this result we concluded that also the hemicellulose component of rotten aspen was degraded by fungi. The residue after water extraction was extracted with 5% NaOH, and in this way the alkali soluble TMAHP–hemicelluloses were isolated (Fig. 3). The yield as well as the exchange capacity of this fraction was several times higher in comparison with the fraction obtained from clear aspen wood modified with quarternary ammonium groups. But when we compared the sums of yields of alkali and water soluble TMAHP–hemicelluloses of clear (15.8%)[3] and rotten aspen (14.1%), the difference was not so pronounced. From the PC analysis of the hydrolysates it was evident that both water- and alkali-soluble hemicellulose fractions from rotten aspen wood consisted predominantly of TMAHP–xylan contaminated by low molecular cellulose fraction. The IR spectra of water- and alkali-soluble TMAHP–hemicelluloses were both similar to NH_4OH extracts and the bonds at 1600 and 1425 cm^{-1} (COO^- stretching salt) proved the presence of (4-O-methyl-D-glucurono)-D-xylan. The higher exchange capacity of alkali-soluble TMAHP–hemicelluloses from rotten aspen in comparison with the same fraction from clear aspen[3] confirmed better accessibility of fungi degraded materials.

The residue after alkaline extraction was extracted with dioxane and separated in two (lignin-rich, yield 3.8%, and cellulose-rich, yield 22.9%) fractions with ion exchange capacities of 0.15 and 0.19 mmol g^{-1}, respectively. From the residue after water extraction also the TMAHP–holocellulose with the yield of 38.4% and $Q = 0.29$ mmol g^{-1} was isolated. Also in this case the yield of holocellulose from rotten aspen was lower in comparison to clear wood meal.[3]

So from the obtained results we can see that the highest quantity of polysachharides can be extracted from the unmodified rotten, aspen holocellulose sample, 24.4% of the material. Less can be extracted from unmodified clear wood holocellulose, 20.9%. The lowest yield (14.1%) of extracted polysaccharide was obtained from the TMAHP–wood of rotten aspen, which was not delignified prior to extraction. But the highest quality hemicelluloses suitable as an additive for paper industry were the TMAHP extracts.[9]

CONCLUSIONS

TMAHP derivatives with exchange capacity of 0.40 mmol g^{-1} and yield of 78.0% were prepared from rotten aspen wood meal. From the results of fractional extraction we can see that the yield of alkali soluble TMAHP–hemicelluloses is higher (8.7%) in comparison with the yield from clear TMAHP–wood meal sample (1.3%). On the other hand, we can extract more polysaccharides from unmodified rotten aspen holocellulose meal (24.4% of the o.d. wood) than from holocellulose of clear aspen (20.9%). The hemicelluloses isolated from the rotten aspen wood meal are contaminated with low molecular cellulose fraction, the degradation products of cellulose attacked by fungi. The lignin component of rotten aspen seems to be less intensively attacked by fungi than the polysachharidic one.

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