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STATISTICALLY DESIGNED EXPERIMENTS FOR THE OPTIMISATION OF FURFURAL PRODUCTION FROM CORN COBS

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ABSTRACT

The dilute hydrochloric acid hydrolysis of corn cobs for the production of furfural was investigated in this study using statistically designed experiments under the following conditions: acid concentration (2-6 %w/w), temperature (120-150 ^{o}C), time (5-30 minutes) and solids loading (5-15 g). A statistical model was developed and validated to predict the yield of furfural during hydrolysis. Response Surface Methodology (RSM) was used to optimise the hydrolysis conditions. The model was statistically significant, did not show lack of fit and was able to predict the production of furfural. After applying RSM, the maximum furfural concentration predicted by the model was 16.1 g/l. The optimum temperature, acid concentration, hydrolysis time and solids loading were obtained as 150 ^{o}C, 5.94 %w/w, 11.23 minutes and 16.15 g respectively. Validation of the model indicated no significant difference between experimental observations and model prediction.

1. INTRODUCTION

Corn cobs, a waste material from the harvesting of corn, is an abundant and low-cost lignocellulosic material from which useful value added products can be recovered (Agbro and Ogie et al., 2012). An important example of such products is furfural. It is an important product of lignocellulosic materials because of its numerous applications in oil refining, plastics and pharmaceuticals (Kottke, 2006). Its annual production volume has been estimated to be around 200,000 tonnes.

In theory, every pentosan containing material could be used for the production of furfural. However, production of furfural on an industrial scale requires that the feedstock have a minimum pentosan content of 18-20% (Mansilla et al., 1998). The global furfural demand is almost exclusively satisfied by producing it from lignocellulosic feedstocks as there is currently no synthetic route for the production of furfural (Vasquez et al., 2007). Production of furfural from lignocellulosic feedstocks occurs in two steps. In the first step, the feedstock is subjected to acid catalysed hydrolysis at high temperature to yield monomeric pentoses in the solution. Furfural is produced in the second step by the dehydration of the pentose sugars (Mansilla et al., 1998).

It is important to optimise the variable upon which the yield of furfural is dependent in order to maximise it. Response surface methodology based on statistically designed experiments has been found to be very useful in optimising multivariable processes. It is employed for multiple regression analysis of quantitative data obtained from statistically designed experiments (Montgomery, 2005). Hence, the aim of this study was to optimise the effect of acid concentration, hydrolysis temperature, hydrolysis time and solid loading on the hydrolysis of corn cobs to produce furfural. A four variable Box-Behnken design was adopted to design the hydrolysis experiments.

2. MATERIALS AND METHODS

2.1. Lignocellulosic Feedstock Preparation

Corn cobs were obtained from a local market in Benin City, Edo state, Nigeria. The cobs were sun dried to reduce moisture and prevent biodeterioration. The dried corn cob was milled to a particle size of about 2 mm, homogenised in a single lot to avoid differences in compositions among aliquots and stored under dry conditions prior to use.

2.2. Furfural Production

Acid hydrolysis of corn cobs was carried out in a 500 ml round bottom flask to which a reflux condenser was connected. The conditions of hydrolysis were as determined by the experimental design. Acid concentration, temperature, time and solids loading were set in the following ranges 2-6 %w/w, 120-150 ^{0}C, 5-30 minutes and 5-15 g respectively. At the end of the hydrolysis reaction, the solid residue was separated using a filter paper. The clear solution was collected in conical flask. The presence of furfural in the extracted solution was ascertained by conventional chemical test.

2.3. Analytical Methods

Determination of furfural concentration of the hydrolysate was carried out spectrophotometrically by measuring an absorbance at 530 nm using the method reported by Sattar et al. (2007). A sample of the hydrolysate (5 ml) was taken in a 25 ml volumetric flask and made up to the mark with 50% ethanol. To this was added 3 ml of 90% aniline and 0.25 ml of 37% hydrochloric acid. The mixture was allowed to stand for 15 minutes at room temperature in dark to develop a red colour. The absorbance of the solution was measured at

530 nm. The concentration of furfural in the hydrolysate was then determined using a standard curve.

2.4. Experimental Design

A four variable Box-Behnken design (BBD) for response surface methodology was used to develop a statistical model for the production of furfural. The range of the variables that were optimised is shown in Table 1. The experimental design made up of 29 runs was developed using Design Expert® 7.0.0 (Stat-ease, Inc. Minneapolis, USA). The coded and actual values of the independent variables were calculated as follows.

$$x_i = \frac{X_i - X_o}{\Delta X} \quad (1)$$

Where x_i and X_i are the coded and actual values of the independent variable respectively. X_o is the actual value of the independent variable at the centre point and ΔX_i is the step change in the actual value of the independent variable. The following generalised second order polynomial equation was used to estimate the response of the dependent variable.

$$Y_i = b_o + \sum b_i X_j + \sum b_{ij} X_i X_j + \sum b_{ii} X_i^2 + e_i \quad (2)$$

Where Y_i is the dependent variable or predicted response, X_i and X_j are the independent variables, b_o is offset term, b_i and b_{ij} are the single and interaction effect coefficients and e_i is the error term.

Table 1: Experimental range and levels of independent variables

Independent Variable	Symbols	Coded and Actual Levels		
		-1	0	+1
Temperature (°C)	X_1	120	135	150
Acid concentration (%w/w)	X_2	2	4	6
Solids loading (g)	X_3	5	10	15
Time (min)	X_4	5	17.5	30

3. RESULTS AND DISCUSSION

3.1. Statistical Modeling

The four-level Box-Behnken design resulted in 29 experimental runs as shown in Table 2. The response or dependent variable was chosen as the yield of furfural. Equation (3) is the quadratic statistical model in terms of actual variables that was obtained after applying multiple regression analysis to the experimental data presented in Table 2.

$$\begin{aligned} Y = {} & 317.15 - 4.29X_1 - 15.71X_2 - 0.13X_3 - 0.23X_4 + 0.10X_1X_2 \\ & - 0.17X_2X_3 - 0.0086X_2X_4 - 0.0024X_3X_4 + 0.015X_1^2 - 0.041X_3^2 \end{aligned} \quad (3)$$

Table 2 also show the yield of furfural as predicted by Equation (3). Tables 3 and 4 show the results of analysis of variance (ANOVA) carried out to determine the fit of the statistical model.

Table 2: Box-Behnken design matrix for the optimisation of variables and the response values

Run No	Factors								Response	
	Coded values				Actual values				Furfural produced (g/l)	
	X_1	X_2	X_3	X_4	X_1	X_2	X_3	X_4	Experiment	Predicted
1	-1	-1	0	0	120	2	10	17.5	9.5	8.4
2	0	1	0	-1	135	6	10	5.0	8.6	6.3
3	0	0	-1	-1	135	4	5	5.0	6.5	7.3
4	-1	0	0	1	120	4	10	30.0	1.6	1.2
5	1	0	1	0	150	4	15	17.5	10.1	9.0
6	0	0	0	0	135	4	10	17.5	5.2	4.2
7	1	0	-1	0	150	4	5	17.5	9.9	11.0
8	0	-1	0	-1	135	2	10	5.0	7.7	8.2
9	0	0	0	0	135	4	10	17.5	1.6	4.2
10	-1	0	-1	0	120	4	5	17.5	3.5	4.2
11	0	-1	1	0	135	2	15	17.5	1.5	1.6
12	0	0	0	0	135	4	10	17.5	5.9	4.2
13	1	1	0	0	150	6	10	17.5	12.9	12.8
14	0	0	0	0	135	4	10	17.5	3.6	4.2
15	1	-1	0	0	150	2	10	17.5	10.0	9.2
16	0	0	0	0	135	4	10	17.5	2.6	4.2
17	1	0	0	-1	150	4	10	5.0	13.1	14.1
18	-1	0	0	-1	120	4	10	5.0	6.7	7.3
19	0	0	1	1	135	4	15	30.0	0.5	0.7
20	0	-1	-1	0	135	2	5	17.5	9.6	7.1
21	-1	0	1	0	120	4	15	17.5	1.5	2.2
22	0	0	1	-1	135	4	15	5.0	6.0	5.1
23	-1	1	0	0	120	6	10	17.5	0.5	0.0
24	0	-1	0	1	135	2	10	30.0	0.5	2.5
25	0	0	-1	1	135	4	5	30.0	0.5	0.9
26	0	1	0	1	135	6	10	30.0	0.5	0.3
27	1	0	0	1	150	4	10	30.0	8.1	7.9
28	0	1	1	0	135	6	15	17.5	0.5	2.8
29	0	1	-1	0	135	6	5	17.5	1.6	1.2

The model Fisher *F-test* of 16.96 with low probability value ($p< 0.0001$) shows a high statistical significance for the regression model as shown in Table 3(Kunamneni and Singh, 2005). The lack-of-fit p value of 0.7053 was not significant relative to the pure error. A non-significant lack of fit is desirable as it implies that the model could be used for theoretical prediction of the production of furfural (Vázquez et al., 2009). The goodness of fit of the model was assessed by checking the coefficient of determination (R^2). According to Guan and Yao (2008), the R^2 value should be at least 0.80 for a model to be considered to have a good fit. Table 4 shows an R^2 value of 0.904 which implies that the model proved suitable for the adequate representation of the actual relationship between the selected variables (Betiku et al., 2013).

Table 3: Analysis of variance (ANOVA) for quadratic model

Sources	Sum of Squar	df	Mean Squares	F value	p value
Model	424.54	10	42.45	16.96	< 0.0001
X_1	138.24	1	138.24	55.24	< 0.0001
X_2	16.71	1	16.71	6.68	0.0187
X_3	11.02	1	11.02	4.40	0.0502
X_4	112.79	1	112.79	45.07	< 0.0001
X_1X_2	36.00	1	36.00	14.39	0.0013
X_2X_3	12.53	1	12.53	5.01	0.0381
X_2X_4	0.18	1	0.18	0.07	0.7889
X_3X_4	0.09	1	0.09	0.04	0.8517
X_1^2	81.37	1	81.37	32.51	< 0.0001
X_3^2	7.15	1	7.15	2.86	0.1082
Residual	45.05	18	2.50		
Lack of Fit	32.39	14	2.31	0.73	0.7053
Pure Error	12.66	4	3.16		
Cor Total	469.58	28			

Table 4: Statistical information for ANOVA

Parameter	Value
R^2	0.904
Adjusted R^2	0.851
Predicted R^2	0.704
Mean	5.19
Standard deviation	1.58

3.2. Optimisation of Furfural Production

Response surface curves were generated from the statistical model to examine the interactions between the independent variables and to determine the optimum levels of the variables. Figure 1 shows the response surface and corresponding contour plot illustrating the effect of temperature and acid concentration on furfural production. There was a high statistical influence of temperature on furfural production compared to acid concentration indicating that furfural production was more affected by temperature compared to acid concentration. This is also corrobotated by the fact that temperature had a much smaller p value compared to acid concentration as shown in Table 3. Figure 1 shows that the concentration of furfural produced increased with temperature. At a temperature of 150 ^{o}C, the maximum furfural concentration was observed at an acid concentration of 6 %w/w. These observation conform to those reported by other researchers (Mansilla et al., 1998; Riera et al., 2007; Sangarunlert et al., 2007). Figure 1 also show that low acid concentration favoured furfural production. The decline in furfural production at high values of acid concentration can be attributed to the fact that at severe hydrolysis conditions, furfural undergoes side reactions and its degradation to succine anhydride and carbon dioxide may become significant (Avci et al., 2013). Bamufleh et al. (2013) and Mao et al. (2012) both studied the production of furfural from midrib of date palm tree and corn cobs respectively. They also attributed the loss of furfural at severe hydrolysis conditions to low hydrolysis of lignocellulosic substrates as well as side reactions.

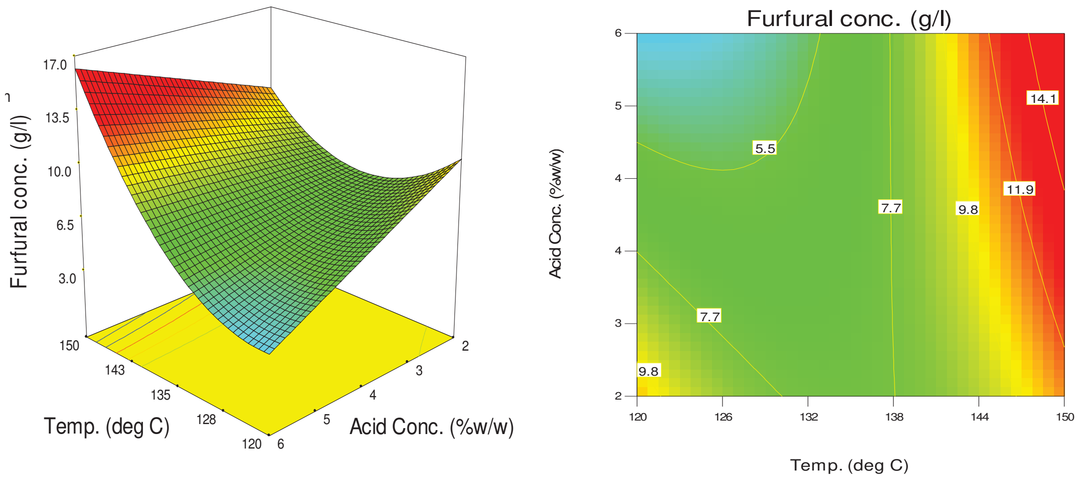
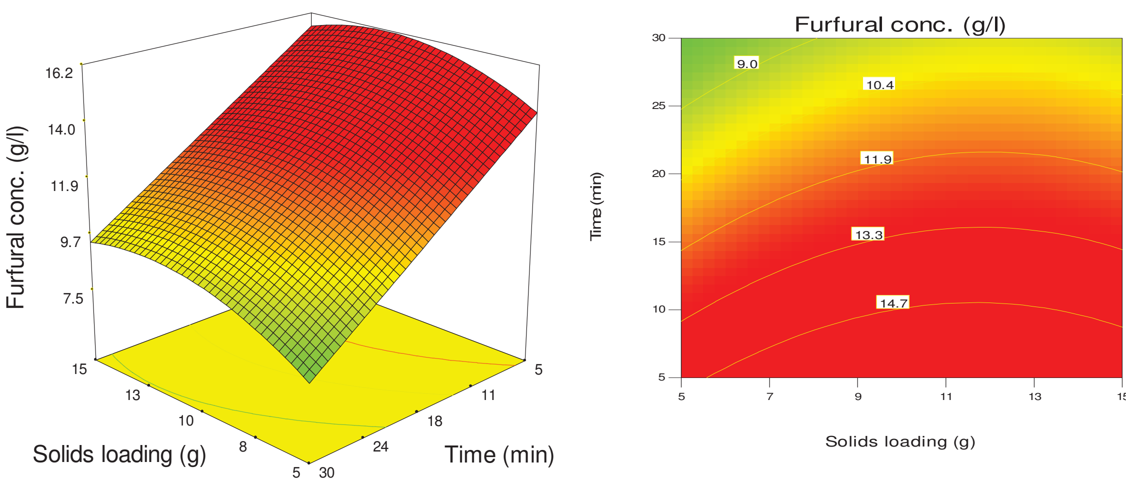


Figure 1: Response surface and contour plot showing the effect of temperature and acid concentration on furfural production

The solids loading and hydrolysis time are considered to be important variables during furfural production. Figure 2 shows the furfural production as function of solids loading and hydrolysis time. The trend observed could be attributed to the degradation of furfural to products such as levulinic acid, formic acid, succine anhydride etc (Avci et al., 2013). The solids loading had an overall positive effect on furfural production while the reverse was the case for hydrolysis time. Similar observation have been reported by other researchers (Riera et al., 2007; Sangarunlert et al., 2007).



`**Figure 2:** Response surface and contour plot showing the effect of solids loading and time on furfural production

The values of acid concentration, hydrolysis temperature, hydrolysis time and solids loading were optimised based on the statistical model (Equation 3). The maximum furfural concentration predicted by the model was 13.11 g/l. The optimum temperature, acid concentration, hydrolysis time and solid loading were obtained as 150 ^{o}C, 5.94 %w/w, 11.23 minutes and 16.15 g respectively.

4. CONCLUSION

The hydrolysis of corncobs was carried out using dilute hydrochloric acid according to a four variable Box-Behnken design for the purpose of producing furfural. The Box-Behnken design was used to develop a statistical model which was subsequently used to investigate the effect of temperature, acid concentration, hydrolysis time and solids loading on furfural production. The model was statistically significant ($p<0.0001$) and was able to describe the relationship between furfural production and the independent variables. RSM was used to optimize the process. Optimisation of furfural production using RSM revealed that the maximum furfural yield predicted by the model was 16.1 g/l. The optimum temperature, acid concentration, hydrolysis time and solids loading were obtained as 150 ^{o}C, 5.94 %w/w, 11.23 minutes and 16.15 g respectively. Validation of the model indicated no significant difference between experimental observations and model prediction.

5. CONFLICT OF INTEREST

There is no conflict of interest associated with this work.

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