FURFURAL PRODUCTION AND KINETICS OF PENTOSANS HYDROLYSIS IN CORN COBS

ALTAF H. BASTA and HOUSSNI EL-SAIED

Cellulose and Paper Dept., National Research Centre, Dokki, Cairo, EGYPT

Received December 4, 1998

The highest furfural yield in the corn cob hydrolysate was of 84.93% (based on pentosans of corn cobs), using 3 % HCl (based on corn cobs) as a catalyst, at a raw material: aqueous acid ratio of 6/1 and temperature of 170°, for 30 minutes. The polynominal correlations of the hydrolysis parameters with the yield of furfural were determined. The yield of furfural in the corn cob hydrolysate was higher than in other agricultural materials such as corn stalks, corn hulls, bagasse and rice hulls. Generally, the maximum efficiency of furfural extracted from the hydrolysate was obtained by using chloroform as an organic solvent, either individually or as a mixture with diethyl ether in a ratio of 10% to 90%, compared to the conventional process using ether solvent. The purity of the produced furfural was determined by IR- and Mass- Spectra. The maximum yield of the extracted furfural was of 49.93 %, based on pentosans of corn cobs.

The kinetic parameters of pentosan hydrolysis using different catalysts indicated that the hemicellulose of corn cobs is more easily hydrolyzed if using HCl instead of H_2SO_4, followed by $Al_2(SO_4)_3$.

Key words: furfural, corn cobs, hydrolysis, pentosans.

INTRODUCTION

Furfural (2-furaldehyde) and its derivatives have a wide range of utilizations. Furfural is mostly used as an extraction solvent to remove the aromatic and other undesirable polar materials from the petroleum fractions used as lubricating oil base stocks, as well as in resin manufacture, especially of the phenol-aldehyde type.[1-4]

The hydrolysis reaction was carried out in two steps. In the first step, the pentosan chains are cleaved and separated into pentoses. As the reaction goes on, at high temperature and pressure, the pyranose ring is cleaved between the O-atom and the next C-atom bearing a hydroxy group, under migration of a H-atom, a carbonyl group being formed. In the slower second step, furfural is formed by dehydration of pentoses. Dehydration can be accelerated by varying the reaction conditions.[5] Furfural is obtained from the hydrolysis of pentosans in the lignocellulosic materials.

Numerous by-products of agricultural crops have been studied for the preparation of furfural using acid hydrolysis.[6-12] Only few publications have been devoted to furfural prepared from harvest residues using acid salts as catalysts, or to the kinetics of hydrolysis.[13, 14]

In the present work, corn cobs were studied for the production of furfural, due to their high percentage of hemicellulose.[10, 15] In Egypt, the dry corn cobs residues amount to ~24696.5 t /harvest, being at present utilized as animal fodder and /or in the preparation of charcoal.

The present work attempts at establishing the optimal conditions for the production of furfural from corn cobs, in comparison with other agricultural residues. The kinetic parameters of pentosans hydrolysis using different catalysts [H_2SO_4, HCl, and $Al_2(SO_4)_3$] were also studied.

EXPERIMENTAL

Analysis of the raw material

Crushed (size 2 mm) corn cobs were chemically analyzed for their hollocellulose.[16] lignin.[17] pentosans,[18] total nitrogen or protein content[19] and extractives.

Hydrolysis of corn cobs

Crushed corn cobs were hydrolyzed in a rotary, electrically heated pulping unit (Model CCL). The desired temperature was achieved in 65 minutes in all experiments (zero time). Each experiment was performed on 100 g oven dry corn cobs, in a 2.5 L stainless steel autoclave. In the end of the experiment, 100 mL of hydrolysate were sucked out and analyzed for furfural, according to Tollens.[20] The furfural yield was also calculated as the percentage of the pentosans of corn cobs.

Different reaction variables were applied, such as the concentration of acid catalyst, material: acid ratio, time, temperature, type of catalyst and type of raw material.

The furfural formed in the hydrolysate was removed by solvent extraction using diethyl ether and chloroform, either alone or in mixtures. The efficiency of solvent extraction was determined by estimating the furfural remaining in the hydrolysate.

Polynomial correlation and regression of the experimental data

To describe the dependence between the yield of furfural based on the pentosans of corn cobs, Y, and the independent variables, X (concentration of acid, material:acid ratio, temperature, time, or temperature at different periods), the following polynominal models were proposed :

one variable

$$Y = B_o + B_1 X_1$$

or

$$Y = B_o + B_1 X_1 + B_{11} X_1^2 + B_{11} X_1^2 + B_{111} X_1^3 + \text{-----}$$

two variables

$$Y = B_0 + B_1 X_1 + B_2 X_2 + B_{11} X_1^2 + B_{22} X_2^2 + B_{12} X_1 X_2$$

or

$$Y = Bo + B_1 X_1 + B_2 X_2 + B_{12} X_1 X_2$$

By the multiple regression technique, the values of the regression constant B_o and the other coefficients B_i of models[21, 22] were obtained. The Bs are coefficients which indicate the relative importance of their associated X values. If B is large, it indicates the importance of its associated X value. Conversely, if the B value is small, it indicates the lack of importance of its X value.

The most probable model was selected on the basis of the correlation coefficient (R^2) and minimum standard error (SE) values.

Spectral analysis

Identification and purification of the furfural thus obtained were carried out using IR- and Mass- spectra.

– IR-spectra (4000–200 cm^{-1}) were recorded on an Insco FT/IR- Infra red spectrophotometer.

– Mass- spectra were recorded on a Finnigan- Mat 55Q 7000. The ionization voltage applied was of 70 ev, mass range (EI) m/e 50–250.

RESULTS AND DISCUSSION

Chemical analysis of corn cobs showed that they contained 30.1% pentosans (Table 1).

TABLE 1

Chemical analysis of corn cobs

Analyses	Value
Holocellulose, %	85.915
Lignin, %	13.900
Pentosans, %	30.097
Protein, %	3.450
MeOH-Benzene extracted residue, %	1.781
Water extracted residue, %	4.711

The hydrolysis of pentosans of corn cobs into furfural was studied under different experimental conditions, as mentioned above, for establishing the optimal conditions for the maximum yield of furfural.

Effect of acid concentration

The influence of acid concentration was studied between 1% to 20% wt /wt H_2SO_4, based on oven dry corn cobs. The hydrolysis was done at 140° and an aqueous acid: material ratio 6/1, for 1 hour. The results of furfural yield in the hydrolysate are illustrated in Figure 1. It is clear that the maximum furfural yield was obtained at 3% H_2SO_4, while further increase in the acid concentration from 3 to 20% had no effect on increasing the hydrolysis rate of pentosans and, consequently, on the percent yield of furfural. Thus, 3% H_2SO_4 was chosen as a catalyst for further experiments.

The regression equation correlated the yield of furfural, Y (based on pentosans of corn cobs) with acid concentration, X, is as follows :

$$Y = -42.48 + 82.807X - 20.650X^2 + 2.299X^3 - 0.115X^4 + 0.002X^5$$
$$(R^2 = 0.99677 \text{ and } SE = 2.7740).$$

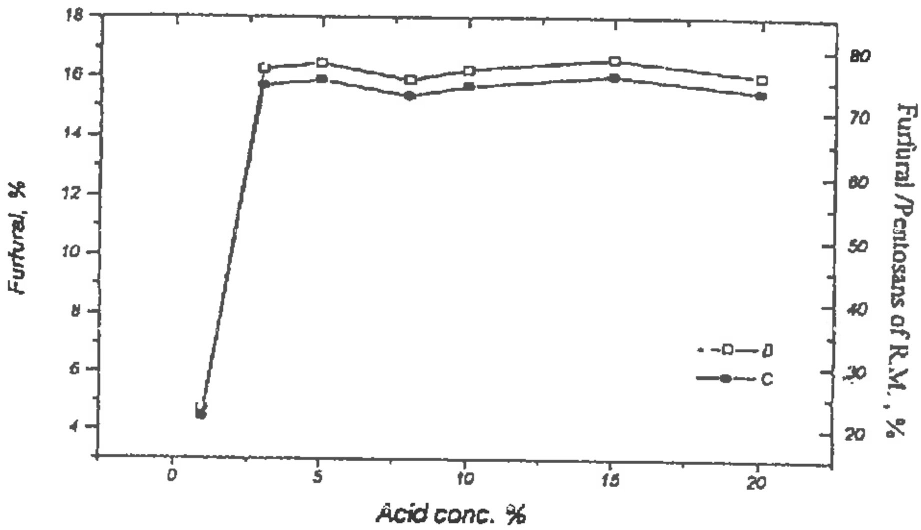

Fig. 1 – Effect of acid concentration.
[-B- Furfural, % and -C- Furfural /Pentosans of R.M., %]

Effect of the acid: material ratio

Figure 2 shows the percent of furfural formation (% furfural in the hydrolysate and % furfural yield based on pentosans in the raw material) as a function of the acid: material ratio, namely: 4/1, 5/1, 6/1, 7/1, 8/1 and 10/1. The other hydrolysis conditions are: 3% H_2SO_4 (based on O.D. corn cobs), at 140°, for 1 hour. It is clear that the yield of furfural gradually increased as the liquor ratio increased from 4/1 up to 6/1. Further increase in the liquor ratio from 6/1 to 10/1 was accompanied by a decrease in the furfural yield in the hydrolysate, which is attributed to the dilution of acid catalyst which decreases the degree of pentosans hydrolysis in corn cobs.

The regression equation correlating the yield of furfural, Y (based on pentosans of corn cobs) with the variation of the aqueous acid: material ratio, X, is as follows:

$$Y = -352.2 + 197.98X - 29.37X^2 + 1.35X^3$$
$$(R^2 = 0.95557 \text{ and } SE = 4.5598)$$

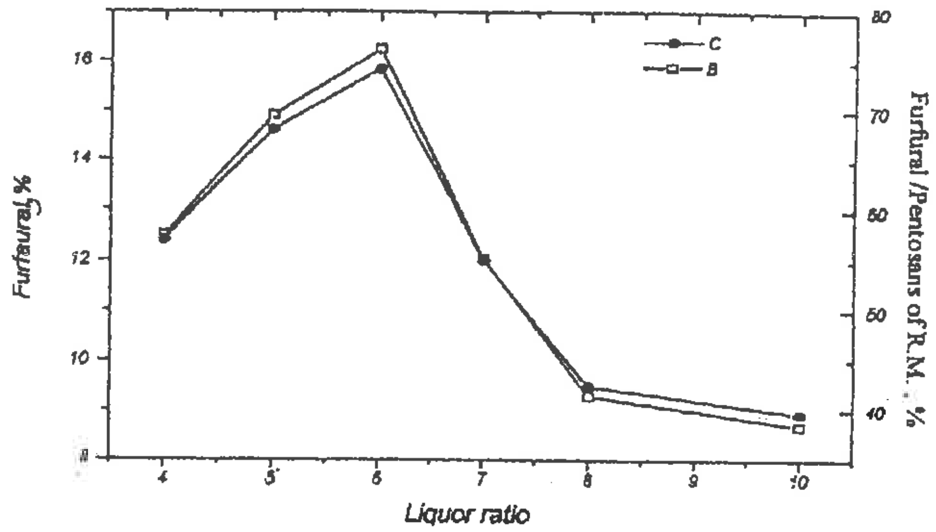

Fig. 2 – Effect of acid to corn cobs ratio.
[-B- Furfural, % and -C- Furfural /Pentosans of R.M., %]

Effect of the catalyst type

Hydrolysis was carried out using 3% (based on O.D. corn cobs) of different catalysts type, i.e. acids, such as H_2SO_4, HCl, H_3PO_4, and acid salts like Na_2SO_4, $MgSO_4$, $Cr_2(SO_4)_3$ and $Al_2(SO_4)_3$. Other hydrolysis conditions are: aqueuos acid: material ratio 6/1, temperature 140° and reaction time 1 hour. The results are registered in Table 2.

TABLE 2

Influence of the catalyst type

Catalyst type	Furfural in hydrolysate, %	Furfural / pentosans of corn cobs, %
HCl	16.056	73.352
H_2SO_4	16.262	74.296
H_3PO_4	14.541	66.430
Na_2SO_4	1.442	6.589
$MgSO_4$	1.883	8.602
$Al_2(SO_4)_3$	15.255	69.694
$Cr_2(SO_4)_3$	6.862	31.350

It is clear that the use of mineral acids as catalyst of hydrolysis had a more pronounced effect on the furfural yield than salts of acid, except the case of $Al_2(SO_4)_3$, where the yield was close to that with H_3PO_4. The maximum yield of furfural in the hydrolysate was obtained with the use of HCl and H_2SO_4.

Therefore, the hydrolysis of hemicellulose of corn cobs using 3% catalyst [H_2SO_4, HCl, and $Al_2(SO_4)_3$], at an aqueous catalyst:material ratio of 6/1 was chosen for studying the influence of temperature.

Effect of temperature

The influence of temperature was studied at 140°, 150°, 160° and 170°, for different time intervals (0–1 hr.).

From Figures 3–5 it is clear that, at relatively short hydrolysis time, temperature has a positive influence (increase) on the furfural yield in the hydrolysate. A slight change in the furfural yield accompanied the hydrolysis at relatively longer times. The time needed to obtain a maximum yield was reduced with the increase in temperature from 140° to 170°. In other words, the hydrolysis of hemicellulose was faster at higher temperature (170°).

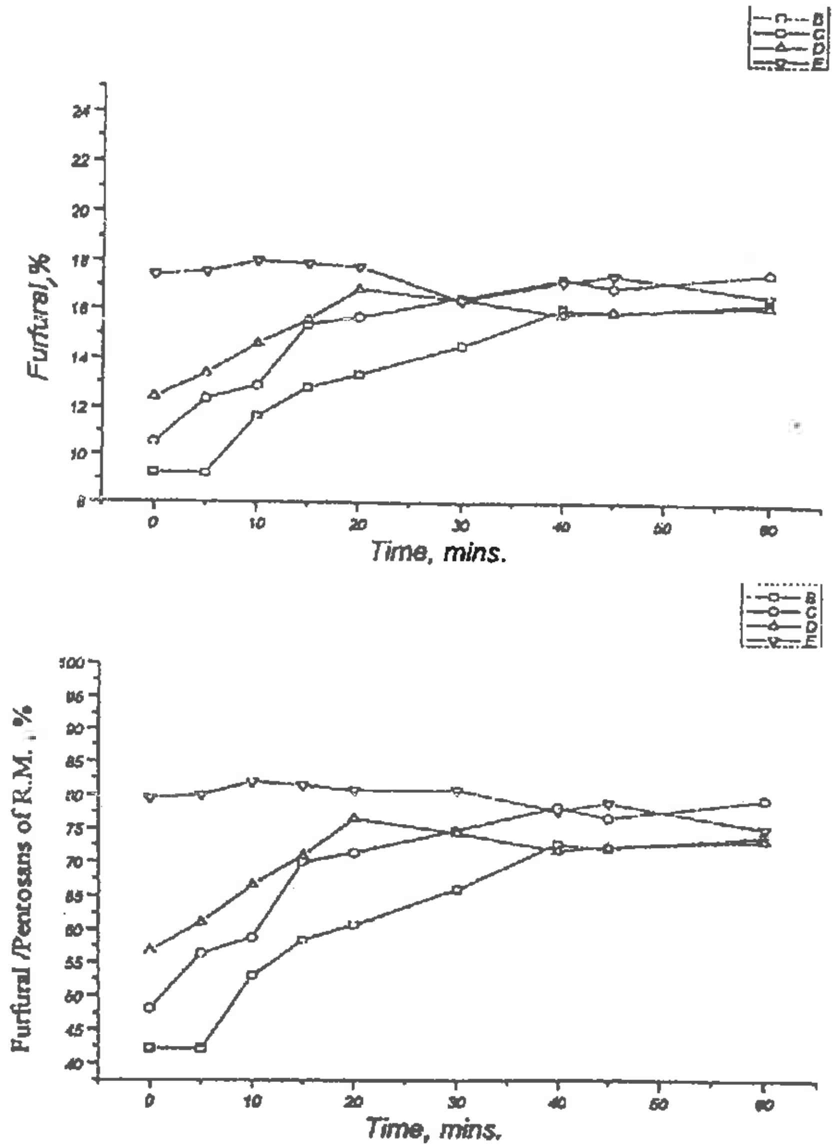

Fig. 3 – Effect of acid hydrolysis time (by H_2SO_4) on Furfural, % and Furfural /Pentosans of corn cobs %, at different temperatures. [-B- 140°, -C- 150°, -D- 160° and -E- 170°]

The maximum yield of furfural was of 84.93%.

The polynomial regression models correlating the yield of furfural,Y (based on pentosans of corn cobs), with the variation of the hydrolysis time, X, at a hydrolysis temperature of 140°, are as follows:

For $Al_2(SO_4)_3$ as a catalyst

$$Y = 3.562 + 2.282X - 0.295X^2 + 0.021X^3 - 5.076X^4 + 3.883X^5$$
$$(R^2 = 0.9965 \text{ and } SE = 0.75931)$$

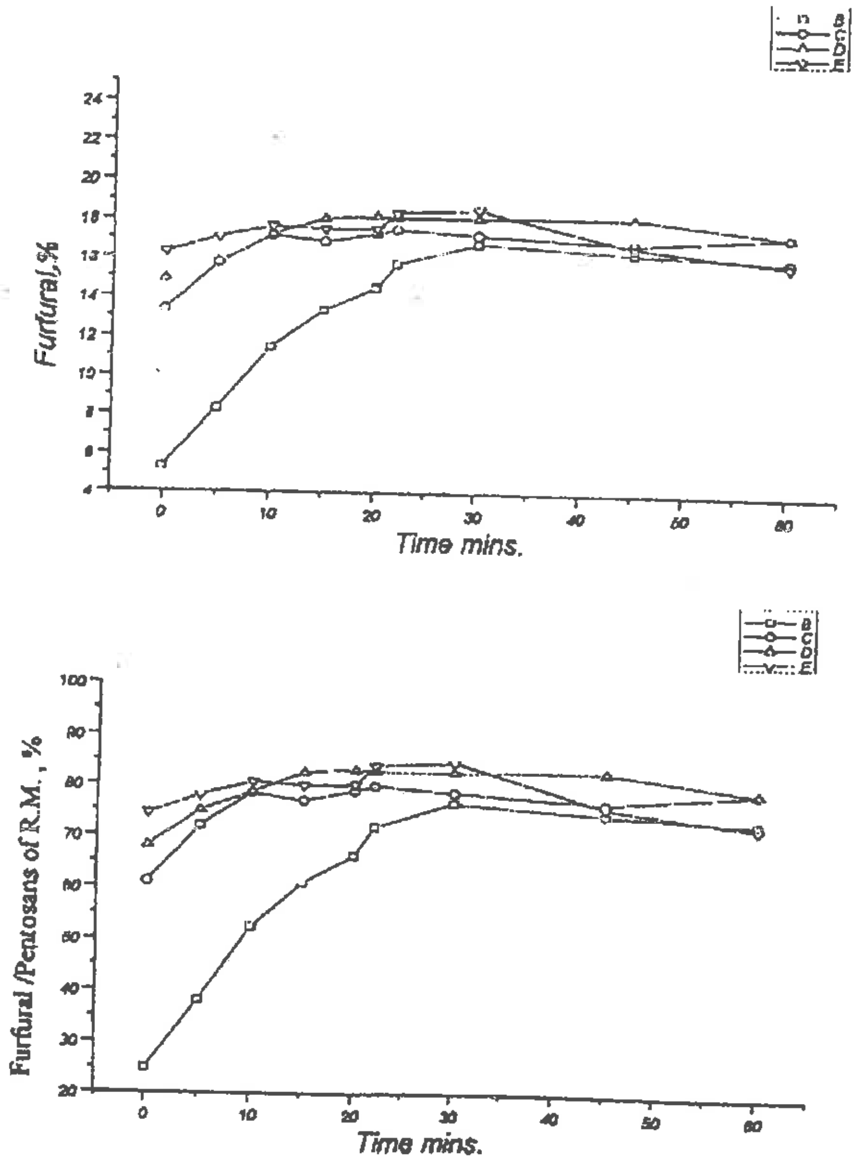

Fig. 4 – Effect of acid hydrolysis time (by HCl) on Furfural, % and Furfural /Pentosans of corn cobs %, at different temperatures. [-B- 140°, -C- 150°, -D- 160° and -E- 170°]

For HCl as a catalyst

$$Y = 24.623 + 3.001X - 0.029X^2 - 7.363X^3 + 1.042X^4$$
$$(R^2 = 0.9966 \text{ and } SE = 1.4902)$$

For H_2SO_4 as a catalyst

$$Y = 40.484 + 1.241X - 0.011X^2$$
$$(R^2 = 0.9721 \text{ and } SE = 2.2574)$$

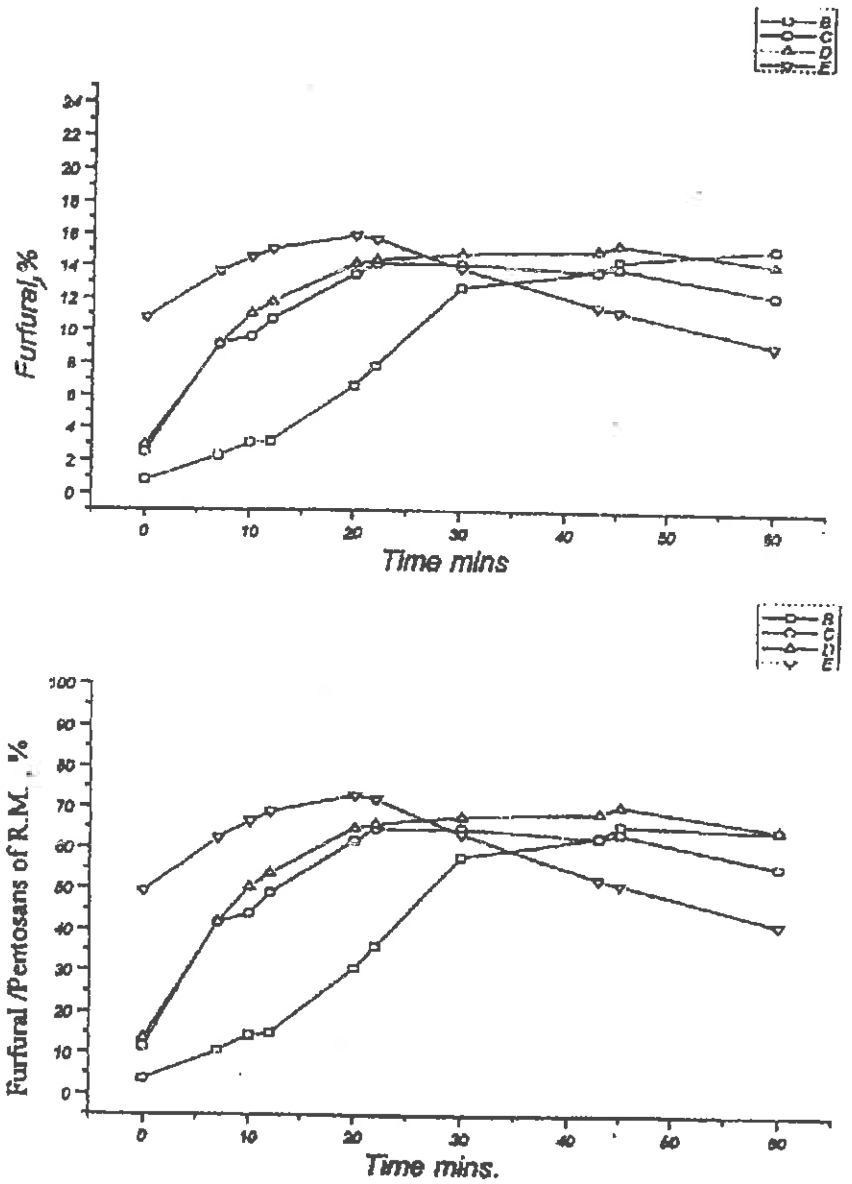

Fig. 5 – Effect of acid hydrolysis time (by $Al_2(SO_4)_3$) on Furfural, % and Furfural /Pentosans of corn cobs %, at different temperatures. [-B- 140°, -C- 150°, -D- 160° and -E- 170°]

The polynomial regression models correlating the yield of furfural, Y (based on pentosans of corn cobs) with the variation of hydrolysis temperature, X, at a hydrolysis time of 20 minutes, are as follows:

For $Al_2(SO_4)_3$ as a catalyst

$$Y = -1536.5 + 19.363X - 0.0582X^2$$
$$(R^2 = 0.9463 \text{ and } SE = 0.7465)$$

For HCl as a catalyst

$$Y = -925.004 + 12.534X - 0.039X^2$$
$$(R^2 = 0.99927 \text{ and } SE = 0.3495)$$

For H_2SO_4 as a catalyst

$$Y = -338.00 + 4.644X - 0.012X2$$
$$(R^2 = 0.99997 \text{ and } SE = 0.072)$$

For the effect of temperature (X_1) on the furfural yield percentage (Y) at different periods (X_2), the following polynomial models are proposed:

For $Al_2(SO_4)_3$ as a catalyst

$$Y = -209.827 + 1.524X_1 + 8.056X_2 - 4.455X1X_2$$
$$(R^2 = 0.9999 \text{ and } SE = 1.58 \times 10^{-2})$$

For HCl as a catalyst

$$Y = -207.161 + 1.657X_1 + 8.204X_2 - 0.046X1X_2$$
$$(R^2 = 1.00 \text{ and } SE = 0.036)$$

For H_2SO_4 as a catalyst

$$Y = -132.431 + 1.247X_1 + 4.301X_2 - 2.501X_1X_2$$
$$(R^2 = 1.000002 \text{ and } SE = 1.304 \times 10^{-3})$$

From all the above polynomial models, it is clear that the importance of hydrolysis variables on furfural yield has the following sequence :

aqueous acid to raw material ratio > acid concentration > temperature > time.

As to the effect of variation of both hydrolysis temperature (X_1) and hydrolysis time (X_2) on furfural yield, it is obvious the importance of X_2 *versus* X_1.

Effect of agricultural waste type

Results in Table 3 show the percent yield of furfural in the hydrolysates from other agricultural wastes, such as corn hulls, corn stalks, rice hulls containing the remainder of rice grind and bagasse, compared to that produced from corn cobs under the same hydrolysis conditions.

The highest yield was from corn cobs, while the lowest was from rice hulls containing rice grind. The percent furfural yields based on the pentosans of agricultural wastes are of 84.93, 74.30, 66.47, 38.72 and 22.59% for corn cobs, corn hulls, bagasse, corn stalks and rice hulls with grinding rice, respectively.

From the above results, it could be concluded that the use of corn cobs as a harvest waste for the production of furfural is more promising than the other agricultural wastes.

TABLE 3

Influence of the raw material type

Raw material	Pentosans in R.M., %	Furfural in hydrolyzate	Furfural / pentosans of corn cobs, %
Corn cobs	30.097	18.590	84.928
Corn hulls	23.898	12.913	74.296
Corn stalks	15.725	4.429	38.728
Rice hulls*	11.963	1.966	22.594
Bagasse	21.326	10.395	66.471

* Rice hulls contain the remainder of grinding rice.

Effect of the organic solvent type for furfural extraction

To minimize the cost and loss of solvent during the production of furfural by using conventional ether extraction, two solvents, i.e. diethyl ether and chloroform, were investigated.

Tables 4a and 4b show the variation of furfural extracted from the hydrolysate using diethyl ether and chloroform, either individual or in mixtures.

From Table 4a, it is clear that the efficiency of furfural extraction from the hydrolysate produced with HCl as a catalyst is higher when using $CHCl_3$ than ether. Replacement of ether by 10 to 25% $CHCl_3$ also increased the efficiency of furfural extraction compared with the case of ether solvent. Instead, increasing the percent of $CHCl_3$ in the mixture to 50% decreased the efficiency of extraction in comparison to either using ether or $CHCl_3$. The maximum efficiency of furfural extraction was of 10% $CHCl_3$ and 90% ether.

Table 4b shows that, in the case of the hydrolysate obtained from acid hydrolysis with HCl, higher efficiencies of the furfural extracted from the hydrolysate of H_2SO_4 and $Al_2(SO_4)_3$ were obtained by using $CHCl_3$ or mixtures of 10% $CHCl_3$ and 90% ether solvents.

Table 4 also shows that the maximum yield of extracted furfural is 10.9% based on furfural in the hydrolyzate (49.93% based on pentosans of corn cobs), by using 3% HCl as a catalyst, followed by hydrolysate extraction with a mixture of 10% $CHCl_3$ and 90% ether solvents. Data in Tables 4 indicate that 10% $CHCl_3$ + 90% ether is a better extractive of furfural than the conventionally used ether.

TABLE 4

Influence of the organic solvent type on the percent of extracted furfural

a- *Using HCl as catalyst*

Organic solvent type	Furfural remained in the hydrolyzate, %	Furfural extracted by the solvent, %	Efficiency of solvent extraction, %
Original hydrolyzate	18.590	---	---
Ether	12.677	5.913	31.807
$CHCl_3$	8.168	10.422	56.062
10% $CHCl_3$ +90% Ether	7.661	10.929	58.789
25% $CHCl_3$ +75% Ether	10.954	7.636	41.076
50% $CHCl_3$ +50% Ether	16.636	1.954	10.512

b- *Using H_2SO_4 and $Al_2(SO_4)_3$ as catalysts*

Catalyst	Solvent	Furfural remained in the hydrolyzate, %	Furfural extracted by solvent, %	Efficiency of solvent extraction, %
H_2SO_4	Original hydrolyzate	17.954	---	---
	Ether	14.269	3.685	20.916
	$CHCl_3$	8.49	9.455	52.664
	10% $CHCl_3$ + 90% Ether	11.257	6.697	37.300
$Al_2(SO_4)_3$	---	15.987	---	---
	Ether	8.946	7.041	44.043
	$CHCl_3$	6.484	9.503	59.442
	10% $CHCl_3$ +90% Ether	8.213	9.374	58.623

Furfural characterization

IR-spectra of furfural extraction from the hydrolysate using the above mentioned solvents (ether, $CHCl_3$ and mixture of 10% $CHCl_3$ and 90% ether), are illustrated in Figure 6.

In these spectra, in the 3000–2800 cm^{-1} region, a pair of bands appeared, arising from the C-H stretching vibration of α-aldehyde substituting groups, in addition to the C-H stretching of the hetero-aromatic ring. The appearance of an absorption band at ~ 2830 cm^{-1}, accompanied by carbonyl absorption bands at ~1697 cm^{-1}, is a good evidence for the presence of an aldehyde group.

The spectrum of extracted furfural by ether solvent (spectrum 1) exhibits four bands in the region 1600–1300 cm^{-1}, which are due to the absorption involving stretching and contraction of all bonds in the ring and interactions between these modes, in addition to the C-H bending vibration of the aldehyde groups. The skeletal C = C bond appears as a doublet, due to the α-aldehyde substitution. The spectrum also shows that the C-H out of plane and ring bending (β-ring) absorption of furan ring appears at 925 cm^{-1}, 880 cm^{-1} and 840 cm^{-1}. The other band at 760 cm^{-1} corresponds to the C-H out of plane bending of the aldehydic groups present in O-position of the furan ring.

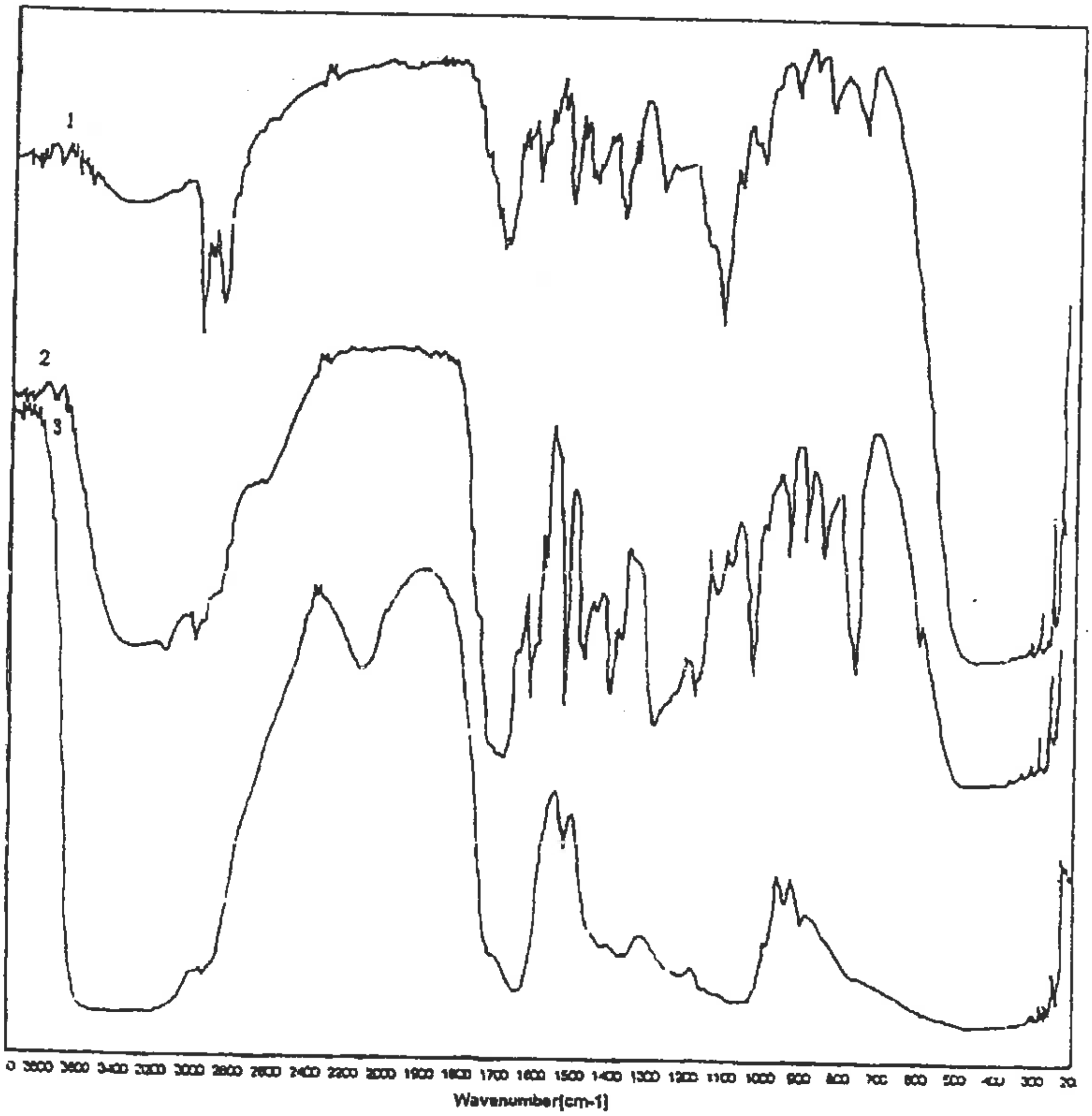

Fig. 6 – IR-spectra of extracted furfural by organic solvents
(1) ether, (2) 10% $CHCl_3$ + 90% ether and (3) $CHCl_3$.

The spectrum of extracted furfural using a mixture of 10% $CHCl_3$ and 90% ether solvents (spectrum 2) has the same bands as the furfural extracted by ether (spectrum 1). The difference between the two spectra was the shift of the band corresponding to the C-H stretching vibration at 2977.5 cm^{-1} to higher frequency (3131.8 cm^{-1}), with increasing the intensity of the bands in the 1300–1200 cm^{-1} region. This may be due to the impurities of extracted furfural, such as organic acids, e.g., AcOH, of the hydrolysate.[23, 24] This evidence was emphasized from the spectrum of furfural extracted using $CHCl_3$ as an extracting agent (spectrum 3), whereas the broad bands in the regions 4000–3000 cm^{-1} and 1800–1600 cm^{-1} apparently correspond to the carboxylic groups.

Thus, to obtain pure furfural by chloroform either, alone or in mixture with the ether, a treatment by dilute alkali on the chloroform layer must be carried out before fractional distillation, in order to remove the extracted organic acids from the hydrolysate. The purity of the obtained furfural becomes clear from the mass spectra chart (Fig. 7).

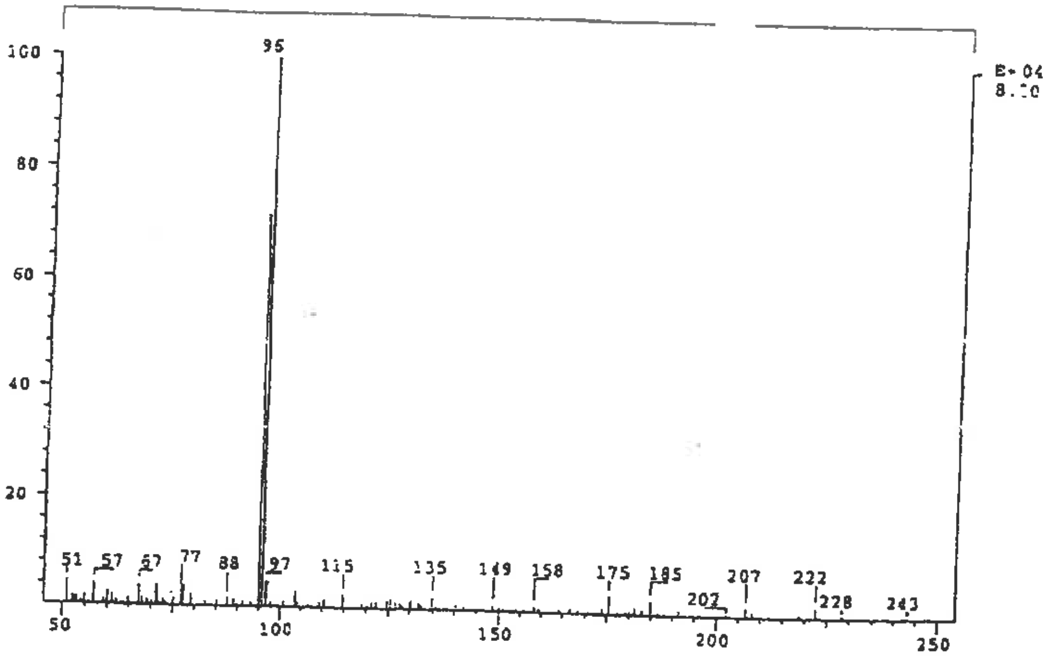

Fig. 7 – Mass-spectrum of produced furfural.

Thermodynamic parameters of pentosans hydrolysis

In this study, the rate constant of the transformation of pentosans of corn cobs to furfural and other thermodynamic parameters, such as activation energy (E_a), enthalpy change (ΔH) and entropy change (ΔS), by a hydrolysis process using H_2SO_4, HCl, and $Al_2(SO_4)_3$ as a catalysts, were calculated from the relations between the concentration of furfural in the hydrolysate, based on the pentosans in the corn cobs, and time, at different temperatures (Figs. 3–5).

Assuming that the rate of hydrolysis is of the first order with respect to pentosans, based on references[25-27] and by applying a linear regression analysis, the kinetic parameters can be calculated from the following equations :

$$-\frac{dP}{dt} = kP_t$$

$$-\int_0^t \frac{dP}{P_t} = k\int_0^t dt \qquad (1)$$

$$\ln\frac{P_0}{P_t} = kt$$

where: P_o is the percent of pentosans of the corn cobs at time zero,
P_t is the percent of pentosans remaing after hydrolysis time t, and
k is the specific rate constant.

$$k = Ae^{-E_a/RT}$$

$$k = \ln A - E_a/RT \quad (2)$$

$$H = E_a - RT \quad (3)$$

$$k = \frac{KT}{h} e^{-\Delta Go_a/RT} \quad (4)$$

$$\Delta G^0 = \Delta H - T\,\Delta S \quad (5)$$

where, E_a : activation energy,
R : gas constant,
A : Arrhenious constant,
K : Boltzman constant,
h : Planck's constant,
ΔH : enthalpy of activation
ΔG^o: Gibbs free energy in the transfer from the initial to the final state, and
ΔS : entropy of activation
T : absolute temperature.

As can be seen from the determination of the correlation coefficient, r, of the relation between ln P_o/P_t against time t (Table 5), the adequacy of equation (1) is very high, as the values of r are close to 1.0. The slope of the straight line is a measure of the hydrolysis rate constant, at a particular hydrolysis temperature.

TABLE 5

Hydrolysis rate constants, k, of the pentosans of corn cobs using different catalysts at different temperatures

Catalyst	H_2SO_4		HCl		$Al_2(SO_4)_3$	
Temp °C	k x 10^{-3} min^{-1}	r^2	k x 10^{-3} min^{-1}	r^2	k x 10^{-3} min^{-1}	r^2
140	20.227	0.986	42.999	0.991	27.840	0.980
150	24.174	0.993	44.275	0.995	35.480	0.964
160	31.808	0.994	46.368	0.985	37.529	0.909
170	7.817	0.951	21.937	0.997	74.4487	0.998

According to Table 5, the values of the first order reaction constants, k, show an increase in the rate of hydrolysis with the increase in hydrolysis temperature. The rate of transformation of pentosans into furfural by HCl as a catalyst is higher than that obtained when using H_2SO_4 and $Al_2(SO_4)_3$. It is also clear that the rate of hydrolysis reaction at 170° using mineral acids (H_2SO_4 and HCl) was very rapid, so that it was very difficult to follow the rate of furfural formation. Therefore, the values of the specific rate constant (k) at 170°, when using mineral acids, were very small compared to that obtained at 140–160°, being far from the straight lines of the relation between ln k against 1/T, used to calculate the activation energies (equation 2).

The values of the thermodynamic parameters (E_a, ΔH and ΔS), given in Table 6, indicate that the reactivity of hemicellulose of corn cobs to hydrolyze with $Al_2(SO_4)_3$ as a catalyst is lower than that of HCl, when using H_2SO_4 on an intermediate position.

TABLE 6

Arrhenius and thermodynamic parameters of the pentosans of corn cobs hydrolysis

Catalyst	Arrhenius parameters			ΔH	ΔS
	A	E_a, kJ/mole	-r	kJ /mole	J /mole
H_2SO_4	301.735	32.999	0.992	30.151	72.972
HCl	0.218	5.571	0.990	2.100	134.509
$Al_2(SO_4)_3$	14293.39	45.333	0.914	18.547	98.012

REFERENCES

[1] R.M. Azeri, P.D. Shikhalizade and S.D. Mirzoev. *Azerb Neft Khoz*, 52, 35 (1972).

[2] A.G. Martynenko, R.A. Gekhovskii, G.E. Ledyashova, G.P. Shiryaeva, N.V. Okhrimenko and V.P. Ivlev, *Neftepererab Neftekhim*, 5, 23 (1977).

[3] A. Sequeira, P.B. Sherman, J.U. Douciere and E.O. McBride, *Oil Gas J.*, 77, 99 (1979).

[4] M. Grayson, "Encyclopedia of Chemistry and Technology", Vol. 10, Wiley-Interscience Publishers, New York. p. 244 (1979).

[5] H.K. Krivanec, "Manufacturing Guide Furfural", UNIDO /ISID /INQ, Sept. 1974, p. 2.

[6] M. Alejandro and C. Elvia, *Cana Azucar*, 3, 21 (1969).

[7] M. Alejandro and C. Elvia, *Assoc. Ted. Azucar Cuba*, 3, 814 (1971).

[8] M.H. Fadl, N.A. Shinnawy and Y. Fahmy, *Research and Industry*, 16, 263 (1971).

[9] S.O. Heikal, N.A. El-Shinnawy and N.A. Fadl, *Cellulose Chem. Technol.*, 14, 81(1980).

[10] M.A. Baoqi and J.I.A. Shuying, *Cellulose Chem. Technol.*, 23, 277 (1989).

[11] H. Sayilkan and B. Cetinkaya, *Chimica Acta Turcica*, 19, 187 (1991).

[12] E. Primo-Yufera, C.I. Gil-Tortosa and F.J. Garcia-Breijo, *Bioresource Technology*, 52 (1995).

[13] N.A. Vedernikov, L.V. Mileeva, I.K. Kroma and A.J. Bucena, *Khim. Drev.*, 5, 30 (1993).

[14] N.A. Vedernikov, A.J. Bucena and V.B. Elge, *Khim. Drev.*, 6, 19 (1993).

[15] M. Grayson, "Encyclopedia of Chemistry and Technology", Vol. 10, Interscience Publishers, New York, p. 243 (1979).

[16] L.E. Wise, M. Murphy and A.A. D'Addiecs, *Paper Trade J.*, 122, 35 (1946).

[17] "The Institute of Paper Chemistry", Appelton, W., Institute Method No. 428 (January 1951).

[18] G. Jayme and P. Sartens, *Biochem.-Zeitung*, 308, 109 (1941).

[19] M.B. Jacobs, "The Chemical Analysis of Foods and Food Products", 2nd ed., D. Van Company, INC. New York, p. 34 (1958).

[20] R. Sieber, "Die Chemisch-Technischen Untersuchungs Methoden der Zellstoff und Papier Industrie", Springer-Velag, Berlin, p. 62 (1951).
[21] K. Mullen and D.M. Ennis, *Food Technol.*, 74 (July 1979).
[22] S.N. Deming and S.L. Morgan, "Experimental Design: Chemometric Approach", Elsevier, New York (1987).
[23] E.R. Rodriguez (Puerto Rico, Commonwealth), U.S. 3, 701, 789 (1972).
[24] H.K. Krivanec, "Manufacturing Guide Furfural", UNIDO /ISID /INQ, p. 32 (Sept. 1974).
[25] S. Glasston, *Textbook of Physical Chemistry*, MacMillan Co., London, p. 828 (1956).
[26] W.F. Wyme, K. Jones and H.J. Eyring, *Chem. Phys.*, 3, 492 (1935).
[27] R. Nishizaki, K. Yoshida and J.H. Wang, *J. Appl. Polym. Sci.*, 25, 2869 (1980).