An Economic Process for Preparation of Xylose and Derivatives by Hydrolysis of Corn Cobs

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ABSTRACT

With the objective of obtaining the most complete recovery of carbohydrate content from agricultural wastes, a process has been studied which involves three stages: (1) water-soluble sugar extraction; (2) pentose preparation by mild hydrolysis; and (3) hydrolysis under more drastic conditions of residual lignocellulose.

In this paper we report on the mild hydrolysis of pentosans from corn cobs in pre-pilot columns. This was done using a process which involved impregnation with sulfuric acid, heating to hydrolyse the wet acidic waste, and watery pentose extraction. The influence of acid concentration and heating time at 100°C on the hydrolysis as well as on sugar degradation and yields has been studied.

The optimum conditions of the process were 9% sulfuric acid and 3 hours heating. Under these conditions, 89% of the total pentosans (t.p.) were hydrolyzed (28% of the raw dry material, r.d.m.); 33% t.p. (9% r.d.m.) were degraded, and 67% t.p. (20% r.d.m.) were recovered in the broths. The broths obtained were purified with ion-exchange resins and good yields of xylose were obtained by crystallization.

Conditions for the direct reduction of the deionized xylose broths to xylitol, as well as yields and the technical properties of the products, were also studied.

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The nitric oxidation of the raw xylose broths and sequestering properties of the raw trioxyglutaric acid obtained were studied. These processes permit the production of cheap humectants and sequestering agents which could have industrial applications.

INTRODUCTION

There is currently considerable interest in the search for new energy sources as a hedge against a petroleum shortage. Equally, there is growing interest in new materials which could substitute for petrochemicals.

The biomass for energy source could be agricultural and forest wastes or from farming, although the latter could adversely affect food supplies for the rapidly growing world population.

For some time, with the objective of obtaining energy or new raw materials for the chemical industry, we have been studying ways of maximizing the recovery of carbohydrates from agricultural wastes, by recovering the three main fractions through a three-stages process: extraction of soluble sugars, pentosan hydrolysis and lignocellulose hydrolysis.

With this process, the pentoses from the second stage could be used as raw materials for chemical derivatives, while the hexose-rich broths could be utilized mainly for the production of fuel alcohol. This process could be suitable in small-scale industries; it reduces to an important extent the degradation of sugars and the energy consumption and does not need expensive autoclaves.

Stage one consists in the extraction of soluble sugars which are present in important amounts in some wastes (García Breijo & Primo, 1986; Gil, 1988).

In this paper the results of experiments on the second stage in order to optimize the hydrolysis of corn cobs for pentose production are described. The production of xylose, xylitol and trioxyglutaric acid from crude extracts and some technical properties of the products have also been studied.

METHODS

Substrate waste

Corn cobs of RX90 cultivar were extracted with water, dried and ground through 2-mm mesh (USA-Standard, ASTM, E-11-611). The meal was percolated with warm water (60°C) and the soluble components were extracted (soluble sugars, salts, etc.). Pentosan content of the raw dry material was 31·8% and that of the dry water-extracted material was 34·7%.

Methods of analysis

The reducing compounds were determined according to the AOAC (1980) method number 31 052, which is based on the Schaffer–Somogyi procedure (1932).

The fermentable sugars were determined according to the AOAC (1980) method number 31 086, which is based on a selective fermentation using a suitable test.

The AOAC (1965) method number 43 021 was used to determine pentoses, pentosans and furfural.

Pentosan hydrolysis

Glass columns (8 × 180 cm), jacketed for heating, were used. The process was developed in two phases. The wet wastes obtained from the previous water extraction were placed in the columns and sulfuric acid was introduced from the bottom. Concentration of 6, 9 or 12% was obtained at the liquid phase; the waste became fully covered at volumes of 20/80 (g of dry waste/ml diluted acid). So as to soak the waste thoroughly, the acid was left in the column for 15 min and the column was then drained (recoveries of acid were about 42% of initial). The wet waste remaining had a solid/liquid ratio of 30/70. It was heated at 100°C for 1·5, 3 or 4 h in order to hydrolyse the pentosans. Sugars in the hydrolysate were removed from the residual solids by recirculating water at 60°C until the sugar concentration stabilized. The solution was drained off and the extraction repeated three times.

The processed damp wastes were compressed and stored until used at the third stage of the general process. The extracts were neutralized with barium hydroxide and filtered.

Determinations carried out on the extracts (crude xylose broth, CXB) and on the residues from the hydrolysis

In extracts were determined: total reducing compounds (hexoses, pentoses plus furfural; initial determinations of hydroxymethylfurfural showed that it was present in negligible proportions); non-fermentable reducing compounds (the fermentable sugars are the difference between the total reducing compounds and nonfermentable reducing compounds); free furfural by neutral distillation; pentoses plus free furfural by acid distillation; pentoses in the extracts by difference.

In residues were determined: pentosans in the initial water extracted waste; non-hydrolysed pentosans in the waste from acid hydrolysis;

hydrolysed pentosans by difference. The amount of pentoses destroyed was calculated by the difference between the hydrolysed pentosans and pentoses in the extract.

Total reducing compounds, non-fermentable reducing compounds, and fermentable-sugar values are given as glucose. Pentoses in the broths, destroyed pentoses, and pentosans in the water-extracted material and in the hydrolysed material are given as xylose.

Purification of crude xylose broths, CXB

The acid solution from hydrolysis was neutralized with barita to pH 5·0, and filtered. The CXB was passed through two columns: acid column, A, Dowex HCR-S (150×5 cm); and basic column, B, Dowex SBR-P (150×7 cm). The flow was kept at 20 ml min^{-1}. The regeneration of column A was performed with 9·5% H_2SO_4 and a 1/1 ratio of vol. acid/vol. resin. The regeneration of column B was performed with 12% NaOH and a 2/1 ratio of vol. base/vol. resin.

Samples were taken periodically from the outlet of every column and pH and conductivity were determined. The xylose was crystallized by concentrating the deionized broths under vacuum, to 65° Brix at 50°C, seeding some crystals into the concentrate and letting it cool.

Catalytic reduction

Xylitol solutions with some sorbitol were obtained directly by catalytic hydrogenation of deionized xylose broth (DXB).

Hydrogenation was performed with Ni-Raney catalyst in an agitated autoclave (Prolabo N-3702) which can reach a pressure of 100 atm. The DXB was concentrated down to 25% xylose and NaOH added to pH 9·0–10·0. Several different pressures and reaction times were tested. Temperature was kept at 25°–35°C. The percentage of hydrogenation was determined by the decrease of the reducing power and by titrating xylitol plus sorbitol by the AOAC method number 20 151 (1980). Hydrogenation of crystallized xylose was carried out under the same conditions.

Viscosity, hygroscopicity and humidity-exchange rate were determined in the hydrogenated deionized broth (HDB) and were compared with those of sorbitol. Humidity-exchange measurements were conducted as described previously by Houston (1952). Each product was placed on a sensor hanging inside a closed chamber at constant humidity and with a mechanism which allowed consecutive weighing in the same chamber. The desired air moisture was achieved by saturated salts solutions maintained at 20°C.

Oxidation of the crude xylose broth, CXB

In order to produce an economic industrial sequestering agent, a process was developed for the direct oxidation of the hydrolysis broths, which were neutralized with barita and used without any other purification. Neutralized and filtered broths were concentrated to 50% xylose, 100 ml of this concentrate was mixed with 50 ml of HNO_3 ($d = 1.495$) in a flask placed in cold water. A small amount of this mixture was put into a reactor and thermostatically heated at 60°C. When the nitrous vapors decreased, the remaining mixture was added slowly, and the reactor maintained at 60°C for 2 h and subsequently at 70°C for 1 h.

Crystalline xylose was oxidized by the same procedure; 100 g of xylose was dissolved in 150 ml of nitric acid ($d = 1.38$). Mixtures of trioxyglutaric acid and xylonic acid were obtained. The proportions of each were determined by fractional precipitation with calcium acetate and by potentiometry of the fractions with K_2MnO_4 (Primo *et al.*, 1961).

Measurement of the sequestering power of crude oxidized broths, COB

100 ml of the liquid product of oxidation was neutralized with NaOH and diluted to 1 litre with distilled water; after adding 3 g pure NaOH, 100 ml was removed and 5 ml of 1% sodium oxalate added. A solution (6%) of calcium acetate was added from a burette until a precipitate of calcium oxalate appeared. Results were given as g Ca^{2+}/100 ml of COB (Primo *et al.*, 1962).

The Fe^{3+} sequestering power was determined by adding, to the diluted solution, 1% $FeCl_3$ and 2% NaOH alternately. When a precipitate of $Fe(OH)_3$ appeared, the amount of Fe^{3+} added was measured.

RESULTS AND DISCUSSION

Pentosan hydrolysis

Table 1 shows the results obtained in the mild hydrolysis of pentosans expressed as percentage of the raw dry material and as percentage of total pentosans in the waste. Under the most extreme of the tested conditions (12% acid and 3 h heating) 95% (30% r.d.m.) of the pentosans were hydrolysed. Under the mildest conditions (6% acid, 3 h) 81% t.p. was hydrolysed (25·8% r.d.m.). However, with the strongest conditions, there was a high degradation of pentoses to furfural (38% t.p.).

TABLE 1
Results Obtained in the Hydrolysis of Pentosans in Waste Corn Cobs

Fraction[a]	Conditions of analyses														
	Acid 12% 3 h			Acid 12% 1·5 h			Acid 9% 3 h			Acid 6% 4 h			Acid 6% 3 h		
	% rdm	%	% tp	% rdm	%	% tp	% rdm	%	% tp	% rdm	%	% tp	% rdm	%	% tp
1. Total pentosans in the water-extracted waste:	31·8 ± 0·9	(2·8)	100·0	31·8 ± 0·9	(2·8)	100·0	31·8 ± 0·9	(2·8)	100·0	31·8 ± 0·9	(2·8)	100·0	31·8 ± 0·9	(2·8)	100·0
2. Unhydrolysed pentosan remaining:	1·80 ± 0·08	(4·4)	5·7	6·01 ± 0·13	(2·2)	18·9	3·53 ± 0·04	(1·0)	11·1	3·3 ± 0·04	(1·0)	12·4	5·71 ± 0·14	(2·5)	18·0
3. Pentosan hydrolysed:	30·0 ± 0·7	(2·3)	94·5	25·8 ± 0·9	(3·5)	81·8	28·3 ± 0·3	(1·1)	89·0	27·9 ± 0·6	(2·2)	87·9	26·1 ± 0·4	(1·5)	82·1
4. Pentoses in the hydrolysate:	18·4 ± 0·4	(1·6)	62·0	17·6 ± 0·4	(2·3)	68·3	19·9 ± 0·1	(0·6)	66·9	18·6 ± 0·7	(3·8)	66·7	18·0 ± 0·4	(2·2)	69·1
5. Pentoses destroyed:	11·4 ± 0·3	(2·6)	38·0	8·2 ± 0·1	(1·0)	31·7	9·37 ± 0·06	(0·6)	31·7	9·3 ± 0·6	(6·4)	33·3	8·1 ± 0·4	(4·9)	30·9
6. Total reducing compounds in the hydrolysate:	22·6 ± 0·5	(2·2)	70·3	20·4 ± 0·8	(3·9)	64·3	23·2 ± 0·7	(3·0)	73·1	21·9 ± 0·4	(1·8)	69·0	22·0 ± 0·5	(2·3)	69·3
7. Non-fermentable reducing compounds in the hydrolysate:	18·8 ± 0·3	(1·6)	59·2	17·9 ± 0·5	(2·8)	56·4	19·43 ± 0·12	(0·6)	61·2	19·1 ± 0·7	(3·7)	60·2	18·4 ± 0·4	(2·2)	57·9
8. Fermentable sugars in the hydrolysate:	3·8 ± 0·3	(7·9)	12·0	2·5 ± 0·2	(8·0)	7·9	3·8 ± 0·2	(5·3)	12·0	2·80 ± 0·12	(4·3)	8·8	3·6 ± 0·2	(5·6)	11·3

[a] Fractions 1 to 5 are given as xylose: fractions 6 to 8 as glucose. The values are an average of 6 analyses and each one is accompanied by interval of confidence ($P = 0.05$) and the variability coefficient (in brackets). Two operations of hydrolysis were done for each condition, with 3 measurements each.

rdm, Raw dry material.

tp, Total pentoses in rdm.

In intermediate conditions (9% sulfuric acid and 3 h heating) the hydrolysis and the degradation in the process produces a high yield. Under these conditions, 89% of pentosans are hydrolysed (28% r.d.m.); 33% t.p. are degraded (9% r.d.m.); and 67% t.p. are recovered in the broth (20% r.d.m.). These conditions are only marginally better than the others. All the conditions tested, including the mildest, produced a significant degradation of pentoses.

Pentoses were recovered by recirculation of warm water (60°C through the column. After three extractions 96% of the sugars produced in the hydrolysis were recovered. Using five columns in counter-current a concentration of 10% of xylose in the watery extract (CXB) was obtained.

Furfural can be recovered as a valuable by-product. There is a proportion of glucose in the extract (15–20% with respect to pentoses) and minimum amounts of other hexoses and pentoses detectable by thin-layer chromatography (data not shown). The hexoses are harmful for the crystallization of pure xylose but not for other industrial applications.

Under the most stringent conditions the amount of pentosans remaining in the hydrolyzed waste is low (1·8% r.d.m.; 5·7% t.p.), but with the selected ones the amount is 3·5% r.d.m. (11% t.p.).

The process could be scaled up by means of a series of 10–15 jacketed, vertical, reactors working at atmospheric pressure. Some would operate in the phase of hydrolysis, others in the phase of extraction and recharge.

Column deionization of CXB and xylose crystallization

The crude sugar solution used had the following characteristics: total reducing sugars, 3·5%; pentoses, 3·1%; conductivity, 16 mmhos; and pH = 5·0. After deionizing, the solution had a conductivity of 4·5 nmhos and the pH was 5·8.

Xylose crystallization gave the following yields: first crystallization, 40% second crystallization (mother liquor), 31%. First crystals had 98% xylose and 0·5% ash. By thin-layer chromatography, arabinose and glucose impurities could be detected (data not shown).

Production of xylitol directly from the deionized broths (DXB); conditions and yields for hydrogenation; properties of the hydrogenated product

Figure 1 shows the yields from the hydrogenation of DXB at different pressures and times (temperature 30°C, 10% catalyst). With 10 h and 75 atm. 98% hydrogenation is reached. The hydrogenation of the non-deionized broths (CXB) gives very low yields. Using crystallized xylose at 25 atm. and 3 h, 98% was hydrogenated (data not shown). The xylitol solutions
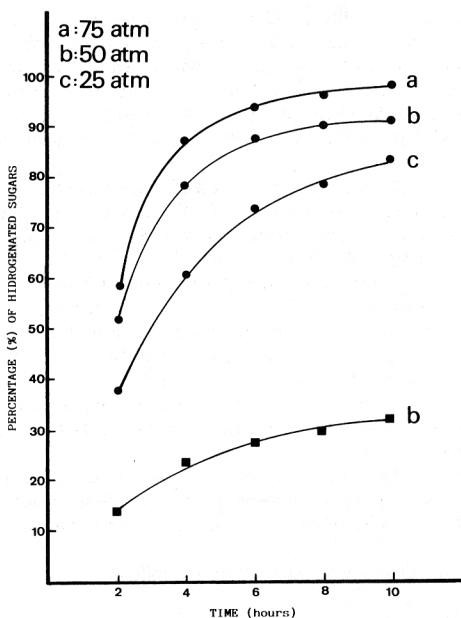
Fig. 1. Yields from hydrogenation of deionized xylose broths (DXB). Solutions of xylitol obtained directly from the deionized broths (●—●). Experiments at different pressures and reaction times, 10% catalyst, 30°C. (■—■, hydrogenation of non-deionized broths, CXB).

contained some sorbitol in accordance with the glucose content of the deionized broths.

Figures 2 and 3 show variations in viscosity against concentration and temperature for the solutions obtained by hydrogenation of deionized broths (HDB). Data are compared with those of sorbitol and xylitol. Curves of HDB are similar to those of sorbitol solutions and higher than those of xylitol, due mainly to other hydrogenated sugars in the HDB.

Figures 4 and 5 show the hygroscopic equilibrium and humidity-exchange rate curves for HDB, xylitol and sorbitol. With relative humidities lower than 85% the HDB retains more water than xylitol and sorbitol and at higher relative humidities the xylitol is more hydroscopic.

The rate of HDB to absorb and lose water is halfway between those of solutions of xylitol and sorbitol, although the differences are small.
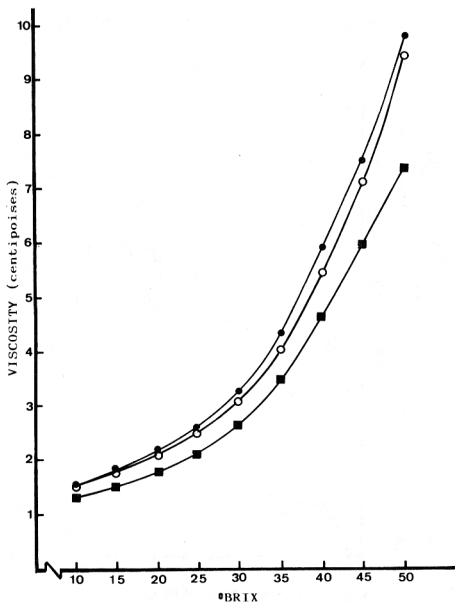
Fig. 2. Relationship between viscosity (in centipoises) and concentration (in °Brix) of (○—○) HDB as compared with those of (■—■) xylitol and (●—●) sorbitol, at 20°C. (Maximum interval of confidence ±0·2). Temperature, 30°C.
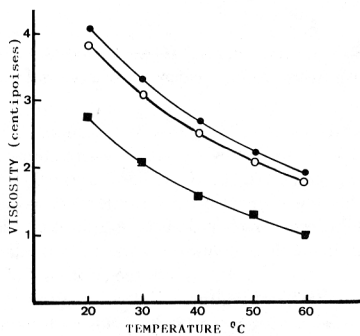

Fig. 3. Viscosity (cp) for concentrated solutions (30° Brix) of (○—○) HDB as compared with (■—■) xylitol and (●—●) sorbitol at different temperatures. (Maximum interval of confidence ±2·5).
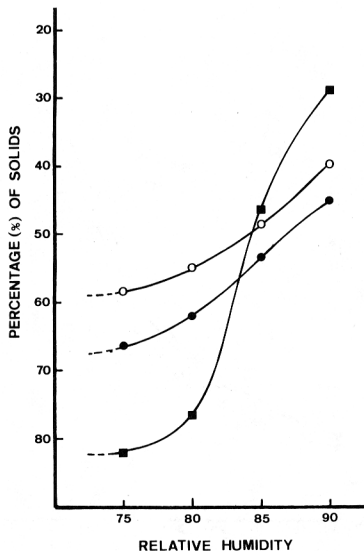
Fig. 4. Relationship between % solids and relative humidity in air (%) for concentrated solutions of (○—○) HDB, (■—■) xylitol and (●—●) sorbitol. (Maximum interval of confidence ± 2·5). Temperature, 25°C.

Production of trioxyglutaric acid (TOGA) by oxidation of non-deionized xylose broth (CXB); Sequestering properties of the crude oxidized product

The CXB was concentrated to 50% xylose and oxidized. On direct oxidation of concentrated CXB the following yields were obtained (in g/litre of concentrated broth): oxalic acid, 6; TOGA, 340; and xylonic acid, 70. Values of TOGA include some saccharic acid formed by oxidation of glucose present in the CXB. Between 15 and 20% of xylose was lost as CO_2. The sequestering power, in alkaline medium, for the crude oxidized broths (COB) was 22–24 g of Ca^{2+}/100 g TOG plus xylonic content (83% TOGA + 17% xylonic) at NaOH concentrations of 3% (around 10 g Ca^{2+}/100 ml concentrated CXB). When concentrations of NaOH were lower than 1% or higher than 5%, sequestering power decreased drastically. Ferric sequestering power was 25–26 g Fe^{3+}/100 g TOG plus xylonic content (around 11 g of
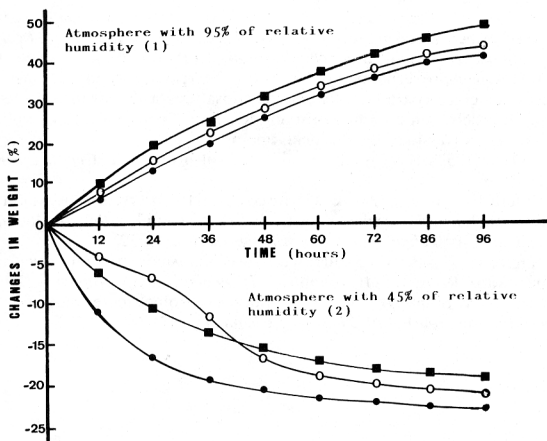
Fig. 5. Changes in water contents for (○—○) HDB, (■—■) xylitol and (●—●) sorbitol with an initial concentration of 50° Brix and atmospheres with 95% and 45% of relative humidity. (1) Maximum interval of confidence 3·0; (2) maximum interval of confidence ± 2·0. Temperature, 25°C.

$Fe^{3+}/100$ ml concentrated CXB) at pH 8; at pH 5·6 the sequestering power was low.

The sequestering power of pure TOGA in the same conditions was 30–35 g Ca^{2+} and 35–38 g $Fe^{3+}/100$ g.

ACKNOWLEDGEMENTS

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