

Production of Furfural by Acid Hydrolysis of Corncobs

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ABSTRACT

Hydrolysis of corncobs for producing furfural was carried out in a pressurized batch reactor using superheated water and diluted sulphuric acid as catalyst. The range of experimental conditions was $T = 140\text{--}200^\circ\text{C}$ and $P = 350\text{--}1550\text{ kPa}$. Yields of furfural are reported as a function of reaction temperature, particle size, acid concentration and liquid/solid ratio. Attention has been focused on the solid residue remaining after the hydrolysis process, so that it can be further used as a humic fertilizer after oxiammoniation treatment.

Key words: furfural, corn-cobs, acid hydrolysis.

1 INTRODUCTION

Agricultural and forestry wastes have long been recognized as feedstocks for the production of useful chemicals. Processes of biomass conversion are specially suited for developing countries, but for efficiency and economy of product recovery integrated processing plants, which can handle different feedstocks and make an efficient use of the process residues, are required.

The production of furfural from agro-wastes has been known since 1830 when Döbereiner discovered furfural¹ and has been extensively reported in the literature.^{2–4} Furfural is produced by hydrolysis to xylose of pentosans contained in wastes such as corncobs, rice hulls, bagasse, oat hulls, etc., followed by dehydration of xylose to furfural.^{5–7} Among the most common catalysts employed in these reactions are acids (e.g. sulphuric, hydrochloric and phosphoric) and salts (e.g. aluminum sulphate and calcium and zinc chlorides). Furfural is entrained by steam injected into the reactor and the overhead stream is condensed to form two

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immiscible phases, a water phase containing about 10 wt % of furfural and the organic phase containing about 84 wt % of furfural.² The water phase can be returned to the process or treated by solvent extraction for furfural recovery.⁸ The furfural-rich phase is usually purified by distillation.⁹

The use of corncobs for the production of furfural has been studied by several researchers and large plants are operated around the world.¹⁰⁻¹²

In the digestion process to hydrolyse agricultural or wood wastes a considerable amount of residues are produced, which are partly used as fuel to produce the steam necessary for the process (20 kg vapour kg⁻¹ furfural). The remainder may present a disposal problem. The acidic treatment results in a loss of fibre quality and furthermore the presence of lignin makes this residue unsuitable as a pulp source.

An alternative use of this residue, once furfural has been recovered, is to return it to the soil as a humic fertilizer after the oxiammoniation process, in order to increase its nitrogen content and neutralize the acid retained from the hydrolysis step.^{13,14}

The aim of this work was to study the recovery of furfural from corncobs in a batch reactor using superheated water ($T = 140\text{--}200^\circ\text{C}$, $P = 350\text{--}1550\text{ kPa}$) and sulphuric acid as a catalyst. Yields of furfural have been obtained as a function of temperature, acid concentration and liquid/solid (L/S) ratio (w/w). Attention has been directed not only to obtaining a high yield of furfural, but simultaneously to rendering the solid residue suitable for a further oxiammoniation step. The quality of the residue must be such that the small size of particles and high degradation of the solids (mainly by carbonization) should be minimized.

2 MATERIALS AND METHODS

2.1 Raw material and analytical techniques

Corn cobs collected locally were ground and sieved to obtain fractions of various particle sizes.

The concentration of furfural in the reactor off-gas was determined by gas chromatography (Hewlett-Packard (Palo Alto, California) GC, model 5710A, FI detector) using a 6.35 mm column of Carbowax 20 wt % on Chromosorb AW (80/100 mesh) at a temperature of 130°C and gas flow rates of $1\text{ cm}^3\text{ s}^{-1}$, $0.5\text{ cm}^3\text{ s}^{-1}$ and $5\text{ cm}^3\text{ s}^{-1}$ for H_2 , N_2 and air respectively. 1,4-Dioxane was used as internal standard.

2.2 Experimental procedure

Samples of corncobs (100 g) of various particle sizes ($<5\text{ mm}$) were soaked in a sulphuric acid solution of defined concentration and a particular/liquid ratio, for 10 min at room temperature. The material was thoroughly mixed in order to obtain a uniform slurry.

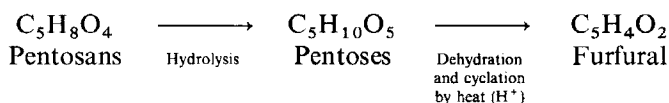
The slurry was then autoclaved in a high-pressure stainless-steel reactor (SOTELEM, Paris) with constant stirring (300 rpm). The reactor had a volume of 3.5 dm^3 and the reaction mixture was heated by circulating thermic oil through the reactor jacket. Temperature control of $\pm 2^\circ\text{C}$ was achieved within a temperature

range of 25–200°C. During the two-hour reaction samples were withdrawn from the vapour stream every 15 min during the first hour and every 30 min during the second hour for furfural analysis.

At the end of the predetermined hydrolysis time, the reactor content was cooled to room temperature for about 20 min and then filtered through a porous ceramic plate. The solid cake so recovered was washed with distilled water until a constant pH was reached in the filtrate, then was dried at 50°C for 12 h. Weight losses and acidity of this residue (by titration with NaOH)¹⁵ were determined.

3 RESULTS AND DISCUSSION

When a dilute mineral acid, such as sulphuric acid, is used as the hydrolysing and dehydrating medium, the formation of furfural from pentosans, present in corncobs, can be described by the following reaction scheme:¹⁶



There are several variables which can be studied in this process; some of the most important are: reaction temperature, particle size of the raw material, catalyst concentration and L/S ratio. Previous experiments showed that high yields of furfural were obtained for sulphuric acid concentrations higher than 0.79 mol dm⁻³, and when reaction temperatures were less than 140°C. However, when superheated water was used in the process, distillate rates were not easily controlled at temperatures less than 140°C. Also, high temperatures and acid concentrations enhanced the degradation of furfural by producing side reactions. As regards the reaction time, a two-hour hydrolysis time was selected in order to avoid side reactions and the increasing amount of fines (particle sizes <0.1 mm) which are produced with longer reaction times.

Analysis of corncobs gave the following results (in wt %): C=48.7, H=5.69, N=0.58, S=0.15 and O=44.9 (the last by difference). The composition of corncobs was determined using a spectrophotometric method¹⁷ for pentosans (32.4 wt %) and by a Soxhlet extraction with alcohol, alcohol–benzene and water. The following results were obtained (wt %):¹⁸ Cathecols–tanins (8.1; alcohol extraction method), resins–waxes–fats (0.22; alcohol–benzene extraction method), lignin (16.4) and extractables (6.0).

3.1 Effect of temperature

Table 1 shows the concentration of furfural in the condensate obtained on reacting corncobs (particle size range 0.084–4 mm) with sulphuric acid (0.079 mol dm⁻³) for a L/S ratio of 20 (w/w) and in the temperature range 150–200°C.

The concentration of furfural in distillates increased at higher reaction temperatures. At 190 and 200°C the maximum yield was observed after relatively short reaction times, due to the fact that furfural was being produced as the temperature reached its maximum value and was being removed in the distillate.

TABLE 1

Furfural Yield (g Furfural Collected 100 g^{-1} Dried Corncobs Treated) and Weight Loss (g Solid Residue 100 g^{-1} Raw Material Treated) in Corncobs as a Function of Hydrolysis Temperature (H_2SO_4 Concentration 0.079 mol dm^{-3})

Temperature ($^{\circ}\text{C}$)	Furfural (wt % dry basis)	Weight loss (wt %)
150	7.8	19.6
160	10.9	22.3
170	10.4	28.6
190	6.5	36.2
200	4.2	39.9

TABLE 2

Furfural Yield and Weight Loss in Corncobs as a Function of Particle Size (H_2SO_4 Concentration 0.079 mol dm^{-3} , Temperature = 180°C)

Size (mm)	Furfural (wt % dry basis)	Weight loss (wt %)
0.5–1.0	13.6	28.2
1.0–2.0	12.9	26.3
2.0–5.0	12.6	23.5
< 5.0	11.0	25.3

The concentrations of furfural achieved were low for each of the reaction temperatures studied here. The highest yield of furfural in condensate was 10.9 wt % based on dried weight of corncobs (that is, g furfural collected from every 100 g of dried corncobs treated) and it was obtained at 160°C . The loss in weight increases as the temperature increases.

3.2 Effect of particle size

Experiments were conducted with samples of four particle size ranges (0.5–1.0, 1.0–2.0, 2.0–5.0 and < 5.0 mm) at 180°C , 0.079 mol dm^{-3} sulphuric acid and a L/S ratio of 15 (w/w). Results are shown in Table 2.

As might be expected, the yield of furfural was greatest from smaller particle sizes, because of the greater surface area per unit volume of the reacting solids. However, more energy is required for the production of smaller particles and the filtration of the final residue is more difficult. With increases in particle size the concentration of furfural in the condensate was lower and the reaction yield decreased. The loss in weight of the solid also decreased slightly with particle size increase, except for the sample size < 5 mm, in which an increase was observed.

3.3 Effect of acid concentration

Preliminary experiments¹⁹ indicated that at low acid concentrations high temperatures are required to obtain a substantial amount of furfural. However, for sulphuric acid concentrations in the range of 0.063 – 0.159 mol dm^{-3} and at 180 –

TABLE 3

Effect of Acid Concentration at Various Temperatures on the Yield of Furfural (g Furfural Collected 100 g⁻¹ Dried Corncobs) in the Condensate and Losses in Weight of Solid

H_2SO_4 concentration (mol dm ⁻³)	Temperature (°C)	Furfural (wt %)	Weight loss (wt %)
0.063	180	10.2	19.9
0.063	200	9.2	26.3
0.063	210	5.5	29.5
0.063	220	4.1	33.6
0.127	180	9.6	21.3
0.127	200	7.1	29.3
0.127	210	6.5	33.3
0.127	220	3.4	36.2
0.159	180	8.7	25.6
0.159	200	4.1	31.2
0.159	210	2.3	34.7
0.159	220	1.3	38.3

L/S ratio, 15 (w/w).

Particle size of ground corncobs, 0.5–4.0 mm.

TABLE 4

Effect of Liquid/Solid Ratio on the Yield of Furfural (wt %)

Liquid/solid ratio (w/w)	H_2SO_4 concentration (mol dm ⁻³)	Furfural (wt %)	Weight loss (wt %)
15	0.063	10.2	19.9
15	0.127	9.6	21.3
15	0.159	8.7	25.6
15	0.400	6.7	27.9
20	0.079	8.1	26.2
20	0.400	5.0	29.3
20	0.794	2.0	32.7
25	0.079	11.5	29.3
25	0.400	5.3	31.4
25	0.794	1.8	36.4

Particle size of ground corncobs, 0.084–3.0 mm.

Temperature, 180°C.

220°C a decrease in the concentration of furfural in the condensate and an increase in the loss in weight as the temperature increases, for a fixed acid concentration, is observed. Results are shown in Table 3.

At high temperatures furfural undergoes side reactions and its degradation to succine anhydride and carbon dioxide may be important.

3.4 Effect of liquid/solid ratio

The liquid/solid ratio (w/w) and hydrolysis time are considered to be important factors in the production of furfural.⁵ Table 4 shows the furfural production per 100 g of dried corncobs and the loss in weight for three liquid/solid ratios and an acid concentration in the range of 0.079–0.79 mol dm⁻³. The effect of L/S ratio on the yield of furfural becomes more important at low acid concentrations. The loss in weight remained within a rather narrow range.

4 CONCLUSIONS

Moderate temperatures and low sulphuric acid concentrations lead to important furfural yields using corncobs as raw material. High temperatures and high mineral acid concentrations damage the hydrolysed residues and decreases furfural yields, due to side reactions. Superheated water improves the economy of the process and particle size and liquid/solid ratio are important for obtaining a constant rate of distillate and avoiding hydrolysed waste carbonization. After the hydrolysis, solid residues can still be processed to obtain nitrogen-enriched fertilizers by means of an oxiammoniation reaction.

REFERENCES

1. Hitchcock, L. B. & Duffey, H., Commercial production of furfural in its twenty-fifth year. *Chem. Eng. Progr.*, **44** (1948) 669–74.
2. Dunlop, A. P. & Peters, F. N., *The Furans*. Reinhold, New York, 1953.
3. Singh, A., Das, K. & Sharma, K. D., Integrated process for the production of xylose, furfural and glucose from bagasse by two-step acid hydrolysis. *Ind. Eng. Chem. Prod. Res. Devl*, **23** (1984) 257–62.
4. Dunlop, A. P., Furfural. In *Kirk-Othmer Encyclopaedia of Chemistry*, Vol. 11, John Wiley & Sons, New York, 1966, pp. 501–10.
5. Mital, J., Studies in the preparation of furfural from *Zea mays* stem pith. *IPPTA*, **14** (1977) 209–17.
6. Strzepek, A., Continuous cellulose saccharification. USA Patent 80 01 097, 1981.
7. Kiminskii, K., Degrading a polysaccharide-containing raw material by acid hydrolysis. German Patent 2 54 119, 1976.
8. Croker, J. R. & Bowrey, R. G., Liquid extractives of furfural from aqueous solution. *Ind. Eng. Chem. Fundam.*, **23** (1984) 480–4.
9. Aly, G. & Zacchi, G., Simulation and design of distillation units for treatment of sulfite pulping condensates to recover methanol and furfural. *Can. J. Chem. Eng.*, **57** (1979) 316–20.
10. Pillai, M. K. S. & Panicker, P. K. N., Pilot-plant studies on manufactures of furfural from cane bagasse. *Chem. Age India*, **30** (1979) 733–5.
11. Kin, Z., Furfural by-product of pulp industry. *Przegląd. Papier.*, **21** (1965) 157–61.
12. Timell, T. E., Wood hemicelluloses. *Adv. Carbohydr. Chem.*, **20** (1965) 247–302.
13. Goldstein, I. S., *Organic Chemicals from Biomass*. CRC Press, Florida, 1981.
14. Riera, F. A., Alvarez, R. & Coca, J., Aprovechamiento integral de residuos agrícolas. Procesos para la obtención de furfural y su interés como materia prima. *Ing. Quím*, **3** (1987) 135–42.

15. Toynbee, D. A. & Fleming, A. K., Air oxidation of subbituminous coal. *Fuel*, **42** (1963) 379–87.
16. Nee, C. I. & Yee, W. F., Hydrolysis of pentosans in bagasse pith. *J. Appl. Chem. Biotechnol.*, **26** (1976) 283–7.
17. Technical Association of the Pulp and Paper Industry (TAPPI) Standard Methods, Pentosans in pulp. T223, Atlanta, Georgia, 1963.
18. Technical Association of the Pulp and Paper Industry (TAPPI) Standard Methods, Acid-insoluble lignin in wood pulp. T222, Atlanta, Georgia, 1954.
19. El-Ashmawy, A. E. & El-Kalyoubi, S., Hemicelluloses of bagasse and rice straw. *Egypt. J. Chem.*, **18** (1976) 149–56.