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Modification of corn cob meal with quarternary ammonium groups

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Corn cob meal was modified with quarternary ammonium groups and subsequently extracted with 80% ethanol, water, and 5% NaOH. The fractions obtained had lower polydispersities, $\overline{M}_w$ values, and yields than unmodified material. The yields are lower than those obtained on bagasse under the same conditions. The modification caused the drastic degradation of the ethanol-lignin (EL) fraction. The one-step extraction with NaOH/H_2O_2 gave 28·8% yield of material (calculated on the starting material) which contained 12·0% Klason lignin, and had the highest polydispersity (4·3, $\overline{M}_w$ = 9540). The water-soluble fractions consisted of arabinoglucuronoxylan and alkali-soluble fractions of xylan without other sugar moieties. The water-soluble fraction from NaOH/H_2O_2 extraction contained arabinoglucuronoxylan with modified arabinose and 4-*O*-methyl-D-glucuronic acid units. By this method higher yields could be obtained than on bagasse treated by the sequential extraction.

INTRODUCTION

Annual plants' residues represent an important source of materials which could be further used in different ways. Corn cobs have the highest content of xylan from all the plant materials (Whistler, 1950). They are already used for furfural production (Barbe *et al.*, 1989) as well as for D-xylose and L-arabinose production (Kubala & Kraus, 1987). (4-*O*-Methyl-*α*-D-glucurono)-*β*-D-xylan could be used as a paper additive to increase the paper strength (Naterová *et al.*, 1986). Xylan from corn cobs was prepared by extraction with NaOH or KOH in combination with $NaOCl_4$ (Ebringerová *et al.*, 1988). In the present paper we studied the fractionation of unmodified corn cobs and the effect of modification on the yield and molecular weight of the fractions obtained without using chlorine-containing compounds.

EXPERIMENTAL

The corn cobs were milled to particles smaller than 0·7 mm prior to the treatment. The sample contained 17·2% Klason lignin (ash content 0·6%, and 2·5% water). The 50 vol.% aqueous solution of 3-chloro-2-hydroxypropyltrimethyl-ammonium chloride (CHMAC) was used.

The material was activated with 17·5% NaOH in 1:10 (w/v) ratio for 20 min and subsequently diluted to 1:20 and tempered and stirred for 4 h at 60°C. The sample was then diluted and washed with 80% ethanol. The eluant obtained was concentrated under reduced pressure, dialysed and freeze dried. The residue was mixed with water (1:20 ratio) and stirred for 2 h. After washing with water the eluant was treated as previously and the residue was extracted with 5% NaOH in 1:20 ratio for 2 h and washed with the same volume of 5% NaOH and eluted with water till neutral reaction on phenolphthalein. The material was treated in the same way when modified with CHMAC but the sample was diluted to 1:20 ratio with 50% CHMAC solution instead of water after activation with 17·5% NaOH. In the case of one step extraction the material was mixed with the solution of 5% NaOH containing 1% H_2O_2 in 1:20 ratio and stirred (500 rpm for 2 h). The sample was eluted with water and the eluant treated as previously. All the extractions were carried out at room temperature in the presence of air and the yields were calculated on the absolute weight of the starting material on the basis of the weights of solid fractions. The water content of

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these samples was determined by thermogravimetry on the basis of residue obtained at 105°C (it was from 3–7 wt % of the material). All the results obtained on unmodified and trimethyl-ammonium-2-hydroxypropyl (TMAHP)-modified samples are listed in Tables 1 and 2, respectively. The Klason lignin was determined according to Tappi Standard T13 m-54. The nitrogen content was determined using Perkin-Elmer elementary analyser, Model 240.

The gel permeation chromatography (GPC) of the fractions was performed on Separon 40-S (52 × 0·8 cm) column (UV detection at 280 nm and parallel refractometric detection) at the flow rate of 0·6 ml/min at 23°C. The eluant was dimethylsulphoxide (DMSO)/water = 1:1 containing 0·01 M CH_3COOH and 0·1 M LiCl under pressure of 6 MPa. The column was calibrated with lignin, dextran and (4-*O*-methyl-α-D-glucurono)-β-D-xylan standards as described previously (Šimkovic *et al.*, 1990). The molecular weights of these standards were determined by mass spectrometry (lignin models) and osmometrically (Knauer, steam-method on water-soluble polysaccharides) and by ultracentrifugation (lignin macromolecular standards). The polydispersity and the molecular weight distribution were measured as described previously (Faix *et al.*, 1981). The accuracy of this method is about 5%.

Proton-decoupled ^{13}C-NMR spectra (75·46 MHz) were recorded at 25°C (70–100 mg/ml) in $(CD_3)_2SO$, D_2O, or D_2O containing NaOH, with Bruker AM-300 FT-NMR spectrometer. In D_2O solutions methanol was used as internal standard (50·15 ppm relative to Me_4Si) whereas in $(CD_3)_2SO$ solutions the reference signal of solvent at 39·5 ppm relative to Me_4Si was used.

Table 1. Yields and Klason lignin contents of fractions obtained from unmodified corn cobs

Fraction	Yield (%)	Klason lignin (%)	Ash content (%)
Ethanol lignin (EL)	5·2	—	3·6
Residue after EL extraction	89·4	12·4	6·0
Water-extracted hemicelluloses (WH)	13·2	5·0	2·2
Residue after WH	59·1	25·1	0·7
Alkali-soluble hemicelluloses (AH)	11·3	0·0	2·5
Residue after AH	25·0	44·0	0·5
One-step $NaOH/H_2O_2$ extract (APH)	28·8	12·0	5·7
Residue after APH	52·4	27·2	1·5

RESULTS AND DISCUSSION

Table 1 gives the results of fractionation of unmodified sample. The ^{13}C-NMR spectrum of the ethanol eluant (EL) fraction in DMSO-d_6 confirmed the presence of lignin (152·6, C—4G—CHO, etherified; 147·8, C-3 guaiacyl; 142·7, C-4 phenylcoumaran; 129·1, C-1 guaiacyl; 122·1, C—6G—CH_2; 119·8, C—6G—CHOH—, β-arylethers; 115·2, C-5 β-arylethers; 111·2, C—2G—CH═CH—; 104·4, syringyl substituted at positions 2 and 6; 55·9, OCH_3; and 29·1 ppm, aliphatic carbon not bonded to oxygen; Nimz *et al.*, 1982; Kringstad & Mörck, 1983). The spectrum also contained characteristic xylan signals at 101·8 (C-1), 75·5 (C-4), 74·1 (C-3), 72·7 (C-2), 63·3 (C-5) and 60·4 (OCH_3; Kováč *et al.*, 1982). The yield of this fraction was only 5·2% and it contained 3·6% ash.

The residue after EL extraction gave 13·2% yield of hemicelluloses by water extraction (Table 1). After isolation and freeze drying this fraction was not completely soluble in water. The ^{13}C-NMR spectrum of this fraction in DMSO-d_6 gave not only the previously mentioned xylan signals (101·7, 75·4, 74·0, 72·6, and 63·2 ppm) but also the signals of 4-*O*-methyl-D-glucuronic acid residue at 97·5 (C-1), 72·0 (C-2, C-3), 82·0 (C-4), 69·5 (C-5), and 59·0 (OCH_3) ppm (the C-6 carbon was not observed) and xylopyranose signals of substituted xylose at 100·7 (C-1), 76·3 (C-2), 73·1 (C-3), 75·4 (C-4), and 63·2 (C-5) ppm (Kováč *et al.*, 1982). The presence of

Table 2. Yields, Klason lignins, nitrogen and ash contents of fractions obtained after modification with CHMAC

Fraction	Yield (%)	Klason lignin (%)	Nitrogen content (%)	Ash content (%)
TMAHP-EL[a]	12·0	—	7·9	0·2
Residue after TMAHP-EL	62·7	5·7	2·3	2·8
TMAHP-WH[b]	7·0	0·1	4·9	0·0
Residue after TMAHP-WH	39·5	43·1	0·4	0·2
TMAHP-AH[c]	13·7	0·1	0·7	0·7
Residue after TMAHP-AH	24·1	56·3	0·0	0·3

[a] Trimethylammonium-2-hydroxypropyl-ethanol lignin.
[b] Trimethylammonium-2-hydroxypropyl-water-soluble hemicelluloses.
[c] Trimethylammonium-2-hydroxypropyl-alkali-soluble hemicelluloses.

arabinose units in this fraction could be confirmed by the signals at 107·1 (C-1), 80·3 (C-2), 77·9 (C-3), 86·1 (C-4), and 61·9 (C-5) ppm (Hromádková *et al.*, 1987). The spectrum also contained some lignin signals at 131·5 (C-1 guaiacyl), 128·6 (olefinic carbon), 61·8, 61·5 ($—CH_2OH$), 55·6 (OCH_3), 29·8, 28·3 ($—CH_2—$), 23·2, 22·3, 13·8, and 10·8 ($—CH_2—$ and/or $—CH_3$) (Kringstad & Mörck, 1983). This fraction contained 5·0% Klason lignin and 2·2% ash.

The extraction of the residue with 5% NaOH gave 11·3% yield of alkali-soluble hemicelluloses (AH). The ^{13}C-NMR spectrum of this fraction in DMSO-d$_6$ contained five D-xylan signals (101·9, C-1; 75·7, C-4; 74·2, C-3; 72·9, C-2; and 63·4, C-5 ppm). The other signals present but with much lower intensity were at 73·3 ppm for C-3 of xylose unit substituted with arabinose and arabinose residue signals at 86·3 (C-4), 80·3 (C-2), 76·5 (C-3), and 62·2 (C-5) ppm. This indicates that most of the arabinose and 4-*O*-methyl-D-glucuronic units on D-xylan polysaccharide were degraded on the AH fraction. The yield of this fraction was 1·9% lower (11·3%) than that of water-extracted hemicelluloses (WH) (Table 1). This sample contained only traces of Klason lignin (0·1%).

When the corn cob meal was extracted with 5% NaOH containing 1% of H_2O_2 without activation with 17·5% NaOH 28·8% of the starting material could be eluted. This water-soluble material contained 12·0% Klason lignin and 5·7% ash (Table 1). The ^{13}C-NMR spectrum of this fraction in D_2O contained the signal of C-1 (102·7 ppm) of unsubstituted xylose units and C-1 (102·4 ppm) of substituted xylose units. The signal of unsubstituted xylose C-1 represented 60·3% of the area of all the anomeric carbons, while the C-1 of substituted xylose represented 19·7%. It means that on average every fourth xylose unit is substituted. There were five other signals observed at the anomeric region at 108·7, 107·5, 103·7, 98·6, and 97·7 ppm. The sample also contained three signals of carboxyl carbons at 177·9, 178·2, and 179·6 ppm. On the basis of known data we attribute the signal at 97·7 ppm to C-1 of 4-*O*-methyl-D-glucuronic acid residue (Kováč *et al.*, 1982), at 103·7 ppm to C-1 of xylose unit substituted with arabinose, and at 107·5 ppm to C-1 of arabinose unit (Hromádková *et al.*, 1987). We suppose that the remaining signals at the anomeric region (98·6 and 107·5 ppm) as well as those at 177·9 and 179·6 ppm are due to changes effected by the action of sodium hydroxide/hydrogen peroxide on arabinose and 4-*O*-methyl-D-glucuronic acid units. This fraction was only partially soluble in DMSO-d$_6$ and the ^{13}C-NMR spectrum of the soluble portion gave only the five signals of unsubstituted xylose units (101·8, 75·4, 74·0, 72·7, and 63·3 ppm). The residue obtained after elution of this fraction represented 52·4% of the starting material, contained 27·2% Klason lignin and 1·5% ash (Table 1).

To find out how the yield of individual fractions will be changed as well as to what extent corn cob material could be modified when it is reacted with quarternary ammonium groups we used CHMAC in the step after activation with 17·5% NaOH (see Experimental). The yield of trimethylammomium-ethanol lignin (TMAHP-EL) is more than doubled in comparison to EL (Table 2). This fraction contained 7·9% nitrogen and was not soluble in DMSO and the ^{13}C-NMR spectrum measured in D_2O in the presence of NaOH gave signals at 169·5, 71·2, 70·6, 64·4, 63·9, 59·4, 53·5, and 46·0 ppm. These signals are not characteristic for lignin or carbohydrate fraction and can be assigned to the macromolecule formed from alkylating agent and degradation products. The $\bar{M}_w$ of this fraction is the smallest from all fractions obtained (Table 3).

The residue after TMAHP-EL contained only 5·7% Klason lignin. By the extraction of this material with water a fraction which represented 7·0% of the starting material was obtained. The ^{13}C-NMR spectrum measured in D_2O confirms the presence of TMAHP-arabinoglucuronoxylan. The C-1 for unsubstituted xylose units at 102·7 ppm represents 55·0% and C-1 of substituted xylose units (102·4 ppm) 16·5% of the area at the anomeric region. It means that on average every fourth xylose unit is substituted with arabinose (108·8 and 107·6 ppm), 4-*O*-methyl-D-glucuronate (98·7 ppm), or TMAHP-group (68·4, 68·9, CHOH; 62·7, CH_2; and 53·4 - 55·3 ppm, CH_3). The signal at 164·4 ppm (C-6 of carboxyl) as well as a small methoxyl signal at 61·0 ppm indicate that most of the methoxyl groups were eliminated during the modification under alkaline conditions (Šimkovic *et al.*, 1986). The additional signals are at 103·7 (C-1 of xylose substituted with arabinose) and 95·7 ppm (C-1 of reducing carbohydrate unit). This fraction contained only 0·1% Klason lignin (Table 2).

The residue after TMAHP-WH extracted with 5% NaOH gave 13·7% yield from the starting material. This fraction was xylan without any attached carbohydrate units or TMAHP-group as confirmed by ^{13}C-NMR. The shifts obtained in D_2O in the presence of NaOH were: 103·6 (C-1), 77·0 (C-4), 76·4 (C-3), 74·7 (C-2), and

Table 3. GPC analysis of individual fractions

Sample	$\bar{M}_w$	D^a	MWD^b		
			<10^3	10^3–10^4	>10^4
EL	6 880	2·1	1	84	15
WH	18 710	2·3	4	54	42
AH	17 580	3·4	20	55	25
APH	9 540	4·3	17	62	21
TMAHP-EL	3 940	1·2	0	99	1
TMAHP-WH	15 900	1·6	4	69	27
TMAHP-AH	16 860	2·0	7	66	27

[a] Polydispersity.
[b] Molecular weight distribution (vol. %).

64·4 (C-5) ppm. This fraction had a very low content of Klason lignin, nitrogen, and ash (Table 2). The residue after TMAHP-AH contained 56·3% Klason lignin.

From the results of GPC analysis (Table 3) we can see lower polydispersity of TMAHP-substituted fractions in comparison to unmodified fractions. The APH fraction which contains 12·0% Klason lignin has the highest polydispersity and the lowest $\overline{M}_w$. This indicates the degradative effect of peroxide on the material. The $\overline{M}_w$ values of modified fractions are only slightly lower at lower polydispersity than those of unmodified fractions (Table 3). For solubility in water the presence of arabinose and 4-*O*-methyl-D-glucuronic unit linked to the linear xylan chain seems to be more important than the polydispersity or $\overline{M}_w$ value.

When comparing the results with those obtained under the same extraction conditions on bagasse (Šimkovic *et al.*, 1990), polymers with higher molecular weights could be extracted from corn cobs. On the other hand the yields of unmodified and modified fractions obtained on corn cobs are smaller than those from bagasse. The yield of $NaOH/H_2O_2$ extraction is higher than those obtained on bagasse.

CONCLUSIONS

The modification of corn cob meal with quarternary ammonium groups slightly lowers the yield of polysaccharide and the $\overline{M}_w$ value at lower polydispersity of the fraction in comparison to unmodified extracts. The yields are lower when compared to bagasse fractions obtained under the same conditions. By the modification most of the ethanol-soluble material was degraded. The one-step extraction with $NaOH/H_2O_2$ gives water-soluble material at 28·8% yield which contained 12·0% Klason lignin with the highest polydispersity (4·3, $\overline{M}_w = 9540$). More material could be extracted from corn cobs than from bagasse with previously used methods. Arabinoglucuronoxylan was soluble in water while the linear xylan which had no other carbohydrates linked to the main chain was soluble only in alkaline solution.

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