Nigerian Research Journal of Engineering and Environmental Sciences 2(2) 2017 pp. 578-587

Nigerian Research Journal of Engineering and Environmental Sciences
Journal homepage: www.rjees.com

RJEES

Original Research Article

EVALUATING THE EFFECT OF ACID MIXTURES AND SOLIDS LOADING ON FURFURAL PRODUCTION FROM SUGARCANE BAGASSE: OPTIMIZATION USING RESPONSE SURFACE METHODOLOGY AND ARTIFICIAL NEURAL NETWORK

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ARTICLE INFORMATION

Article history:
Received 15 August 2017
Revised 30 September, 2017
Accepted 03 October, 2017
Available online 29 December, 2017

Keywords:
Furfural
ANN
Optimisation
RSM
Sugarcane bagasse

ABSTRACT

A three variable Box-Behnken design (BBD) coupled with response surface methodology (RSM) and artificial neural network (ANN) was employed to optimise and evaluate the effect of solids loading and acid concentration for the production of furfural from sugarcane bagasse. The three variables studied were concentration of hydrochloric acid (0-6%w/w), concentration of sulphuric acid (2-6%w/w) and solids loading (5-15g). Statistical analysis of the results showed that all the variables had significant effect on furfural yield. A statistical model was developed by applying regression analysis to the experimental data. The model was statistically significant ($p<0.05$) and showed a good fit with the experimental data. Artificial neural network was also used to optimise the production of furfural with several training algorithm used and quick propagation (QP) yielding the best training to predict the furfural concentration. The RSM model predicted optimal levels of 6.00w/w%, 0.00w/w% and 15.00g for HCl, H_2SO_4 and solids laoding respectively. Furfural produced was obtained to be 7.876g/L. The ANN model yielded optimum levels of 5.999w/w%, 0.001w/w% and 14.997g for HCl, H_2SO_4 and solids laoding respectively. Furfural concentration produced at these optimum values was 8.679 g/L. Both models produced a good fitting with the experimental data. However, ANN proved to be a better optimization tool because of its higher R^2 value (0.99225) and lower RMSE value (0.16905).

1. INTRODUCTION

Agricultural biomass in Nigeria are improperly disposed due to of lack of well-developed technological process for their chemical utilization thereby causing the problem of environmental pollution, wastage of resources and raw materials. However, in developed countries with fast growing economy such as China, attention has been focused on the proper utilization of waste agricultural biomass to obtain useful products. Agricultural biomass serves as a source of industrial chemicals such as furfural (Chughtai et al., 1999). Furfural is a dehydration product of pentosan, a monosaccharide often found in large quantities in the hemicellulose fraction of lignocellulosic biomass from which it is almost exclusively produced (Cai et al., 2014). Furfural is a basic chemical which finds various applications in rapidly developing industries as an intermediate chemical for the production of nylon, pyrrole, lysine, furfuryl and tetrahydrofurfuryl alcohol (Dunlop and Peters, 1953). Many furfural derivatives have been used as pharmaceuticals, fungicides and herbicides. Furfural is also the most commonly used solvent in petroleum refining industries and is in great demand for separating saturated compounds from unsaturated ones for the extraction of lubricating oils, gas oils and diesel fuels (Daous and Yorulmaz, 1989). Furfural is an organic compound which can be derived from several kinds of agricultural by-product including corncobs, wheat bran, oat, sugarcane bagasse, rice husk, straw.

Sugarcane is used worldwide as a feedstock for ethanol and sugar production. After sugar is milled for juice extraction, bagasse is obtained as residue, which corresponds to about 25% of the total weight and contains 60% to 80% of carbohydrates. The fermentation of this carbohydrates could significantly improve bioethanol productivity and sustainability but instead, bagasse is disposed off as agricultural waste.

This study was focused on the production of furfural from sugarcane bagasse. Response surface methodology and artificial neural network were evaluated for their predictive capabiities in modelling the process.

2. MATERIALS AND METHODS

2.1. Lignocellulosic Feedstock Preparation

Sugarcane bagasse was obtained from Mile 12 market in Lagos State, Nigeria. The bagasse was sun dried for three days to reduce its moisture. The dried bagasse was milled and sieved to a particle size of about 2mm, homogenized 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 sugarcane bagasse 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. The concentration of hydrochloric acid, sulphuric acid and solids loading were set in the following ranges 2-6%w/w, 0-6%w/w and 5-15 g respectively. The reaction time and temperature were constant and set at 30 minutes and 150^{o}C 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 (Sattar et al., 2007).

2.3. Analytical Methods

Determination of furfural concentration in the hydrolysate was carried out spectrophotometrically at 530 nm using the method reported by Sattar et al. (2007). A sample of the hydrolysate (5 ml) was

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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 the 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. Design of Experiment

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 17 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.

$$x_i = \frac{X_i - X_o}{\Delta X} \tag{1}$$

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.

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

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. (Amenaghawon et al., 2015).

Table 1: Experimental range and levels of independent variables

Independent Variable	Symbols	Coded and Actual Levels		
		-1	0	+1
HCl concentration (%w/w)	X_1	2	4	6
H_2SO_4 concentration (%w/w)	X_2	0	3	6
Solids loading (g)	X_3	5	10	15

2.5. Artificial Neural Network Design

Commercial ANN Software, Neural Power, version 2.5 (C.P.C-X Software USA) was used to model and optimize the production of Furfural. The concentration of furfural produced was predicted using the Multilayer Full Feed Forward and the Multilayer Normal Feed Forward neural networks. Both network architectures were trained using different learning algorithms including: Incremental Back Propagation IBP, Batch Back Propagation BBP, Quick Propagation QP, Generic Algorithm GA, and Levenberg-Marquadt Algorithm LM. The training algorithm that best describes the furfural yield was selected based on their R^2 value. The network topology contained a single hidden layer while the number of neurons of this layer, the transfer function of the hidden and the output layers were determined iteratively by developing several neural networks with transfer functions of Sigmoid, Hyperbolic-tangent, Gaussian, Linear, Threshold, Linear and Bipolar Linear. Each of the network was trained using a stopping criteria of 100,000 iterations (Betiku et al., 2014).

2.6. Comparison of ANN and RSM performance

To check the accuracy of the models from ANN and RSM, coefficient of determination, (R^2) and root mean square error (RMSE) were evaluated using Equations 3 and 4. A very high R^2 and low RMSE value represent a goodness of fit of the model, which suggest that the model proves suitable for the adequate representation of the actual relationship between the response variable (furfural yield) and the independent variables (HCl concentration, H_2SO_4 concentration and Solids loading).

$$R^2 = 1 - \sum_{i=1}^{n} \left[\frac{\left(x_{i,cal} - x_{i,\exp}\right)^2}{\left(x_{avg,\exp} - x_{i,\exp}\right)^2} \right] \quad (3)$$

$$RMSE = \frac{\left[\sum_{i=1}^{n} \left(\left| x_{i,\exp} - x_{i,cal} \right| \big/ x_{i,\exp} \right) \right]}{n} \times 100 \quad (4)$$

Where:
n = number of experimental data while
$x_{i,cal}$ = calculated values,
$x_{i,exp}$ = experimental values
$x_{avg,exp}$ = average experimental values

3. RESULT AND DISCUSSION

3.1. RSM Modelling

This study investigated the modelling and optimization of furfural yield from sugarcane bagasse. The actual variables as well as the experimental and predicted values of furfural yield obtained are shown in Table 2. The response or dependent variable was chosen as the yield of furfural. Equation (5) 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.

$$Y = 5.07287 - 1.24194X_1 + 0.31738X_2 - 0.35340X_3 - 0.18750X_1X_2 + 0.086875X_1X_3 - 0.019250X_2X_3 + 0.13856X_1^2 + 0.13714X_2^2 + 0.012220X_3^2 \quad (5)$$

Where Y is the predicted response (furfural concentration) and X_1, X_2 and X_3 are the actual values of HCl concentration, H_2SO_4 concentration and solids loading respectively. Tables 3 and 4 show the results of analysis of variance (ANOVA) carried out to determine the fit of the statistical model. The analysis of variance (ANOVA) for quadratic model are shown in Table 3 while Table 4 shows the result of the R^2 value of the model, Adjusted R^2 value and the standard deviation, mean and coefficient of variation (C.V %) of the model variables. Table 4 shows a reasonable agreement between the R-Squared value of the model and its Adjusted R-Squared value. The F-value of the model is 9.84 and the p-value is <0.05, which showed that the model was significant (Zaida and Mohd Zulkhairi, 2014). The coefficient of determination (R^2) was 0.9268 suggesting that 92.68% of the variability in furfural concentration can be explained by this model. Regression also provides a way to evaluate the nature and the degree of correlation between dependent and independent variables. The closer the R^2 value is to 1.00, the stronger the model and the better the response predictions. The lack of fit F-value of 4.99 with p>0.05 implies that the lack of fit was not significant relative to the pure error. A non-significant lack of fit was considered good and was desired for the model to fit. Hence, the model could be used in theoretical prediction of the furfural produced from sugarcane bagasse.

Table 2: Experimental and predicted values of furfural yield

Run No	Factors (Actual values)			Response
	X_1	X_2	X_3	Furfural produced (g/l)
1	2	3	15	3.41
2	4	3	10	2.81
3	4	3	10	2.57
4	6	6	10	4.15
5	2	3	5	2.67
6	6	3	5	2.27
7	4	0	15	4.68
8	4	3	10	3.02
9	4	6	5	4.67
10	2	0	10	2.87
11	4	3	10	3.33
12	6	3	15	6.48
13	2	6	10	6.35
14	4	0	5	2.95
15	6	0	10	5.17
16	4	6	15	5.24
17	4	3	10	2.50

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

Sources	Sum of squares	df	Mean square	F value	p value
Model	27.45	9	3.05	9.84	0.0032
X_1	0.96	1	0.96	3.08	0.1225
X_2	2.81	1	2.81	9.08	0.0196
X_3	6.53	1	6.53	21.09	0.0025
X_1X_2	5.06	1	5.06	16.34	0.0049
X_1X_3	3.02	1	3.02	9.74	0.0168
X_2X_3	0.33	1	0.33	1.08	0.3340
X_1^2	1.29	1	1.29	4.17	0.0803
X_2^2	6.41	1	6.41	20.70	0.0026
X_3^2	0.39	1	0.39	1.27	0.2972
Residual	2.17	7	0.31		
Lack of Fit	1.71	3	0.57	4.99	0.0772
Pure Error	0.46	4	0.11	9.84	0.0032
Cor Total	29.62	16	3.05	3.08	0.1225

Table 4: Statistical information for ANOVA

Parameter	Value
Standard deviation	0.56
Mean	3.83
C.V. %	14.54
PRESS	28.10
R^2	0.9268
Adjusted R^2	0.8326
Predicted R^2	0.0512
Adeq precision	8.733

3.2. ANN Modelling

Multilayer Normal Feed Forward MNFF and Multilayer Full Feed Forward MFFF and a topology of the ANN which is the number of neurons in the hidden layer, transfer functions for both the hidden and output layers were selected, tested and used for the prediction furfural concentration produced. Training algorithms used include; Incremental Back Propagation IBP, Quick Propagation QP, Genetic Algorithm GA, Batch Back Propagation BBP and Levenberg-Marquadt Algorithm LM were all used to train the experimental data. The R^2 and RMSE values obtained from these trainings are shown in Table 5. Table 5 shows that QP was found to be the best training algorithm to predict the furfural concentration produced. In order to determine the optimum network topology, several iterations were carried out on the various transfer functions. The best transfer function was also used to find the optimum number of neurons for the network based on the R^2 value (Figure 1). The Hyperbolic-Tangent function for hidden layer and linear function for the output layer gave higher R^2 values compared all other transfer functions. The optimum number of neurons was determined to be three. The optimum network topology is therefore 3-3-1 i.e. three input factors for the input, three neurons in the hidden layer, one output layer and a transfer function of Hyperbolic-Tangent for the hidden and linear function for the output layer. The network was chosen because it gave the least RMSE value and an R^2 value closest to 1 (R^2 = 0.99225). ANN model developed in this present study is the MNFF Quick Propagation QP network with Hyperbolic-Tangent as the transfer function for the hidden and linear function for the output layer. The structure of the ANN model is shown in Figure 2.

Table 5: R^2 and RMSE values of MNFF and MFFF using different training algorithms

Learning algorithm	MNFF		MFFF	
	R^2	RMSE	R^2	RMSE
IBP	0.99163	0.17573	0.99226	0.16908
BBP	0.9900	0.18124	0.98814	0.17825
QP	**0.99225**	**0.16908**	0.99224	0.16908
GA	0.97362	0.18223	0.96251	0.18352
LM	0.97122	0.24264	0.97212	0.23254

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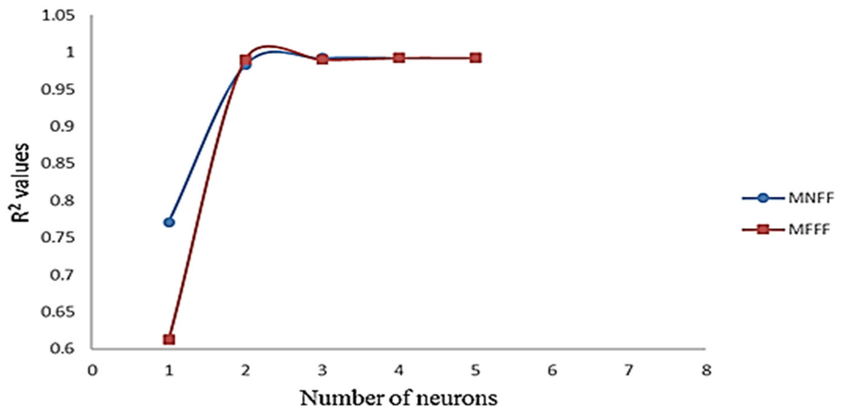

Figure 1: R^2 values and corresponding number of neurons for MNFF and MFFF using Hyperbolic-Tangent function for hidden layer and linear function for output layer

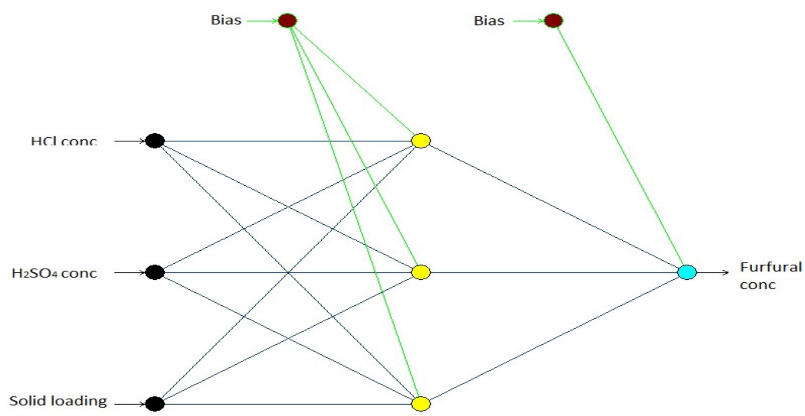

Figure 2: Final artificial neural network model

Predicted values of furfural concentration calculated has been found to have fitted well to the experimental data as shown in Table 6. This means that the model obtained from ANN could describe the relationship between the input variables: concentration of HCl, concentration of H_2SO_4 and solids loading and the furfural concentration produced. The optimum values of the variables that maximized furfural concentration produced was determined using the ANN model to be conc. of HCl of 5.999 w/w%, conc. of H_2SO_4 of 0.001 w/w% and solid loading of 14.997g. Furfural concentration produced at these optimum values was 8.679 g/L.

3.3. Comparison of RSM and ANN Model Performance

To determine the best model that better optimizes the variables, the R^2 and RMSE values of RSM and ANN models were evaluated and their results are shown in Table 3.5. These results have proved that ANN produces better accurate predictions due to it higher R^2 value (0.83 and 0.99 for RSM and ANN) and lower RMSE value (0.20147 and 0.16905 for RSM and ANN). Both models have been tested and it is observed that both models produced good fitting. But, ANN also proved to be a better optimization tool over RSM because of it higher R^2 value and lower RMSE value as shown in Table 6.

Therefore, ANN has been proved to be better than in the modelling and optimization of furfural production.

Table 6: Comparison of RSM and ANN performance models

Model	Conc of HCl (%) w/w	Conc of H_2SO_4 (%) w/w	Solids Loading (g)	Furfural Conc. (g/L)	R^2	RMSE
RSM	6.000	0.000	15.000	7.877	0.8326	0.20147
ANN	5.999	0.001	14.997	8.679	0.99225	0.16905

3.4. Effect of Factors on 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 3 shows the effect of the acid mixtures on furfural production. The results showed that at low value of HCl concentration (2w/w%), increase in H_2SO_4 concentration results to a mild decrease in furfural concentration till it gets to a value of (3w/w%) were further increase in H_2SO_4 led to an increase in furfural concentration. At high value of HCl (6w/w %), there is a mild decrease in furfural concentration as H_2SO_4 increases, thereafter a slight increase in furfural concentration is observed. At low value of H_2SO_4 (0 w/w%), increase in HCl results to a rapid increase in furfural concentration. At high value of H_2SO_4 (6w/w%) increase in HCl concentration results in a mild increase in furfural concentration. This shows that the concentration of hydrochloric acid has more statistical influence on furfural yield than sulphuric acid.

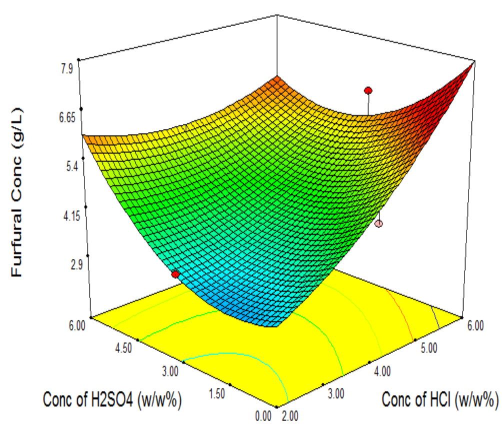

Figure 3: Response surface andshowing the effect of sulphuric acid and hydrochloric acid on furfural yield

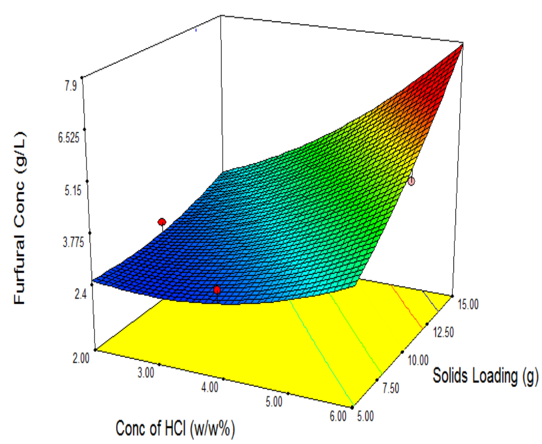

Figure 4: Response surface showing the effect of hydrochloric acid and solids loading on furfural yield

Figure 4 shows the response surface and contour plot illustrating the effect of solids loading and HCl concentration on furfural production. There was a high statistical influence of solids loading on furfural production compared to HCl concentration indicating that furfural production was more affected by solids loading compared to acid concentration. This is also corroborated by the fact that solids loading had a much smaller p value (0.0025) compared to HCl concentration as can be confirmed in Table 3. Figure 4 shows that the concentration of furfural produced increased with increase in solids loading. At a solid loading of 15 g, the maximum furfural concentration was observed at a constant HCl concentration of 6 %w/w. A similar result was reported by Mansilla et al. (2007) who reported an optimum liquid to solid ratio (a variant of solid loading) of 25 mL/g for the production of furfural from rice hull via acid hydrolysis. Similarly, Amenaghawon et al. (2014) reported an optimum liquid to solid ratio of 25 mL/g during a reaction time of 20.5 minutes and acid concentration of 2 %w/w to obtain a sugar yield of 81.65% from dilute sulphuric acid hydrolysed cassava bagasse. The generally mild 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) 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. The optimal levels of the independent variables were determined to be 6.00 w/w% of HCl, 0.00 w/w% H_2S0_4 and 15g of solids loading, after numerical optimization by RSM was carried out. The maximum concentration of furfural produced was also obtained to be 7.876g/L.

4. CONCLUSION

This study evaluated the performance of RSM and ANN on the modeling and optimization of furfural production from sugarcane bagasse. The effect of the three independent variables and their interactions on furfural concentration were established. The three variables showed significant influence on furfural production. A significant quadratic model with a p value of 0.0032 (i.e $p<0.05$) was obtained to predict furfural production as a function of the three variables using RSM. The optimal levels of the independent variables were determined to be 6.00w/w% of HCl, 0.00 w/w% of H_2S0_4 and 15g of solids loading, after numerical optimization by RSM was carried out. The maximum concentration of furfural produced was also obtained to be 7.876g/L. ANN was also used in modelling, it showed that multilayer normal feed forward (MNFF) and quick propagation (QP) with Tanh as hidden and linear as output layer transfer functions was the most successful learning algorithm for the furfural production. The optimum values of the variables that maximized furfural concentration produced was determined using the ANN model to be conc. of HCl of 5.999 w/w%, conc. Of H_2SO_4 of 0.001 w/w% and solids loading of 14.997g. Furfural concentration produced at these optimum values was 8.679 g/L. ANN also proved to be a better optimization tool over RSM because of it higher R^2 value (0.99225) and lower RMSE value (0.16905).

5. CONFLICT OF INTEREST

There is no conflict of interest associated with this work.

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