New Aspects in Cationization of Lignocellulose Materials. VII. Modification of Spruce Wood Meal with Quarternary Ammonium Groups

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Synopsis

Trimethylammonium-2-hydroxypropyl (TMAHP) derivatives of spruce wood meal (SWM) and holocellulose of this specia were prepared by the reaction of wood meal with 3-chlor-2-hydroxypropyltrimethylammoniumchloride (CHMAC) in alkaline medium. The TMAHP samples were fractionated and yields and exchange capacity (Q) of individual fractions were compared with beech and aspen fractions obtained under the same conditions. As it is evident from ^{13}C-NMR spectroscopy and GPC analysis the water soluble fraction from TMAHP–SWM consists only of lignin–saccharide degradation products. The NaOH extracts of TMAHP–SWM and TMAHP–holocellulose as well as the water-soluble fraction from TMAHP–holocellulose are polymeric materials. From TMAHP–SWM only 3.1% of alkali-soluble material could be extracted, while from TMAHP–holocellulose 15.7% of water-soluble and 7.9% of alkali-soluble materials were obtained.

INTRODUCTION

Spruce wood is the most abundant wood species in Czechoslovakia. The composition of spruce hemicelluloses and lignin differs from hard wood components.[1] The use of these materials as polymers is still negligible, although some activities in this direction are known.[2]

After the study of beech[3] and aspen[4] wood, this study presents the use of spruce wood meal for the chemical modification and fractionation with the purpose to isolate TMAHP–hemicelluloses, as well as to prepare ion exchangers from lignocellulose materials and also to characterize different wood species as possible sources of hemicelluloses.

EXPERIMENTAL

Materials. Spruce wood meal (SWM; 0.2–0.4 mm) from specia *Picea excelsa L.* extracted with mixture of benzene/alcohol and holocellulose from SWM were used as lignocellulose material (Klason lignin 23.5 and 1.2%, respectively). The 50% (vol) aqueous solution of CHMAC was used as alkylating agent.

Methods. The quantitative content of quaternary groups was determined using potentiometric titration as described previously.[5] The nitrogen content was controlled using the Perkin-Elmer elementar analyzer, Model 240. The

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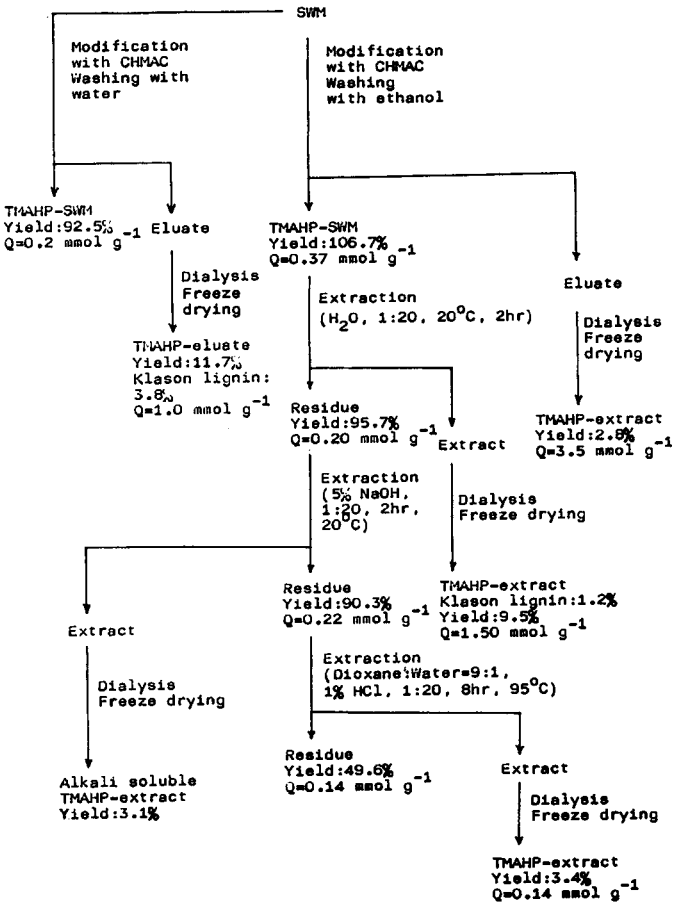

Fig. 1. Fractionation scheme of TMAHP–SWM.

isolation of individual fractions was done according to the schemes in Figures 1 and 2. The polydispersity of obtained fractions was determined by gel permeation chromatography (GPC). Sephadex LH-60 on a 53 × 0.8 cm column with dioxane/water = 7 : 3 eluant and UV analyzer (280 nm) were used for lignin fractions characterization. The polysaccharide fractions were analyzed on a 91 × 0.8 cm column filled with Spheron 40 (25–40 μm) using 0.005M NaOH solution and registrated by differential refractometry. The gel LH-60 was calibrated with polystyrene standards and lignin fractions isolated from waste liquors, respectively. The molecular weight of these standards was determined by ultracentrifugation. The gel Spheron 40 was calibrated with poly(ethylene glycol) standards with defined molecular weight (Fluka and Janssen Chemicals, respectively). The constant $K_{av} = (V_e - V_0)/(V_t - V_0)$ was calculated from the measured elution volumes and the parameters of column. ^{13}C-NMR spectra were measured at 25°C (100 mg/mL) in water and 5% NaOH, respectively, using a Bruker AM-300 spectrometer. The infrared spectra were measured with Perkin-Elmer, Model 983, in the form of KBr pellets.

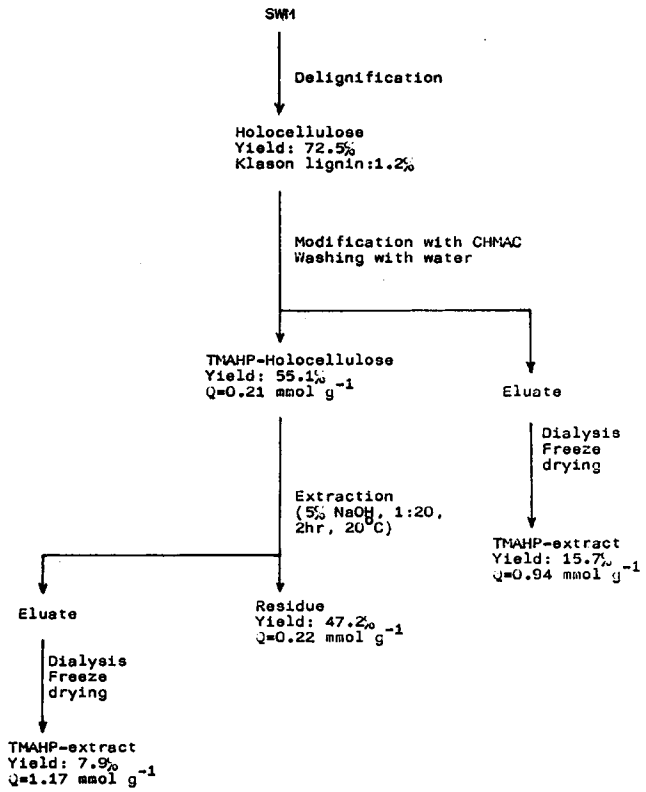

Fig. 2. Fractionation scheme of TMAHP–holocellulose from SWM.

RESULTS AND DISCUSSION

The modification of SWM was done under standard conditions and the reaction was stopped by diluting the mixture with 80% ethanol solution. The yield of obtained solid portion (Fig. 1) (106.8% of absolute dry SWM) was higher as obtained under the same conditions with beech[3] and aspen[4] wood. The exchange capacity (Q = 0.37 mmol g^{-1}) was lower than the value of aspen sample but higher as obtained when beech wood was used. The IR spectra of SWM and TMAHP–SWM samples were differing only in absorption band at 1732 cm^{-1} (C=O stretching nonconjugated to aromatic ring) present in SWM and absent in TMAHP–SWM. It was probably due to lignin degradation during alkylation.

The ethanolic eluate after dialysis and freeze drying (Fig. 1) with 3.5 mmol g^{-1} and yield of 2.8% was obtained. ^{13}C-NMR spectrum of this fraction in water confirmed the presence of lignin degradation products (132.7, C-1 of β-aryl ethers and pinoresinal; 118.8, C-6 of pinoresinal and phelycoumarane; 115.2, C-5 of β-arylethers; 73.3, C-α in β-O-4; 71.6, C-α in β-arylethers; 67.6 C-γ in phenylcoumarans; 63.8 and 63.3, C-γ in β-O-4; and 24.5 ppm (—CH_2— and/or —CH_3)[6,7] as well as some D-xylane residues (102.8, 77.5, 75.0, 74.4, and 64.9 ppm).[8] The presence of the TMAHP group was also evident (55.6–55.3 ppm).[4]

When SWM was washed directly after modification with water, the yield of TMAHP residue (92.5%) and Q (0.2 mmol g^{-1}) were lower than for the residue after 80% ethanol washing (Fig. 1). This was due to washing out the water-soluble saccharide portion together with lignin water-soluble degradation products into the eluate. TMAHP material eluated with water directly after modification (yield = 11.7% and Q = 1.0 mmol g^{-1}) contained 3.8% Klason lignin. But when the modified material was extracted with water (yield = 9.5% and Q = 1.5 mmol) from TMAHP–SWM fraction which had been washed out after modification with 80% ethanol (Fig. 1), the obtained extract contained only 1.2% of Klason lignin. ^{13}C-NMR spectra of both TMAHP materials soluble in water were identical. It contained two peaks for reducing saccharide anomers (97.6 and 93.5 ppm, respectively) and the composition of monosaccharide after hydrolysis as analyzed by paper chromatography[9] should comprise D-xylose, D-mannose, D-glucose and 4-O-methyl-D-glucuronic acid.

From the results of GPC (Fig. 3) it can be seen that the water-soluble TMAHP-saccharide fraction eluted from SWM by the described procedure represents the degradation products formed and cannot be considered as polymeric material.

The residue after water extraction was separated with 5% NaOH (Fig. 1). The yield of extracted material was only 3.1% and the exchange capacity (Q = 0.71 mmol g^{-1}) was lower as for water-soluble TMAHP material. The ^{13}C-NMR spectrum of this fraction was identical with alkali degraded D-xylan consisting only of β-D-xylopyranose units without any substituents.[10] The insoluble portion after NaOH extraction was treated with acidified dioxane/water solution and the cellulose (yield = 49.6%, Q = 0.14 mmol g^{-1}) and lignin (yield = 3.4%, Q = 0.14 mmol g^{-1}) fractions were obtained. The GPC analysis of TMAHP–dioxane lignin fraction showed higher molecular weight in comparison to TMAHP extract eluted with 80% ethanol (Fig. 3). The IR spectra of these two fractions were identical.

To obtain the TMAHP–polysaccharid soluble in water, holocellulose from SWM as substrate for modification was used (Fig. 2; yield = 72.5%; Klason lignin = 1.2%). The yield of TMAHP material eluted by water was higher (15.7%, Fig. 2) in comparison to TMAHP eluates from SWM. This is due to absence of lignin in the substrate as was shown previously.[3] The distribution of molecular weight as determined by GPC was also different from TMAHP eluate from SWM. This fraction could be considered as polymer, although it contained three maxima of lower molecular weight (Fig. 3). The ^{13}C-NMR spectrum of this fraction in water contained five resonances of unsubstituted β-D-xylopyranose units (C-1: 102.0, C-2: 73.9, C-3: 74.9, C-4: 77.5, and C-5: 64.1 ppm), substituted β-D-xylopyranose units at C-2 (C-1: 101.7, C-2: 83.6, C-3: 73.9, C-4: 77.5, and C-5: 64.1 ppm), and D-glucuronic acid residues (C-1: 98.7, C-2: 73.5, C-3: 73.5, C-4: 82.7, C-5: 72.4, C-6: 177.9, and OMe: 61.0 ppm).[11] The presence of the TMAHP group was confirmed by resonances at 55.3 ($(CH_3)_3$), 69.3 (CHOH), and 66.3 ppm (two CH_2 groups) on the basis of ^{13}C-NMR spectrum of CHMAC (C-1: 66.9, C-2: 69.7, C-3: 48.7, and $(CH_3)_3$: 55.7 ppm).

The yield of eluate obtained from holocellulose by the extraction with NaOH was also higher (7.9%) than from SWM. The ^{13}C-NMR spectrum of

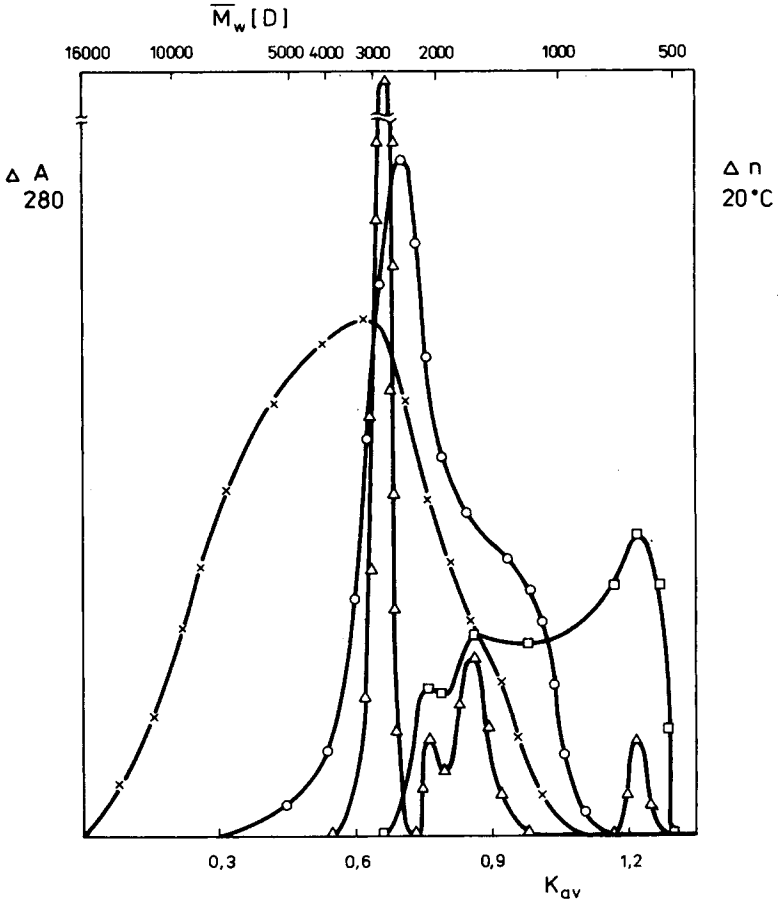

Fig. 3. GPC analyses of TMAHP fractions: (×) TMAHP–dioxane lignin from SWM; (○) TMAHP–extract from SWM with ethanol; (△) TMAHP–extract from holocellulose with water; (□) TMAHP–extract from SWM with water.

this fraction in 5% NaOH showed in the anomeric region, besides the signals of C-1 carbons of unsubstituted, β-D-xylopyranose units (103.4 ppm), substituted β-D-xylopyranose units at C-2 (102.0 ppm), D-glucuronic acid units (98.8 ppm), and also C-1 atoms from β-(1-4) linked D-glucose (104.5 ppm) and β-(1-4) linked D-mannose (101.4 ppm) residues of D-gluco-D-mannan.[12] The resonance of three methyl groups linked to quarternary ammonium group is at 55.4 ppm.

So the hemicelluloses extracted from TMAHP–holocellulose with NaOH contained (4-O-methyl-D-glucurono)-D-xylan and D-gluco-D-mannan while the NaOH extract from TMAHP–SWM contained only D-xylan without D-glucuronic acid units. So from the TMAHP–SWM only 3.1% of polymeric material can be extracted with NaOH, while from TMAHP–holocellulose 15.7% of water-soluble and 7.9% of alkali-soluble polysaccharide with ion-exchanging properties can be obtained. This is the same quantity as obtained from beech sawdust,[3] but more than from aspen wood meal.[4]

CONCLUSIONS

TMAHP derivatives with exchange capacity of 0.37 mmol g^{-1} and yield of 106.7% were prepared from SWM. The water-soluble TMAHP–SWM material consisted only from lignin–saccharide degradation products. The alkali-soluble fraction from TMAHP–SWM and TMAHP–holocellulose as well as water eluate from TMAHP–holocellulose were TMAHP–hemicellulose polymeric materials. From TMAHP–SWM only 3.1% of alkali-soluble material could be extracted while from TMAHP–holocellulose 15.7% of water-soluble and 7.9% of alkali-soluble material were obtained.

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