# New Aspects in Cationization of Lignocellulose Materials. VI. Modification of Steam-Exploded Aspen Wood Chips with Quarternary Ammonium Groups

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## Synopsis

Holocellulose prepared from steam-exploded aspen wood was gradually fractionated with 2.5% $NH_4OH$, 4.5% NaOH, and 17.5% NaOH, respectively. Some residual polysaccharides were extracted from the material in this way, but their yield was only about 5%. Trimethylammonium-2-hydroxypropyl (TMAHP)-derivatives, exploded aspen wood (EXAW), were prepared by the reaction with 3-chlor-2-hydroxypropyl trimethylammoniumchloride (CHMAC) in alkaline medium. The quantity of water and alkali extracted TMAHP–polysaccharides (yield 2.6%) was lower than the yields from modified healthy beech and aspen, as well as rotten aspen. On the other hand, we can obtain more modified cellulose-rich and lignin-rich material than from previously mentioned species. The steam-explosion process is suitable for increasing the accessibility of cellulose component in lignocellulose material for chemical modification.

## INTRODUCTION

The steam-explosion process was used for pretreatment of lignocellulose materials to isolate wood components[1-4] or to produce monosaccharides or other chemicals.[5,6] It was stated that the hemicelluloses[1,2] and lignin[3,4] were degraded while the cellulose[1,2] was attacked only slightly when temperatures up to 220°C were used. We hope there are still some new unknown possibilities for the utilization of steam exploded lignocellulose material.

In this paper we discuss the changes which occurred during steam-explosion process and how they affect the extractibility and chemical accessibility of this material.

## EXPERIMENTAL

Aspen wood chips (debarked) were treated with steam under pressure of about 43 atm at a temperature of 255°C. The time of treatment (inside the gun) was 55 s. The obtained material which contained 37.2% of o.d. lignocellulose was placed into plastic bags and was not dried prior to modification or extraction. A 50% (vol) aqueous solution of 3-chloro-2-hydroxypropyl-trimethylammoniumchloride (CHMAC) was used as alkylating agent. The

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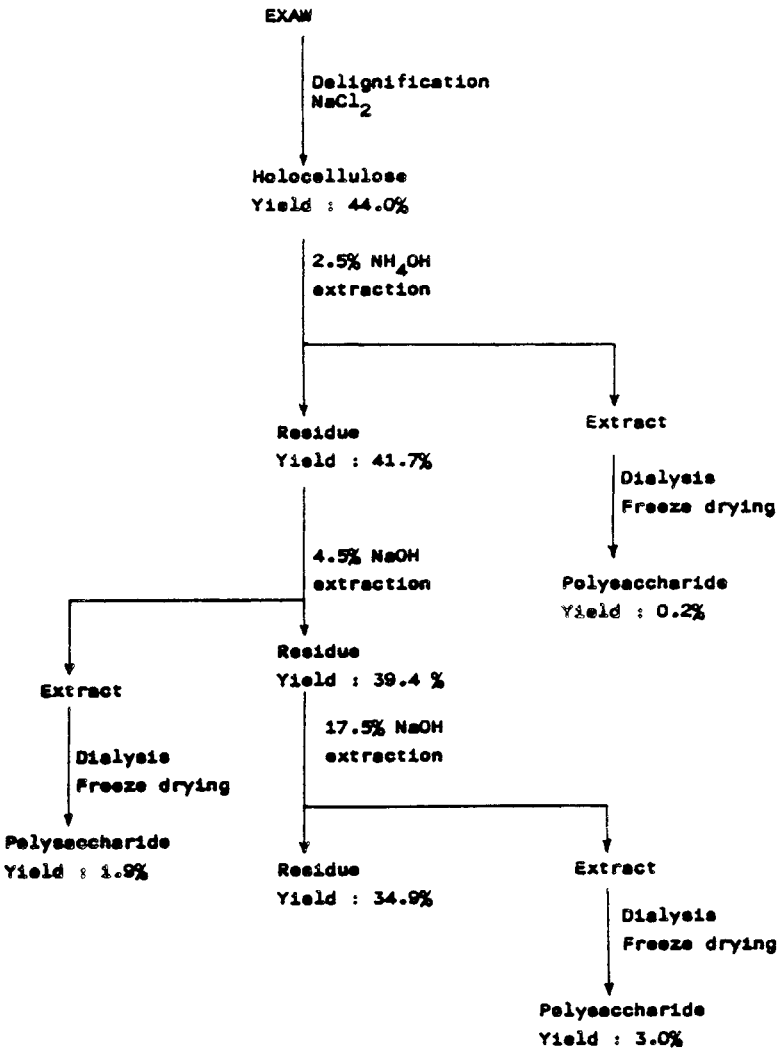


Fig. 1. Fractionation scheme of EXAW holocellulose.

holocellulose sample as well as dioxane lignin were prepared as described previously.[7]

## Methods

The isolation of individual fractions was done as described in Figures 1 and 2. Klason lignin was determined according to Tappi Standard T 13 m-54. All other methods were described or cited previously.[7]

## RESULTS AND DISCUSSION

Pure aspen wood contains 57.2% of cellulose, 25.6% of hemicelluloses, and 17.2% of lignin.[8] The yield of holocellulose from pure aspen was 71.5%, and from steam-exploded aspen the yield of holocellulose material (with Klason

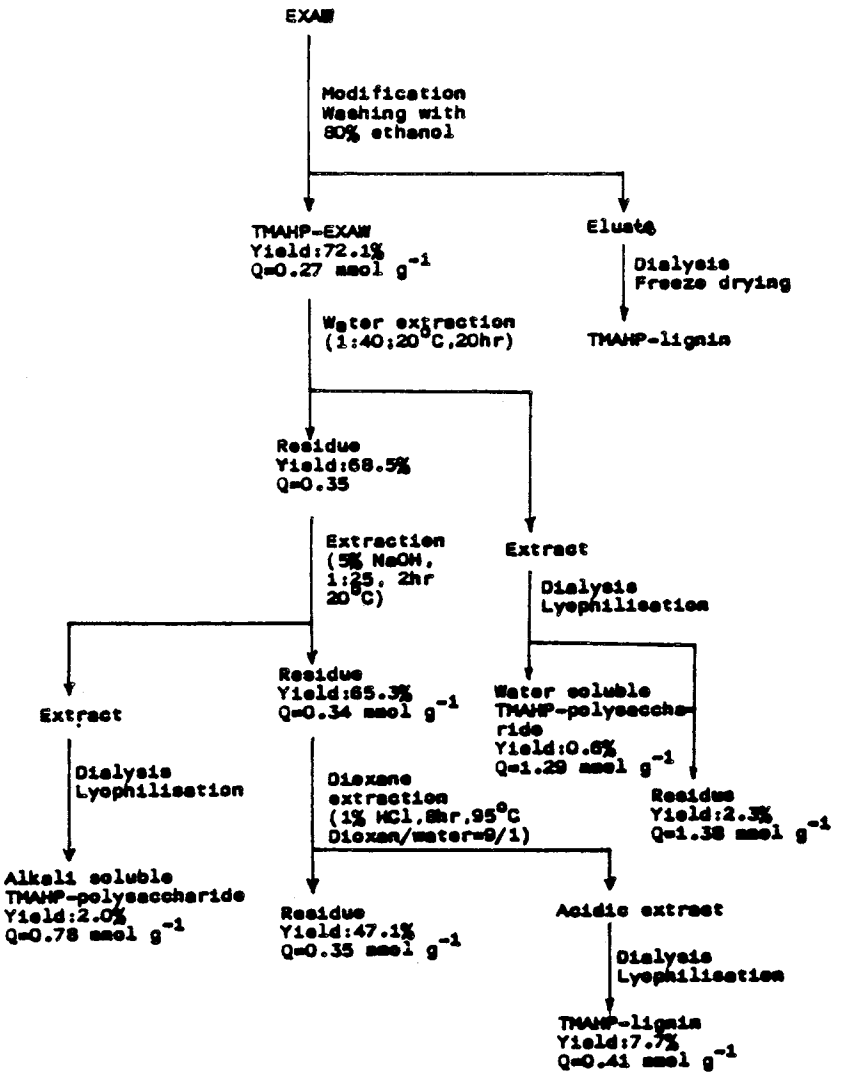


Fig. 2. Fractionation scheme of TMAHP-EXAW.

lignin content 0.2%) was 44.0%. It is less than the content of cellulose. The total yield of material obtained after fractional extraction with 2.5% solution of $NH_4OH$, 4.5% NaOH, and 17.5% NaOH solutions, respectively, was only 5.1% from the starting material (Fig. 1).

The infrared (IR) spectrum of exploded aspen wood (EXAW) is not differing from the spectrum of the nondegraded sample. Also the spectra of holocellulose samples are identical. The IR spectrum of $NH_4OH$ extract with absorption bands at 1725 (C=O acid), 1600 ($COO^-$ antisymmetric stretching), and 1405 $cm^{-1}$ ($COO^-$ symmetric stretching) suggests the presence of (4-O-methyl-D-glucurono)-D-xylan.[9] The same absorption bands but with lower intensity are also present in the IR spectra of both samples, the 4.5% NaOH and 17.5% NaOH extracts, respectively. As determined by paper chromatography (PC) (ethylacetate:pyridine:water = 8:2:1) D-xylose was the predominant

sugar in the soluble portion of all hydrolysates (using 2*M* $CF_3COOH$).[10] In both NaOH extracts there was a residue after hydrolysis. According to IR spectra (3414, $\nu$OH; 2903,$\nu$CH; 1632, C=O; 1429,$\delta CH_2$; 1373 and 1318 $cm^{-1}$, $\delta$CH; 1160, $\delta$COC; 1113, $\nu_{as}$ ring; 1060, $\nu$—C—O—; and 896 $cm^{-1}$, $\nu_{as}$ ring) this residue consists of extracted cellulose component. These results confirm the presence of extractable polysaccharides in EXAW, but their content is only about 5%.

To find out how the accessibility was changed when the material was activated by the steam-explosion process, we alkylated EXAW with CHMAC under optimal conditions.[10] The yield (72.1%) as well as the exchange capacity ($Q$ = 0.27 mmol $g^{-1}$) were lower in comparison with healthy beech and aspen, or rotten aspen.[7,8] This is probably due to the fact that more material is degraded by explosive pretreatment and subsequent modification than in the other previously studied materials. The unmodified EXAW contained 25.8% of Klason lignin. This is more than in pure aspen, and it confirms the fact that most part of hemicellulose component was degraded during the steam-explosion process. The sample of TMAHP–EXAW contained 23.8% of Klason lignin. From the eluate (Fig. 2) a material with exchange capacity ($Q$ = 0.88 mmol $g^{-1}$) and yield of 5.2% from the starting material was prepared. The IR spectra of EXAW and TMAHP–EXAW differ in absorption bands at 1715 and 1683 $cm^{-1}$ (C=O nonconjugated and conjugated stretching with aromatic ring), which were observed on EXAW and were absent in modified material. The IR spectrum of ethanolic eluate after dialysis and freeze drying did show the characteristic absorption bands for lignin (1585, 1425, aromatic ring vibration; 1460 C—H asymmetric deformations, 1330, 1225, 1115, syringyl vibrations, and 1030 $cm^{-1}$, guaiacyl band). In this way higher quantity of lignin degradation products could be isolated in comparison with rotten aspen.[7]

By extraction of TMAHP–EXAW with water a very small portion (0.6% of EXAW; see Fig. 2) of TMAHP material with high exchange capacity ($Q$ = 1.29 mmol $g^{-1}$) was obtained. The IR spectrum of this sample showed characteristic absorption bands at 1600 ($COO^-$ antisymmetric stretching) and 1420 $cm^{-1}$ ($COO^-$ symmetric stretching) for uronic acid groups. The predominant saccharide in hydrolysate was D-xylose as was determined by PC. The residue after hydrolysis consisted of lignin degradation products (IR spectra bands: 1677, C=O stretching in conjugation to the aromatic ring; 1634 and 1504, aromatic ring vibrations; 1458, C—H deformations asymmetric, 1428, aromatic ring vibration; 1371, C—H deformations symmetric; 1335, syringyl ring breathing; 1060, C—O deformations; and 1073 $cm^{-1}$, C—H aromatic in plane deformations). The dialyzed portion represented 2.3% of EXAW material with the highest exchange capacity of all obtained samples ($Q$ = 1.38 mmol $g^{-1}$). The $^{13}$C-NMR spectrum of this sample in water exhibited peaks with shifts at 162.0, 102.8, 77.5, 74.1, 73.9, 64.0, and 55.3 ppm. It is possible that this shifts belong to TMAHP–glycoside of glucuronogalactone formed from (4-0-methyl-D-glucurono)-D-xylan during alkylation. The sample did not contain unmodified saccharides as proved by PC (butanol : pyridine : water = 6 : 4 : 3).[7]

Also a very small part of the material was extracted with 5% solution of NaOH (yield 2.0%). The exchange capacity of this portion was 0.78 mmol $g^{-1}$. The IR spectrum was similar to water-soluble TMAHP fraction, but the bands at 1600 and 1420 $cm^{-1}$ were less intensive. In this case, also, D-xylose

was the predominant component of acid hydrolysate. The residue after hydrolysis, as can be seen from IR spectra, consists of lignin degradation products (1677, C=O stretching in conjugation to the aromatic ring; 1464 and 1059 $cm^{-1}$, C—H and C–O deformations). The residue after NaOH extraction exhibited exchange capacity of 0.35 mmol $g^{-1}$. It gave a higher value as was obtained from healthy beech, aspen, and rotten aspen.[7,8,10] The next step of fractionation was dioxane extraction (Fig. 2). The residue (yield = 47.1%; $Q$ = 0.35 mmol $g^{-1}$) was a cellulose-rich fraction (IR spectra bands: 1430, $CH_2$; 1370, CH; 1200, OH; 1150, COC; 1100 and 1000 pyranose ring; and 900 $cm^{-1}$ asymmetric ring) and the extract (yield = 7.7%; $Q$ = 0.41 mmol $g^{-1}$) a lignin-rich fraction (IR spectra bands: 1590, aromatic ring vibration; 1450, C—H asymmetric deformations; 1380, C—H symmetric deformations; 1155, OH vibration of polysaccharides; 1110, COC vibration; 1065, CO of pyranose ring; and 900 $cm^{-1}$ asymmetric vibration of saccharide ring). From IR spectra we concluded that this lignin fraction contains more saccharide component in comparison with TMAHP–lignin from ethanol eluate.

So from the obtained results it can be seen that after steam-explosion pretreatment, a higher quantity of cellulose-rich and lignin-rich materials can be extracted in comparison with healthy beech and aspen, as well as rotten aspen.[7,8,10] The exchange capacities of these two fractions are also higher. The steam-explosion process is suitable for pretreatment of lignocellulose material prior to chemical modification.

## CONCLUSIONS

TMAHP derivatives with exchange capacity of 0.27 mmol $g^{-1}$ and yield of 72.1% were prepared from EXAW. From the results of fractional extraction we can see that the yield of water- and alkali-soluble TMAHP–polysaccharides (2.6%) is lower in comparison with the yields from modified healthy beech and aspen, as well as rotten aspen. On the other hand, we can obtain more modified cellulose-rich and lignin-rich materials. The steam-explosion process is suitable for pretreatment of lignocellulose material prior to chemical modification to prepare TMAHP–cellulose or TMAHP–lignin.

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