

## HYDROLYSIS OF CORN-COB LIGNOCELLULOSIC RESIDUE FROM PENTOSE PREPARATION

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### Abstract

The use of agricultural wastes for energy and intermediary chemicals has economic, ecological and strategic interest. The strong hydrolysis of the lignocellulose residue remaining after mild hydrolysis of pentosans from corn-cobs is described. The process avoids the use of autoclaves by pressing the acidified lignocellulosic mass at a moderate temperature. The effects of different variables on the yields were studied. Under the best conditions tested, 65% of polymeric potential sugars in the residue were recovered as fermentable sugars in the extract.

This is the last stage of a complete procedure set up to obtain maximum yields of carbohydrates from agricultural wastes (soluble sugars, pentoses for chemicals, and glucose from cellulose for fermentations).

**Key words:** Corn-cobs, sugars from chemicals, hydrolysis, lignocellulose.

### INTRODUCTION

The use of biomass as a source of energy and intermediary materials for the chemical industry is a possible alternative for petroleum and could decrease the environmental pollution.

The annual production of biomass represents 10 times the annual world consumption of energy: the agricultural raw materials for energy and chemical applications are specific crops or wastes. The use of specific crops such as sugar cane, corn and other crops, to obtain fuel alcohol has been problematic because of its possible effect on the food supplies for the growing world population. Therefore, the exploitation of waste seems the best way.

Most of the processes used are hydrolytic, and the resistance of the lignocellulosic materials is an important problem. Most of the hydrolysis processes for wood and lignocellulosic-residues use low concentra-

tions of acids and high pressures and temperatures, in expensive autoclaves (Scholler, Meunier, Madison and other processes developed in the former Soviet Union). Other processes use open reactors and concentrated acids, mainly HCl (Rhein, Bergius, Udio-Rhein, Hereng, Woguchi-Chisso, Chaloo processes). The Hokkaido and Nikon-Mokuzai-Kagaku processes use 80% H<sub>2</sub>SO<sub>4</sub>. The use of HF or HNO<sub>3</sub> has also been proposed. Some authors have published reviews of these methods (Dupui, 1980; Goldstein, 1981; 1983). The enzymatic hydrolysis of cellulose has received more attention in recent years (Wald *et al.*, 1984; Wilke *et al.*, 1984; Beltrame *et al.*, 1984; Gusakov & Sinitsyn, 1987; Vallauder & Eriksson, 1990).

The corn crop produces stalks and cobs, amounting to 10 ton ha<sup>-1</sup>. In previous papers we reported on the potential pentose and hexose content of different wastes: corn-cobs and stalks, rice straw, wine shoots, etc. (García-Breijo & Primo-Yúfera, 1986; 1987; 1989).

An industrial process for the optimum recovery of these potential sugars must meet some requirements: to reduce the degradation of sugars during the different operations as much as possible; to avoid the use of expensive autoclaves, resistant to acids at a high temperature and pressure; to use uncomplicated technology suitable for small-scale industries which could be adapted to rural areas and thus avoid the long-distance transport of wastes.

In order to approach these conditions and to recover the different fractions of carbohydrates, a process was examined in three phases: (1) extraction of soluble sugars; (2) mild hydrolysis of the pentosans and extraction of hydrolyzed pentoses and (3) strong hydrolysis of the lignocellulosic residue and extraction of sugars obtained.

In a previous paper, Gil-Tortosa *et al.* (1990) reported the conditions for the extraction of soluble sugars, hydrolysis of the pentosans, purification of xylose and production of useful derivatives (humectants, sequestering, detergent and emulgent agents). In this paper, the hydrolytic process for the lignocellulosic residue derived from the second phase, above, was examined.

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## METHODS

### Hydrolysis

Air dried corn-cobs (Rx90 cultivar) were ground to 2 mm-particle size, extracted with water and the solid residue submitted to mild hydrolysis according to the previously-established methods (Gil-Tortosa *et al.*, 1990). In the washed and pressed residue from the hydrolysis, the water content was determined in order to calculate the solid-liquid ratio in every process stage.

The process for the strong acid hydrolysis of the lignocellulosic residues had three stages:

(a) Acidification of the moist mild hydrolysis residue with 98% sulfuric acid, added to obtain the calculated concentrations (4, 6, 8 and 10%) in the aqueous phase. Then the material was dried at 70°C until the concentration of  $H_2SO_4$  in the liquid phase reached 72%.

(b) Addition to the dry material of 80, 85, 90 and 95% sulfuric acid to reach a solid-liquid ratio of 1:0.5, and mixing. The mass was then pressed in a hydraulic press at 30 bar and at a moderate temperature, in order to make the acid penetrate into the cellulosic structure. The variables considered in this stage were: concentration of the added acid: 80, 85, 90 and 95%; pressing temperature: 40 and 50°C; pressing time: 5, 10 and 15 min.

(c) Water was added to the material to dilute the acid to 8% in the aqueous phase and the suspension was heated at 105°C for 3 h, at atmospheric pressure to hydrolyze the previously-formed oligomers.

The final, acidic, sugar solution (acid broth), after filtration, was neutralized with barium hydroxide and analyzed. The solid residue retained in the filter was dried at 80°C for 6 h for the dry weight determination.

### Analytical methods

The reducing compounds in the final solution of hydrolyzed sugars were determined by the 31052 method (AOAC, 1980), which is based on the Schaffer-Somogyi procedure (1932).

The fermentable sugars were determined by the 31086 method (AOAC, 1980), based on selective fermentation with *S. cerevisiae*.

The polymerized potential sugars in the lignocellulosic residue were determined by the Dunning and Dallas method (1949).

The carbohydrates of the lignocellulosic residue hydrolyzed during the strong hydrolysis process were calculated through the difference between the dry weight of the residue, before and after the hydrolysis (a + b + c stages).

Hydrolyzed sugars, total reducing compounds and fermentable-sugars values are given as glucose and expressed as percentage of the initial dry, raw corn-cobs (r.d.c.c.) or respective to the polymerized sugars in the lignocellulosic material remaining from the pentosan hydrolysis after the mild hydrolysis above (r.p.s.).

Each value is the mean of two hydrolysis experiments and three analytical determinations.

## RESULTS AND DISCUSSION

### Stage (a)

The lignocellulosic residue from the mild hydrolysis contained 3.5% pentosans and 38% total polymerized potential sugars (dry matter basis).

The variable assayed in stage (a) was the sulfuric acid concentration in the liquid phase (4, 6, 8 and 10%). After stage (a), the hydrolysis was completed by a second stage (b) run under the following standard conditions: concentration of  $H_2SO_4$  added, 90%; pressing time, 10 min; pressing temperature, 40°C. The final analyses, dependent on the variations in stage (a), are given in Table 1.

The amount of hydrolyzed sugars increased with the acid concentration, but the fermentable sugars obtained reached a maximum at 8% sulfuric acid concentration (18.7% r.d.c.c. or 44.4% r.p.s.). Higher concentrations gave lower yields because of the greater degradation of the sugars. When the acid concentration increased from 8% to 10%, the sugar degradation was doubled (Table 1).

### Stage (b)

According to the previous results, stage (a) was standardized at 8%  $H_2SO_4$  while the acid concentration and pressing temperature and time were varied in stage (b). Table 2 shows the results obtained.

The hydrolysis of sugars increased with increases in each of the three variables tested. The greatest hydrolysis was obtained with 95% acid and 15 min pressing time at 50°C (31% r.d.c.c., or 86% r.p.s.). The results mean that the pressing stage has a decisive influence on the hydrolysis of the lignocellulosic residue. The most important variable was the acid concentration; when it was increased from 80 to 95% the hydrolysis of sugars doubled. The second main variable was the pressing time, whose influence was higher at greater acid concentration and pressing temperature.

An important fraction of the sugars from the strong hydrolysis was degraded during the process. Under the strongest conditions, this fraction amounted to 7.7% r.d.c.c. (21.40% r.p.s.) (given as glucose: HS-FS; Table 2). A part was found in the final aqueous solution of stage (c), as non-fermentable reducers; it was mainly hydroxymethylfurfural and, in a minor proportion, furfural. Another part was lost with the vapours produced in the process, or oxidized.

The most important compounds for obtaining fuel ethanol are the fermentable sugars in the final solution (FS). Under the strongest conditions the yield of FS was 63% r.p.s., or 23% r.d.c.c.; under the mildest conditions, it was 25% and 9% respectively. The fermentable sugars: hydrolyzed sugars (FS:HS) ratio was greatest under the mildest conditions (0.778) and smallest under the strongest ones (0.753), but the decrease in the FS:HS ratio from the mildest to the strongest con-

Table 1. Effect of variables on the first stage, with hydrolysis completed by standard conditions in stage (b)

Acid concentration <sup>a</sup>	H.S. <sup>b</sup>		R.C. <sup>c</sup>		F.S. <sup>d</sup>	
	% r.d.c.c. <sup>e</sup>	% r.p.s. <sup>f</sup>	% r.d.c.c.	% r.p.s.	% r.d.c.c.	% r.p.s.
4	19.7 ± 0.4(2.0%)	46.8	16.8 ± 0.6(3.6%)	39.9	15.2 ± 0.2(1.3%)	36.1
6	22.6 ± 0.6(2.7%)	54.2	19.5 ± 0.3(1.6%)	46.3	17.8 ± 0.4(2.2%)	42.3
8	23.7 ± 0.5(2.1%)	59.5	21.4 ± 0.4(1.9%)	50.8	18.7 ± 0.3(1.6%)	44.4
10	25.8 ± 0.5(1.9%)	67.8	19.1 ± 0.2(1.0%)	45.4	16.7 ± 0.4(2.4%)	39.7

<sup>a</sup>Percentage in the aqueous phase.<sup>b</sup>Hydrolyzed sugars.<sup>c</sup>Total reducing compounds in the sugar solution (final broth).<sup>d</sup>Fermentable sugars in the sugar solution (final broth).<sup>e</sup>Respective to raw dry initial corn cob weight.<sup>f</sup>Respective to polymerized sugars in the lignocellulosic residue.

Values given as glucose.

Table 2. Effect of variables on the second stage

Acid <sup>a</sup> (%)	Temp. <sup>b</sup> (°C)		Pressing time					
			5 min		10 min		15 min	
			% r.d.c.c. <sup>f</sup>	% r.p.s. <sup>g</sup>	% r.d.c.c.	% r.p.s.	% r.d.c.c.	% r.p.s.
80	40	HS <sup>c</sup>	11.7 ± 0.4(3.4%)	32.5	12.2 ± 0.2(1.6%)	33.9	14.5 ± 0.3(2.1%)	40.2
		RC <sup>d</sup>	11.3 ± 0.3(2.7%)	31.4	11.9 ± 0.4(3.4%)	33.0	13.5 ± 0.5(3.2%)	37.6
		FS <sup>e</sup>	9.1 ± 0.4(4.4%)	25.3	9.4 ± 0.6(6.4%)	26.1	11.1 ± 0.4(3.6%)	30.9
80	50	HS	12.0 ± 0.3(2.5%)	33.4	13.7 ± 0.3(2.2%)	38.1	15.7 ± 0.5(3.2%)	43.7
		RC	11.4 ± 0.4(3.5%)	31.7	12.8 ± 0.5(3.9%)	35.5	14.2 ± 0.2(1.3%)	39.5
		FS	9.3 ± 0.4(4.3%)	25.9	10.5 ± 0.2(1.7%)	29.3	12.0 ± 0.1(0.8%)	33.4
85	40	HS	13.2 ± 0.6(4.6%)	36.7	15.3 ± 0.4(2.6%)	42.5	17.7 ± 0.6(3.4%)	49.2
		RC	12.2 ± 0.5(4.1%)	33.8	13.8 ± 0.4(2.9%)	38.3	15.8 ± 0.4(2.5%)	43.9
		FS	10.2 ± 0.1(1.1%)	28.3	11.7 ± 0.4(3.4%)	32.5	13.5 ± 0.4(2.9%)	37.5
85	50	HS	18.9 ± 0.2(1.1%)	52.5	20.2 ± 0.3(1.5%)	56.2	23.0 ± 0.5(2.2%)	63.9
		RC	16.5 ± 0.6(3.6%)	46.0	17.5 ± 0.7(4.0%)	48.7	19.6 ± 0.4(2.0%)	54.6
		FS	14.5 ± 0.1(0.7%)	40.4	15.4 ± 0.2(1.3%)	42.9	17.4 ± 0.4(2.3%)	48.5
90	40	HS	19.7 ± 0.3(1.5%)	54.8	22.4 ± 0.2(0.9%)	62.4	24.8 ± 0.5(2%)	68.0
		RC	17.2 ± 0.7(4.1%)	47.7	19.1 ± 0.4(2.1%)	53.0	21.5 ± 0.7(3.3%)	59.8
		FS	15.2 ± 0.3(0.3%)	42.2	17.1 ± 0.4(2.3%)	47.5	18.8 ± 0.3(1.6%)	52.3
90	50	HS	22.7 ± 0.3(1.3%)	63.1	23.8 ± 0.6(2.5%)	66.2	27.1 ± 0.7(2.6%)	75.2
		RC	19.9 ± 0.6(2.8%)	55.3	20.5 ± 0.5(2.4%)	56.8	22.9 ± 0.8(3.4%)	63.6
		FS	17.4 ± 0.6(3.5%)	48.4	18.1 ± 0.4(2.2%)	50.2	20.5 ± 0.7(3.4%)	56.9
95	40	HS	22.5 ± 0.4(1.8%)	62.6	24.6 ± 0.2(0.8%)	68.5	27.8 ± 0.3(1.0%)	77.2
		RC	19.5 ± 0.2(1.0%)	54.2	21.3 ± 0.8(3.8%)	59.2	23.5 ± 0.9(3.8%)	65.6
		FS	17.2 ± 0.5(2.9%)	47.8	18.7 ± 0.9(4.8%)	52.0	20.9 ± 0.8(3.8%)	58.3
95	50	HS	23.5 ± 0.7(3.0%)	65.4	26.0 ± 0.5(1.9%)	72.2	31.2 ± 0.8(2.6%)	86.7
		RC	20.6 ± 0.9(4.4%)	57.0	22.1 ± 0.6(2.7%)	61.4	25.6 ± 0.4(1.6%)	71.1
		FS	17.9 ± 0.4(2.2%)	49.5	19.7 ± 0.7(3.6%)	54.7	23.5 ± 0.8(3.4%)	65.3

<sup>a</sup>Concentration of acid added.<sup>b</sup>Pressing temperature.<sup>c</sup>Hydrolyzed sugars.<sup>d</sup>Total reducing compounds in the sugar solution (final broth).<sup>e</sup>Fermentable sugars in the final broth.<sup>f</sup>Respective to raw dry initial corn cob weight.<sup>g</sup>Respective to polymerized sugars in the lignocellulosic residue.

Values given as glucose.

ditions was 3.2%, whereas the increase in fermentable sugars was 158%. The FS concentration in the final broth was higher when the conditions were stronger (2.8% w/v with the mildest and 6.9% with the strongest conditions).

When the acid sugar solution from the last operation of stage (b) (sugar broth), was reused with new pressed material in stage (c), in a counterflow process, the sugar concentration in the final broth increased to 12.5%, but an excessive amount of sugars was degraded.

The process could fit the requirements of small plants covering the waste productions of limited rural areas where corn is grown.

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