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STATISTICAL OPTIMIZATION OF THE TOTAL REDUCING SUGARS YIELD FROM THE DILUTE ACID HYDROLYSIS OF CORN STOVER

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ABSTRACT

The dilute acid hydrolysis of corn stoverusing sulphuric acid at different concentrations (2.32-5.68% w/w), hydrolysis times (18-52 min) and hydrolysis temperatures (76-144°C) were studied. The total reducing sugar present in the hydrolysate was quantified using DNS Method. A 2^3 five level Central Composite Design (CCD) was used to develop a statistical model for the optimization of process variables which are acid concentration, hydrolysis time and hydrolysis temperature. Response Surface Methodology (RSM) was employed for the optimization of the dilute acid hydrolysis conditions. The optimal hydrolysis conditions that resulted in the maximum total reducing sugar concentration were acid concentration of 4.99% (w/w), hydrolysis temperature of 90.09°C and hydrolysis time of 44.99 minutes. Under these conditions, the total reducing sugar concentration was obtained to be 20.9575 g/L. Quadratic model selected for the analysis was then validated.

INTRODUCTION

In recent years, more attention has been paid to the utilization of lignocellulosic materials. Lignocellulosic materials are plant biomass having the potential to be converted to value added by-products. It is composed of two carbohydrate polymers (cellulose and hemicellulose), and an aromatic polymer (lignin). Generating bioethanol from lignocellulosic biomass, which comprises of materials like agricultural residues (corn cobs and stover, crop straws, and bagasse), herbaceous crops (alfalfa, switch grass), short rotation woody crops, forest residues, wastepaper and other wastes (municipal and industrial) is potentially viable and economically sustainable because of their low cost, widespreadavailability, sustainable production and environmental friendliness (Feher et al., 2017).

Corn stover biomass stands out amongst the most plenteous feedstock materials for creating second generation bioethanol since it is readily available and sustainable (Yang et al., 2013). Notwithstanding, the change of corn stover to bioethanol is quite testing as a result of the unpredictable structure of the lignocellulosic biomass, consequently effective pre-treatment is important in order to adjust its structural and chemical composition to facilitate efficient hydrolysis of carbohydrates to fermentable sugars. These sugars are then converted to ethanol through fermentation (Amenaghawon et al., 2013).Dilute acid hydrolysis is the most generally utilized pre-treatment technique for lignocellulosic biomass. Dilute acid hydrolysis involves the breakdown of cellulose and hemicellulose polymers of the lignocellulosic biomass by acids at concentrations of about 1-10% using a moderate temperature to form individual sugar molecules which can be fermented to ethanol (Lenihan et al., 2011).

Turning waste to wealth has received a lot of attention globally. Agricultural wastes such as corn stover have the potential to be turned into value adding products. Biomass fuel is ever more appealing as it is a reasonable substitute to non-renewable fuels. The use of corn stoveras a potential source for reducing sugars which are raw materials for biofuel production and other applications, has vital effects on the international policy, the economy and rural development (J. Ben-Iwo et al, 2016). It reduces Nigeria's dependence on oil producing countries, it supports the recycling of agricultural waste thereby reducing pollution to the environment, and more importantly, it creates employment and provides an additional source of income for the country.

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This study was limited to the production of reducing sugars from thelignocellulosicbiomass alone. It did not pay any attention to the fermentation of these sugars to produce bioethanol. It was a small scale laboratory study where only small measured quantities were studied.

MATERIALS AND METHODS

2.1 Materials

A. 2.1.1 Reagents and Raw Materials

- Corn Stover
- Dilute Sulphuric Acid (2.32 to 5.68 %w/v)
- Distilled water
- 3,5 dinitrosalicylic Acid
- Analytical Glucose
- 2M Sodium hydroxide
- Rochelle salt (Potassium sodium tatarate)

B. 2.1.2 Equipment and Apparatus

- Grinding machine
- Scout Pro Electronic weighing balance SPU20001, S/N 7129151748
- Vision scientific Oven Model LDO-201-E
- Filter paper
- Jenway 6405 UV- Vis Spectrophotometer S/N 3976
- Stuart UC152 Hot plate magnetic stirrer S/N R60000548
- Funnel
- Test Tubes and Holder
- Beaker
- Conical Flask
- Thermometer (0 -360 degree Celsius)
- Pipette and Pipette sucker
- Measuring Cylinder
- Volumetric flask
- Reagent Bottles
- Round and flat bottom flasks
- Wash bottle

2.2 Methods

2.2.1 Pretreatment of Substrate

The substrate(Corn stover) was air dried for 2 weeks, after which it was ground and sieved.

2.2.2 Preparation of DNS Reagent

1g of DNS Acid was dissolved in 20ml of 2M Sodium Hydroxide and 50ml distilled water. To this mixture, 30g of Rochelle salt was added after which distilled water was added to make the volume up to 100ml. The solution was then filtered off to remove any precipitates.

2.2.3 Dilute Acid Hydrolysis

Dilute acid hydrolysis of substrate was carried out using sulphuric acid concentration range of 2.32%-5.68%, hydrolysis temperature range of (76-144) °C and an hydrolysis time range of (18-52) minutes. In a beaker 1.5g of substrate was weighed to which 50ml of sulphuric acid added. The mixture was placed on a hot plate magnetic stirrer with the magnet inserted and set to the hydrolysis temperature. The mixture was left to hydrolyze for a time range of 18 to 52 minutes after which the mixture removed and filtered. The filtrate (also known as the hydrolysate) was then analyzed for total reducing sugar by calorimetric method using a UV Spectrophotometer.

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2.2.4 Total Reducing Sugar Analysis by Calorimetric Method

2.2.4.1 Preparation of Glucose Standard Curve

5 glucose solutions of the concentrations of 20g/L, 40g/L, 60g/L, 80g/L and 100g/L were prepared. To a test tube, 1.8ml of distilled water was added to 0.2 ml of 20g/L glucose solution. 2ml of DNS Reagent was added and the mixture was then boiled for 5 minutes in a water bath, after which it was cooled to room temperature and then diluted to 24ml as shown in plate 3. The absorbance of the resulting solution was then measured at wavelength of 540 nm using a UV spectrophotometer. The process was repeated for glucose concentrations of 40g/L, 60g/L, 80g/L and 100g/L.

The resulting absorbance gotten for the different glucose solutions were then plotted against their concentrations.

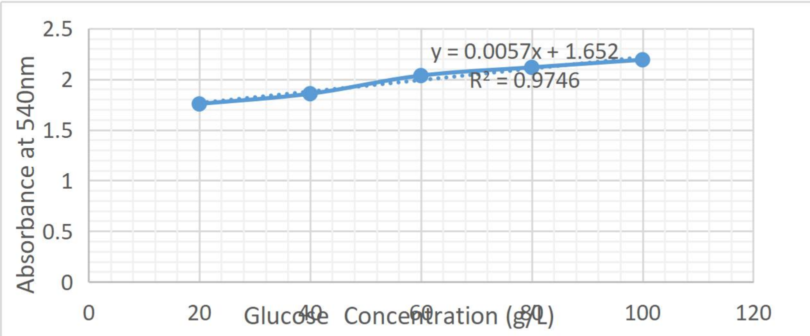

Figure 2.1: Glucose standard concentration curve

2.2.4.2 Determination of Total Reducing Sugar Content of Hydrolysate

To a test tube, 0.2ml of hydrolysate (reducing sugar solution), 1.8ml of Distilled water and 2ml of DNS Reagent were added. The mixture was then boiled for 5 minutes in a water bath, after which it was cooled to room temperature and then diluted to 24ml. The absorbance of the resulting solution was then measured at a wavelength of 540nm using a UV Spectrophotometer. The absorbance gotten from the spectrophotometer was used to obtain the concentration of total reducing sugars from the Glucose standard concentration curve. The process was repeated for all the hydrolysates gotten after each hydrolysis.

2.2.5 Design of Experiment

A Central Composite Design (CCD) with three factors was used to examine the response pattern and to determine the optimum combination of acid concentration, hydrolysis temperature and hydrolysis time for maximizing the sugar recovery from corn stover. The range and levels of variables optimized are as shown in Table 2.1. The Central Composite Design combines the vertices of the hypercube whose coordinates are given by a 2^n factorial design with star points. The star points provide the estimation of curvature of the nonlinear response surface (Amenaghawon et al., 2013). The experimental design was developed using Design Expert® 7.0.0 and it resulted in 20 runs as shown in Table 2.2. The 20 experimental runs were randomized to maximize the effects of unexplained variability in the responses observed.

Table 2.1: Coded and Actual Levels of the factors for the 3 Factor Central Composite Design

Independent Variables	Symbols	Coded levels				
		-1.68	-1	0	1	1.68
		Actual Levels				
Acid Concentration (%w/v)	X_1	2.32	3	4	5	5.68
Hydrolysis temperature (°C)	X_2	76	90	110	130	144
Hydrolysis Time (min)	X_3	18	25	35	45	52

RESULTS AND DISCUSSION

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3.1 Result Presentation

Table 3.1: Experimental results for the dilute acid hydrolysis of corn stover

Runs	Factors						Response
	Coded Values			Actual Values			Total Reducing Sugar Concentration (g/L)
	X_1	X_2	X_3	X_1	X_2	X_3	Y_1
1	1	1	1	5	130	45	20.89
2	1	1	-1	5	130	25	13.96
3	1	-1	1	5	90	45	20.28
4	1	-1	-1	5	90	25	12.02
5	-1	1	1	3	130	45	17.75
6	-1	1	-1	3	130	25	13.27
7	-1	-1	1	3	90	45	18.60
8	-1	-1	-1	3	90	25	8.28
9	-1.68	0	0	2.32	110	35	12.09
10	1.68	0	0	5.68	110	35	16.18
11	0	-1.68	0	4	76	35	16.99
12	0	1.68	0	4	144	35	18.09
13	0	0	-1.68	4	110	18	7.99
14	0	0	1.68	4	110	52	20.75
15	0	0	0	4	110	35	14.86
16	0	0	0	4	110	35	14.57
17	0	0	0	4	110	35	15.02
18	0	0	0	4	110	35	14.99
19	0	0	0	4	110	35	16.82
20	0	0	0	4	110	35	13.98

3.1.1 Linear Model Fit

Final Equation in terms of the coded values:

Sugar Concentration = $15.27 + 1.18X_1 + 0.62X_2 + 3.75X_3$ 3.1

Final Equation in terms of actual factors:

Sugar Concentration = $-5.99826 + 1.18098X_1 + 0.031060X_2 + 0.37505X_3$ 3.2

Table 3.2: ANOVA table for the Linear model fit for the hydrolysis of corn stover

Source	Sum of Squares	Df	Mean Square	F value	p-value Prob. > F	Inference
Model	218.20	3	72.73	40.96	< 0.0001	Significant
X_1	19.05	1	19.05	10.73	0.0048	
X_2	5.32	1	5.32	2.99	0.1028	
X_3	193.83	1	193.83	109.17	< 0.0001	
Residual	28.41	16	1.78			
Lack of Fit	27.65	11	2.51	16.50	0.0031	Not significant
Pure Error	0.76	5	0.15			
Cor Total	246.61	19				

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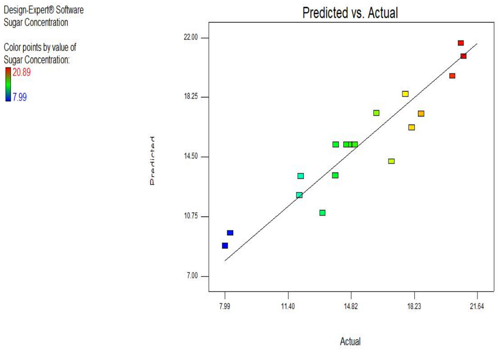

Figure 3.1: Predicted vs Actual Response values for the Linear Model Fit for the dilute acid hydrolysis of corn stover

Table 3.3: Data for the Linear model fit

R squared	0.8848
Adj R squared	0.8632
Pred. R squared	0.7958
Adeq. Prec.	21.398
Standard deviation	1.33
Mean	15.27

3.1.2 Two Factor Interaction Model Fit

Final Equation in terms of the coded values

Sugar Concentration = 15.27 + 1.18X_1 + 0.62X_2 + 3.75X_3 – 0.20X_1X_2 + 0.049X_1X_3 - 0.90X_2X_3…. 3.3

Final Equation in terms of actual factors

Sugar Concentration = -26.94107 + 2.10348X_1 + 0.22765X_2 + 0.84849X_3 – 9.93750E-003X_1X_2 + 4.87500E-003X_1X_3 – 4.48125E-003X_2X_3…… 3.4

Table 3.4: ANOVA table for the Two Factor Interaction model fit for the hydrolysis of corn stover

Source	**Sum of Squares**	**Df**	**Mean Square**	**F value**	**p-value Prob. > F**	**Inference**
Model	224.96	6	37.49	22.52	< 0.0001	Significant
X_1	19.05	1	19.05	11.44	0.0049	
X_2	5.32	1	5.32	3.19	0.0973	
X_3	193.83	1	193.83	116.40	< 0.0001	
X_1X_2	0.32	1	0.32	0.19	0.6703	
X_1X_3	0.02	1	0.02	0.01	0.9165	
X_2X_3	6.43	1	6.43	3.86	0.0712	
Residual	21.65	13	1.67			
Lack of Fit	20.89	8	2.61	17.14	0.0031	Not significant
Pure Error	0.76	5	0.15			
Cor Total	246.61	19				

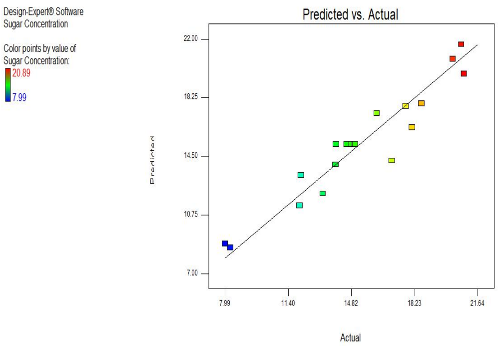

Figure 3.2: Predicted vs Actual Response values for the Two Factor Interaction Model Fit for the dilute acid hydrolysis of corn stover

Table 3.5: Data for the Two Factor model fit

R squared	0.9122
Adj R squared	0.8717
Pred. R squared	0.7505
AdeqPrec	16.9995
Standard deviation	1.29
Mean	15.27

3.1.3 Quadratic Model Fit

Final Equation in terms of the coded values

Sugar Concentration = 14.70 + 1.18X_1 + 0.62X_2 + 3.75X_3 – 0.20X_1X_2+ 0.049X_1X_3 - 0.90X_2X_3 -0.15X_1^2 + 1.03X_2^2 -0.063$X_3^2$3.5

Final Equation in terms of actual factors

Sugar Concentration = 0.64658 + 3.27483 X_1 - 0.34093 X_2 + 0.89266 X_3 – 9.93750E-003 X_1X_2 + 4.87500E-003X_1X_3 – 4.48125E-003X_2X_3 - 0.14642X_1^2 + 2.58447E-003X_2^2 -6.30970E-004$X_3^2$3.6

Table 3.6: ANOVA table for the Quadratic model fit for the hydrolysis of corn stover

Source	**Sum of Squares**	**Df**	**Mean Square**	**F value**	**p-value Prob. > F**	**Inference**
Model	242.19	9	26.91	60.85	< 0.0001	Significant
X_1	19.05	1	19.05	43.07	< 0.0001	
X_2	5.32	1	5.32	12.02	0.0060	
X_3	193.83	1	193.83	438.28	< 0.0001	
X_1X_2	0.32	1	0.32	0.71	0.4177	
X_1X_3	0.02	1	0.02	0.04	0.8399	
X_2X_3	6.43	1	6.43	14.53	0.0034	
X_1^2	0.31	1	0.31	0.70	0.4232	
X_2^2	15.92	1	15.92	36.00	0.0001	
X_3^2	0.06	1	0.06	0.13	0.7218	
Residual	4.42	10	0.44			
Lack of Fit	3.66	5	0.73	4.81	0.0549	Not significant
Pure Error	0.76	5	0.15			
Cor Total	246.61	19				

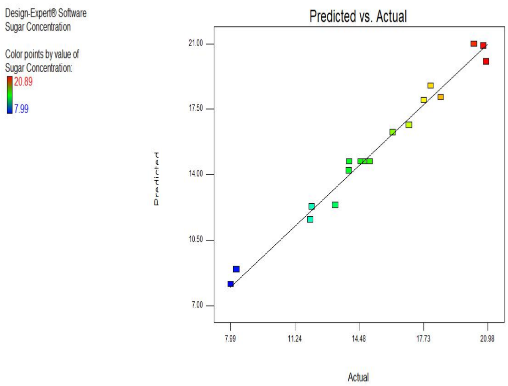

Figure 3.3: Predicted vs Actual Response values for the Quadratic Model Fit for the dilute acid hydrolysis of corn stover

Table 3.7: Data for the Quadratic model fit

R squared	0.9821
Adj R squared	0.9659
Pred. R squared	0.8676
AdeqPrec	27.298
Standard deviation	0.67
Mean	15.27

3.1.4 Cubic Model Fit

Final Equation in terms of the coded values

Sugar Concentration = 14.7 + 1.22X_1 + 0.32X_2 + 3.75X_3 – 0.20X_1X_2+ 0.049X_1X_3 - 0.90X_2X_3 -0.15X_1^2 + 1.03X_2^2 - 0.063X_3^2 +0.56$X_1X_2X_3$ +0.51$X_1^2X_2$ – 4.191E-003$X_1^2X_3$ -0.060$X_1X_2^2$ 3.7

Table 3.8: ANOVA table for the Cubic model fit for the hydrolysis of corn stover

Source	**Sum of Squares**	**Df**	**Mean Square**	**F value**	**p-value Prob. > F**	**Inference**
Model	245.62	13	18.89	114.97	< 0.0001	Significant
X_1	8.36	1	8.36	50.89	0.0004	
X_2	0.61	1	0.61	3.68	0.1035	

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X_3	81.41	1	81.41	495.35	< 0.0001	
X_1X_2	0.32	1	0.32	1.92	0.2149	
X_1X_3	0.02	1	0.02	0.12	0.7454	
X_2X_3	6.43	1	6.43	39.10	0.0008	
X_1^2	0.31	1	0.31	1.88	0.2198	
X_2^2	15.92	1	15.92	96.88	< 0.0001	
X_3^2	0.06	1	0.06	0.36	0.5700	
$X_1X_2X_3$	2.54	1	2.54	15.47	0.0077	
$X_1^2X_2$	0.88	1	0.88	5.37	0.0597	
$X_1^2X_3$	0.00	1	0.00	0.00	0.9855	
$X_1X_2^2$	0.01	1	0.01	0.07	0.7976	
$X_1X_3^2$	0.00	0				
$X_2^2X_3$	0.00	0				
$X_2X_3^2$	0.00	0				
X_1^3	0.00	0				
X_2^3	0.00	0				
X_3^3	0.00	0				
Residual	0.99	6	0.16			
Lack of Fit	0.22	1	0.22	1.47	0.2789	Not significant
Pure Error	0.76	5	0.15			
Cor Total	246.61	19				

Table 3.9: Data for the Cubic model fit

R squared	0.9960
Adj R squared	0.9873
Pred. R squared	0.7968
AdeqPrec	37.62
Standard deviation	0.41
Mean	15.27

3.1.5 Optimization of the Dilute Acid Hydrolysis of Corn Stover

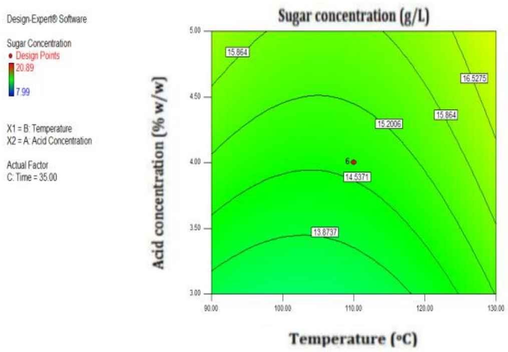

Figure 3.4a:Contour plot showing the effect of acid concentration and temperature on thetotal reducing sugar concentration

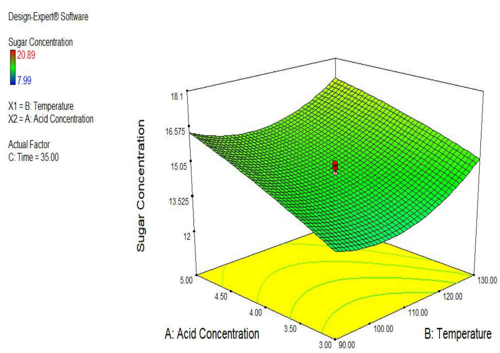

Figure 3.4b: Response surface plot showing effect of acid concentration and temperature on the total reducing sugar concentration

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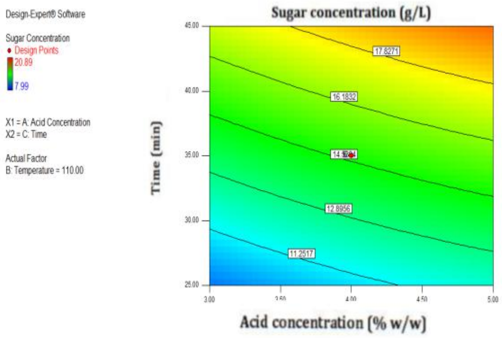

Figure 3.5a: Contour plot showing the effect of reaction time and acid concentration on the total reducing sugar concentration

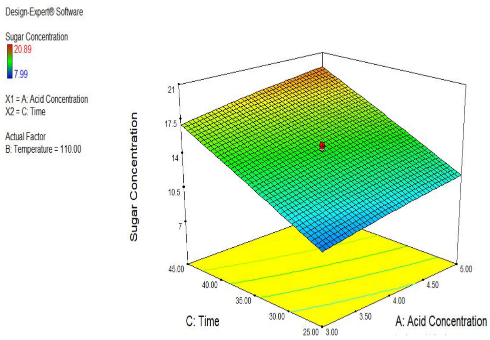

Figure 3.5b: Response surface plot showing the effect of reaction time and acid concentration on the total reducing sugar concentration

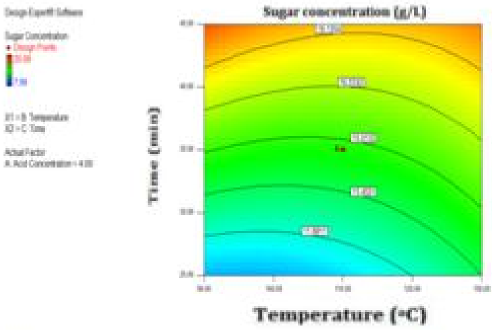

Figure 3.6a:Contour plot showing the effect of reaction time and hydrolysis temperature on the total reducing sugar concentration

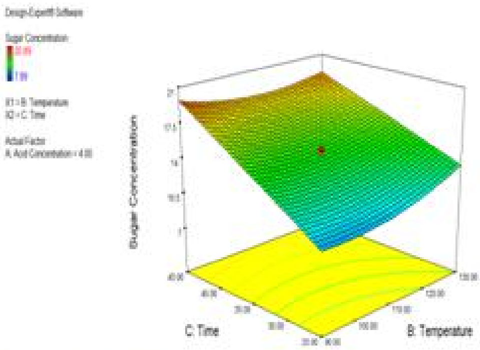

Figure 3.6b:Response surface plot showing the effect of reaction time and hydrolysis temp. on the total reducing sugar concentration

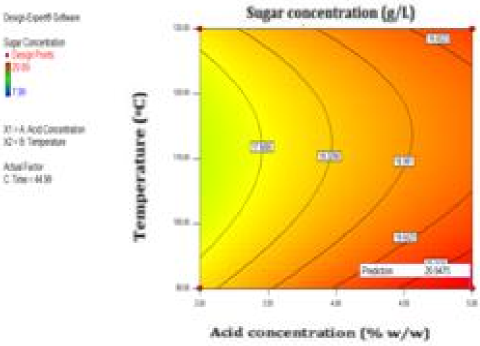

Figure 3.7a: Optimum reaction time for thehydrolysis of corn stover

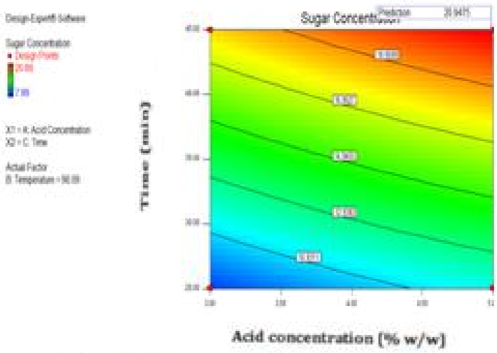

Figure 3.7b: Optimum reaction temperature for the hydrolysis of corn stover

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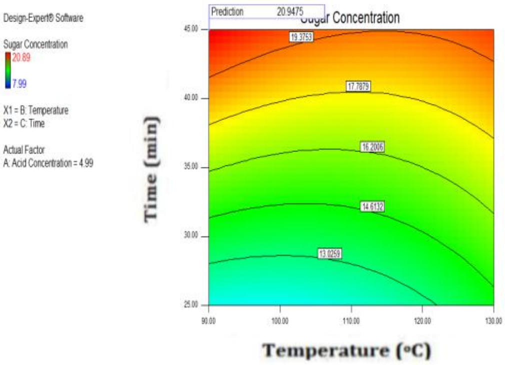

Figure 3.7c: Optimum acid concentration
For the hydrolysis of corn stover

Table 3.10: Optimum conditions for the hydrolysis of corn stover

Factor	Value
X_1- Acid Concentration (%w/w)	4.99
X_2- Temperature (°C)	90.09
X_3- Time (min)	44.99

3.2 Discussion

3.2.1 Statistical Analysis of the Results obtained from the Dilute Acid Hydrolysis of Corn Stover

Similar statistical analysiswas done for the corn stover. The experimental results for reducing sugar concentrations obtained for the dilute acid hydrolysis of corn stover are shown in Table 3.1. From Table 3.1, it was observed that the highest reducing sugar concentration yields were obtained at very high concentrations, very high reaction time and moderately high temperatures.

3.2.2 Linear Model Fit

The linear model fit for the experimental results obtained for the dilute acid hydrolysis of the corn stoverproduced equations 3.1 and 3.2 in terms of the coded and actual values.

From table 3.3, the model coefficient of determination (R^2) , adjusted R^2, predicted R^2 and adequate precision values obtained were 0.8848, 0.8632, 0.7958 and 21.398 respectively. The R^2 value of 0.8848 indicates the model could explain 88.48% of the response data variability. The adjusted $R^2$and predicted R^2values of 0.8632 and 0.7958 showed that the predicted and adjusted R^2 values are in reasonable agreement (within 0.2). The adequate precision value of 21.398 indicates an adequate signal and a desirable ratio, hence the model can be used to navigate the design space.

A standard deviation of 1.33 and mean of 15.27 were also obtained for the model. Table 3.2 shows the ANOVA table for the linear model fit. The Model F-value of 40.96 implies the model is significant. The linear model generated has a p-value less than 0.0001, hence $X_1$and X_3 are significantmodel terms. The lack of fit F-value of 16.50 obtained implies that the lack of fit is significant relative to the pure error.Figure 3.1 shows the plot of the predicted versus the actual response values. From the plot, it is observed that the actual values are not so far apart from the predicted values.

3.2.3 Two Factor Interaction Model Fit

The two factor model fit for the experimental results obtained for the dilute acid hydrolysis of the corn stoverproduced equations 3.3 and 3.4 in terms of the coded and actual values.

Model coefficient of determination (R^2), adjusted R^2, predicted R^2 and adequate precision values of 0.9122, 0.8717, 0.7505 and 16.995 were obtained respectively. The R^2 value of 0.9122 indicates that the model could explain 91.22% of the response data variability. Compared to the linear fit, the R^2, adjusted R^2, predicted R^2 and the adequate precision values all decreased. The adjusted $R^2$and predicted R^2values of 0.8717 and 0.7505 showed that the predicted and adjusted R^2 values are in reasonable agreement (within 0.2). The adequate precision value, even though it decreased (comparedto linear fit), it is still greater than 4, hence indicating an adequate signal and a desirable signal to noise ratio, hence the model can be used to navigate the design space.
A standard deviation of 1.29 and mean of 15.27 were obtained for the model. Table 3.4 shows the ANOVA table. From which the model F-value of 22.52 implies the model is significant. X_1, X_3 and $X_2X_3$are significant terms. The lack of fit F-value of 17.14 implies that the lack of fit is not significant relative to the pure error and there is a 0.31% chance that a “Lack of Fit F-value” this large could occur due to noise. Compared to the linear model fit, the “Lack of Fit F-value” obtained was higher, but its probability of occurrence the same.

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This model is more significant than the linear model, as the R^2 values obtained were closer to 1 than that obtained for the linear model. It shows the effects of the interactions of two independent variables on the response. From the ANOVA table, the interaction between the terms X_1,X_2, X_1,X_3 and X_1,X_3 had no significant effect on the response.

Figure 3.2shows the plot of the predicted versus the actual response values. From the plot, it is observed that the actual values are closer to the predicted values, compared to the linear model.

3.2.4 Quadratic Model Fit

The quadratic model fit for the experimental results obtained for the dilute acid hydrolysis of the corn stoverproduced equations 3.5 and 3.6 in terms of the coded and actual values.

From Table 3.7, the model coefficient of determination (R^2), adjusted R^2, predicted R^2 and adequate precision values obtained were 0.9821, 0.9659, 0.8676 and 27.298 respectively. The R^2 value of 0.9821 indicates the model could explain 98.21% of the response data variability, and implies the model is significant. Compared to the linear and two factor model fits, the R^2 and adjusted R^2 values increased. The predicted R^2 value obtained from this model was greater than those of linear and two factor models. The adequate precision value was higher than that of the two factor model but lower than the value for the linear model. The adjusted $R^2$and predicted R^2values of 0.9659 and 0.8676 showed that the predicted and adjusted R^2 values are in reasonable agreement. The adequate precision has a value greater than 4, indicating an adequate signal and a desirable signal to noise ratio, hence the model can be used to navigate the design space.

A standard deviation of 0.67 and a mean of 15.27 were obtained for this model. Table 3.6 is the ANOVA table from which the Model F-value of 60 implies the model is significant. X_1, X_2,X_3, X_2X_3 and $X_2^2$are significant terms. The lack of fit F-value of 4.81 implies that the lack of fit is not significant relative to the pure error, and there is a 5.49% chance that a "Lack of Fit F-value" this large could occur due to noise.

The quadratic model is more significant than both the linear and the two factor model, as the R^2 values obtained were closer to 1 than those obtained for the linear and two factor models. It shows the effects of the interactions of two independent variables, and the quadratic effects of each of the independent variables on the response. From the ANOVA table, the interaction between X_2 and X_3 (i.eX_2X_3) had significant effect on the response, while the interaction between the terms X_1,X_2 and X_1,X_3 had no significant effect on the response. Also, the quadratic effect of the independent variable, X_2 ($i.e\ X_2^2$) had a significant effect on the response.

Figure 3.3shows the plot of the predicted response values versus the actual response values. From the plot, it is observed that the actual values are closer to the predicted values, compared to the linear model and the two factor interaction model.

3.2.5 Cubic Model Fit

The quadratic model fit for the experimental results obtained for the dilute acid hydrolysis of the corn stoverproducedequation 3.7 in terms of the coded values.

The Final Equation in terms of the actual values was not available because some of the model terms were aliased with one another. From Table 3.9, the model coefficient of determination (R^2), adjusted R^2, predicted R^2 and adequate precision values obtained were 0.9960, 0.9873, 0.7968 and 37.62 respectively. The R^2 value of 0.9960 indicates that the model could explain 99.60% of the response data variability, and implies that the model is significant. The model's R^2 value and the predicted R^2 value was the highest compared to the previous models studied. The adjusted R^2 and the predicted R^2 values obtained were in reasonable agreement since their values were within 0.2 of each other. The adequate precision has a value greater than 4, indicating an adequate signal and a desirable signal to noise ratio, hence the model can be used to navigate the design space.

A standard deviation of 0.41 and a mean of 15.27 were obtained for this model. Table 3.8 shows the ANOVA results for the cubic model fit. From the ANOVA table, Model F-value of 114.97 implies the model is significant. X_1, X_3, X_2X_3 and X_2^2 are significant terms. The lack of fit F-value of 1.47 implies that the lack of fit is not significant relative to the pure error, and there is a 27.89% chance that a "Lack of Fit F-value" this large could occur due to noise.

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Also from the table, the model terms $X_1X_3^2$,$X_2^2X_3$, $X_2X_3^2$, X_1^3, X_2^3, and X_3^3 did not have any values because $X_1X_3^2$ aliased $X_1X_2^2$, $X_2^2X_3$ aliased $X_1^2X_3$, $X_2X_3^2$ aliased $X_1^2X_2$, X_1^3 aliased X_1 and $X_1X_2^2$, X_2^3 aliased X_2 and $X_1^2X_2$, X_3^3 aliased X_3 and $X_1^2X_3$.

As aforementioned, although the cubic model studied the effects of interaction of three independent variables, the cubic effects of each independent variable, and gave the highest coefficient of determination (R^2) and adjusted R^2 values, it was not suitable for this optimization problem because of the fact that some of the model terms were aliased with one another.

3.2.6 Optimization of the Dilute Acid Hydrolysis of Corn Stover

Again, the quadratic model was selected for the optimization because it had a very high coefficient of determination (R^2) and had no alias between its model terms. To obtain the optimum conditions for the hydrolysis of corn stover that will yield the maximum total reducing sugar concentration, response surface plots were generated for the quadratic model. The 3-D plots and contour plots were obtained by keeping one variable constant at the centre while varying the other two variables. The response generated from these plots expressed the effects of acid concentration, hydrolysis temperature and hydrolysis time, on the total reducing sugar concentration.

Figures 3.4a and 3.4b show the contour and response plots for the effect of acid concentration and temperature, on the total sugar concentration. From figure 3.4b, the lines at the base of the surface plot are curves and they indicate high interaction and proportionality between acid concentration and temperature. The more curvature, the more interaction. Figure 3.4a and 3.4b show that the total reducing sugar concentration increased as the acid concentration increased from 3 to 5%w/w. Maximum sugar recovery was obtained at an acid concentration of 5%w/w.

Figure 3.5a and 3.5b show the contour plot and response surface plot for the effect of reaction time and acid concentration, on the total sugar concentration. From figure 3.5b, the lines at the base of the surface plot indicate minimal interaction between reaction time and acid concentration and also inverse proportionality because they are straight lines. There is a weak inverse proportionality towards the lower levels of time and acid concentration. Astheir levels increase, their interaction increased. Figure 3.5a and 3.5b show that as the acid concentration increased with the reaction time, the total reducing sugar also increased. Maximum sugar recovery was obtained at a time of 45 minutes.

Figure 3.6a and 3.6b show the contour plot and response surface plot for the effect of reaction time and temperature, on the total sugar concentration. From figure 3.6b, the lines at the base of the response surface plot are curved lines, with the curves not so defined indicating an inverse and quadratic kind of interaction and proportionality between the temperature and time. The figures also show that for all the temperatures that were investigated, the total reducing sugar concentration increased with reaction time.

To select the optimum conditions for the hydrolysis reaction using the quadratic model, the model was analyzed and the maximum response predicted as shown on figure 3.7a, 3.7b and 3.7c respectively.

Figure 3.7a shows curved lines which indicate a high level of interaction and proportionality between temperature and acid concentration. The optimal predicted sugar obtainable is 20.9475g/L and the time taken to get to this concentration as predicted is 44.99 minutes.

Figure 3.7b shows curved lines which indicate a low level of interaction and inverse proportionality between time and acid concentration. The optimal predicted sugar obtainable is 20.9475g/L and the temperature taken to get to this concentration as predicted is 90.09°C.

Figure 3.7c shows curved lines which indicate a moderate level of interaction and inverse quadratic proportionality between time and temperature. The optimal predicted sugar obtainable is 20.9475g/L and the acid concentration taken to get to this concentration as predicted is 4.99%w/w.

From figures 3.7a, 3.7b and 3.7c, the predicted maximum total sugar concentration was 20.9475g/L and it would be achieved under the conditions stated in Table 3.10. The maximum total reducing sugar concentration obtained from the dilute acid hydrolysis of corn stover at the optimum conditions in Table 3.10 from a laboratory test was 20.68g/L which was quite close to the predicted value of 20.95g/L. The result obtained from the laboratory test shows that there is an excellent agreement between the laboratory result and predicted result, hence confirming the validity of the model.

CONCLUSION

In this work, the dilute acid hydrolysis of corn stover was studied quantitatively using a 2^3 central composite design for response surface methodology. The following conclusions were drawn from the study:

- Corn stover is a good feedstock for bioethanol production as the acid hydrolysis produced reducing sugars which can be fermented to produce bioethanol.
- Acid concentration, hydrolysis time and hydrolysis temperature all significantly influenced the dilute acid pre-treatment of corn stover, and the concentration of total reducing sugars produced.
- Reaction time has more impact on the total reducing sugar yield from corn stover compared to acid concentration and reaction temperature.
- A validated quadratic model fully expressed the relation between the total reducing sugar concentration produced during the acid hydrolysis relative to the acid concentration, hydrolysis temperature and hydrolysis time.
- Based on the results obtained for the corn stover hydrolysis, it is a good source of total reducing sugar,producing an optimum yield of total reducing sugars at the respective factor values of 5%w/w, 90°C and 45 minutes.

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