DETERMINATION AND OPTIMIZATION OF EFFECT OF PROCESS PARAMETERS ON FURFURAL YIELD FROM MICROALGAE

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Abstract: This paper reports a study on the production of furfural from algae biomass, optimizing the process parameters using Response Surface Methodology (RSM). Central composite design (CCD) was employed to determine the effect of process parameters: temperature (65 – 140°C), time (30 – 90 min), and concentration of 1MH_2SO_4 (35 mL/g-70 mL/g) on the yield of furfural. The regression analysis showed good fit of the experimental data to the second-order polynomial (Quadratic model) with coefficient of determination (R^2) value of 0.9807 and model *F*-value of 56.54. The model was found to be significant as its Predicted R^2 of 0.8771 was in close agreement with the Adjusted R^2 of 0.9634. Its probability value was greater than F value. A good fit of the model was further validated as F-value of 4.17 was found to be greater than the P-value of 0.0714. Furfural yield of 69.29% was predicted by the model at optimum condition: reaction temperature of 140°C, H_2SO_4quantity of 35.02 mL and reaction time of 65.3 min.Validation experiments conducted at the optimum conditions gave an experimental value of 67.10% which was in close agreement with the predicted value of 69.26%.
Keywords: Acid hydrolysis, Algae biomass, Lignocellulosics, RSM, concentration, models

Introduction

The need to replace fossil-based chemicals by renewable alternatives has led to an increased interest in the production of platform chemicals originating from lignocellulosic biomass (Sweygers*et al*., 2016). However, the search for an efficient process to convert lignocellulosic biomass into platform chemicals is an important challenge, thus it requires process intensification. Lignocellulosic biomass is any organic matter that is available on a renewable basis which includes energy crops, agricultural residues, aquatic plants, wood and wood residues as well as other waste materials (Maity, 2015).Zeitsch (2000) reported that in theory, any material containing a large amount of the pentose (five carbons) sugars arabinose and xylose can serve as a raw material for furfural production.

Furfural, a chemical similar to 5-hydroxymethylfurfural, is one of the furan derivatives produced from the hemicellulosic fraction of lignocellulosic, which is considered a promising commodity bio-based chemical because of the possibility of its use in the production of several products such as antacids, paints, fuel additives and fertilizers and many others that are normally produced from non-renewable resources (Jeon *et al*., 2016). It has been reported by Tong *et al*. (2010) that in recent years, an increasing effort has been devoted to find paths to utilize biomass as feedstock for the production of organic chemical because of its abundance, renewability and worldwide distribution. This is because plant based renewable resources are a strategic option to meet the growing need for industrial building blocks as it offers economic and environmental advantages for the development of this resource base.

Also, it has been established by Jones and Mayfield (2012) that, microalgae offer several advantages over terrestrial plants as a source of transportation biofuels, including high growth rates, high lipid content, the ability to grow large cultures on non-agricultural land, and the ability to rapidly improve strains and produce co-products. Machado *et al*. (2016) has opined that despite these promising characteristics, the economic viability of algae-based biofuels is still uncertain. Recent estimates place a barrel of algae-based oil at US $450–$2300, compared with US $80–110 for crude oil in 2012 (Alabi*et al*., 2009). Efforts to lower the cost of algae oil production are currently focused on nutrient sourcing and usage, harvesting, strain isolation, production management, fuel extraction, co-product development, and residual biomass sourcing such as proteins, furfural and glucose (Hannon *et al*., 2010). After the desired biodiesel have been extracted from harvested algae, a significant portion of residual biomass remains, with several options currently being explored for their usage. These options include anaerobic digestion of biomass to produce methane (Machado *et al*., 2016), pyrolysis of dry biomass to produce bio-oil (Yan *et al*., 2014) or use as a fertilizer (Lopez *et al*., 2012).

This research focus on another alternative, specifically using a portion of the processed biomass to produced furfural. The aim of this research is to study the effect of process conditions on the yield of furfural obtained from microalgae biomass and investigate the conversion of microalgae into furfural. An optimization for the conversion of hemicellulose to furfural by variation of the reaction temperature (A), the H_2SO_4 concentration *(B)* and the reaction time (C) was also investigated. Thereafter, the Response Surface Methodology (RSM) was used in the optimization strategy and the conditions to maximize the yield of furfural were determined.

Materials and Methods

Experimental design for furfural production

In this study, the Response Surface Methodology (RSM) approach was followed for the optimization of furfural production yield (Yemis and Mazza, 2012; Sweygers*et al*., 2016). Reaction temperature (A), the H_2SO_4 concentration (B) and the reaction time (C) are considered the most important influencing parameters for the acid hydrolysis of lignocellulosic polysaccharides, and were chosen as independent variables. Generally, the reaction conditions involved a trade-off between the A, B and C. For the dilute acid hydrolysis, a low H_2SO_4 concentration is desired because of the high cost concerning the reactor materials of construction. These three factors were chosen and varied as shown in Table 1.

Table 1:Factors varied for the CCD design of experiment

S/N	Factor	Low Level	High Level
1	A=Temperature (°C)	65	140
2	B=Concentration of H_2SO_4(ml/g of feedstock)	35	70

3	C=Time (min)	30	90

From the CCD design above in Table 1, A total of twenty (20) experimental combinations were run while statistical analysis was performed on the output response (furfural yield), optimization of the investigated factors was done and optimum conditions were determined.
The microalgae were collected from waste water pond at Ahmadu Bello University (ABU), Zaria and was identified at botany department ABU, Zaria. The identified species of microalgae from the waste pond are *Closterium species*, *ScenedesmusOpoliensis*, *Cosmarium*, *ScenedesmusObliquus*, *ScenedesmusbijugaStaurastrum*SPP, *Oscillatoria*SPP, *Spirulina*, *Merismopedia*and *Ankistrodesmusfalcatus (Cyanobacteria).* The microalgae was then filtered using vacuum filter and dried in oven at about 80°C and finely grounded and sieved to 1000 µm mesh size. The prepared samples were analyzed for dried moisture content, ash contents, lignin, oil content, cellulose and hemicellulose contents (Ameh*et al.*, 2016) after the oven drying at Institute for Agricultural Research (IAR/ABU), Zaria.
Furfural production was carried out using a batch reactor and a distillation system. Sulphuric acid solution (1M of variable quantities), 30 g of sodium chloride and 30 g of microalgae sample, were introduced into a 500 mL 3-necked round bottom flask connected to a Vigreux column and a Condenser and the reaction mixture was heated using heating mantle. The effluent from the batch reactor experienced rapid distillation at 105°C. The distillate from the reaction mixture was collected over 40 mL chloroform in a separating funnel. After 2 h of distillation (after which there was no increase in the distillate collected), the furfural-chloroform layer (collected in the separating funnel) was decanted, then poured into a conical flask (Ameh*et al.*, 2016). The decanted furfural-chloroform mixture was subjected to a rotary evaporation at a temperature of 65°C for 10 min. This procedure was repeated for various reaction temperatures, concentration and reaction time generated by RSM.

$(C_5H_8O_4)n + nH_2O \rightarrow (C_5H_{10}O_5)n$
PentosansPentoses
$(C_5H_{10}O_5)n \rightarrow (C_5H_4O_2)n + 3H_2O$
Pentoses Furfural
Scheme 1: Reaction for the Production of furfural

The experimental set up during the research is shown in Plate 1

Plate 1: Experimental set up for production of furfural from microalgae

Results and Discussion

Table 2 shows the design matrix of the Central Composite Design (CCD) for furfural production from microalgae and the responses obtained after performing the experiment.

Yield of furfural

The yield of furfural was calculated according to Equation 1

$$\text{Furfural (\%)} = \frac{\text{mass of furfural produced (g)}}{\text{mass of microalgae biomass (g)}} \times 100 \qquad (1)$$

The yields of furfural from the various runs is shown in Table 2

Table 2: Experimental (CCD) design and results (conversion of microalgae to furfural)

Exp'tal Run	A	B	C	Response (Furfural yield) (%)
1	102.50	52.50	60.00	55.07
2	65.00	70.00	30.00	27.67
3	39.43	52.50	60.00	20.00
4	140.00	35.00	30.00	60.05
5	102.50	52.50	60.00	54.55
6	105.50	52.50	60.00	54.71
7	102.50	52.50	60.00	56.00
8	65.00	70.00	90.00	51.00
9	102.50	52.50	110.45	45.00
10	102.50	52.50	60.00	60.00
11	102.50	52.50	9.55	15.67
12	140.00	70.00	90.00	58.00
13	65.00	35.00	90.00	43.00
14	65.00	35.00	30.00	7.87
15	165.57	52.50	60.00	73.33
16	140.00	35.00	90.00	64.20
17	102.50	81.93	60.00	57.40
18	140.00	70.00	30.00	67.10
19	102.50	52.50	60.00	54.82
20	102.50	23.07	60.00	49.00

A= Temperature (°C), B= Concentration of H_2SO_4(mL/g) C= Reaction Time (min)

Table 3:Composition of some physicochemical properties of microalgae feedstock

Parameter	Value
Lignin content (%)	13.82
Cellulose content (%)	27.99
Hemicellulose content (%)	58.20
Ash content (%)	30.28
Oil content (%)	0.00
Density (g/ml)	1.17
Moisture content (%)	4.16

The bulk densities, moisture contents, ash contents as well as average crude fibre, oil content analysis are presented in Table 3.
As show in Table 3 the microalgae had high % content of hemicellulose (58.20%) this makes it suitable as a good feedstock for furfural production. This is higher than agricultural feedstock (sugarcane bagasse 32 %) as reported by Ameh*et al.*, (2016); rice husk (19%) reported by Ambalkar and Talib, (2012); maize hemicellulose (32 and 30%) as reported by Wenjuan*et al.* (2016) and Shafeeq*et al.* (2015), respectively. Thus microalgae should give higher % of furfural yield. Also the % oil content of the microalgae is 0.00% which indicates that it contains no biofuels (biodiesel) and hence has high % of biomass which can be converted to furfural.

Statistical analysis of CCD design for furfural production from microalgae

The experimental design had a total of 14 different combinations and 6 repeated (center point) for furfural production from microalgae. Statistical analysis was done on the input response (furfural yield) as presented in Table 4.

Table 4: Model statistical summary of CCD for furfural yield

Source	Std dev.	R-Squared	Adjusted R-Squared	Predicted R-Squared	press	Adequate Precision	Lack Of Fit Value
Linear	10.49	0.7009	0.6448	0.4818	3000.84	11.090	0.0005
Quadratic	3.37	0.9807	0.9634	0.8771	723.07	29.437	0.0714
2FI	9.15	0.8151	0.7298	0.6799	1882.80	12.240	0.0008

As shown above in Table 4, three different models were suggested by the Design of experiment (DOE) and from the Table it can be seen clearly that quadratic model came out the best model hence it is selected for the design and optimization of furfural production from microalgae as the quadratic model has the highest R-Squared value a close value between the R-Squared 0.9807 and Adj R-Squared 0.9634 as well as the Pred. R-Squared 0.8771 compared to linear and 2 factorial models. The differnce (1.73%) between R-Squared 0.9807 and Adj R-Squared 0.9634 is less than 2% hence confirms that qudratic model fitted best. Also the lack of fit value for quandratic model exceeded the 5% for the which is one of the major createria for a model to fit. Likewise the qudratic model has the highest adequate precission of 29.437 copmapred to other models indicating a good signal to noise ratio since a ratio greater than 4 is desired and can be used to navigate the design space.
Also shown in Table 5, is the ANOVA of the selected quadratic model based on the pvalue (0.0001) is less than 0.05 hence the model is significant and the confidence level is 95% while the lack of fit is insignifficant thus confirming the adeuacy of the quadratic model selected.

Table 5: ANOVA for response surface quadratic model for furfural production from microalgae

Model	Fvalue	P Value
	56.54	<0.0001 Significant
A	283.53	<0.0001
B	11.8200	0.0064
C	68.3200	< 0.0001
A^2	6.4600	0.0292
B^2	0.0039	0.9513
C^2	81.9500	< 0.0001
AB	8.0100	0.0178
AC	44.3400	0.0001
BC	6.9200	0.0251
Lack of Fit	4.1700	0.0714*

***=** not significant

From Table 5, it can be seen that, the significant model terms are: A, B, C, A^2, C^2, AB, AC,and BC .However, this does not mean the model term $B^2$is not important in this study but it shows that, the model terms A, B, C, A^2, C^2, AB, AC and BC contributed more in the yield of furfural as compared to B^2model term, Thus the results obtained showed that the model is good.
Where: A= Temperature (°C), B= Concentration of 1MH_2SO_4(mL/g) and C= time (min).

The quadratic model equation selected for furfural yield from microalgae
The model equation is;

$$\text{Yield} = +55.71+15.34*A+3.13*B+7.53*C-2.25*A^2+0.056*B^2-8.03*C^2-3.37*A*B-7.93*A*C-3.13*B*C \quad (2)$$

Equation 2 shows the yield of fururаl from microalgae **where** the linear terms A= reaction temperature (°C), B= Concentration of of 1M H_2SO_4 Catalyst (mL/g) And C= reaction time (min). A, B and C represent the liner terms , A^2,B^2 and C^2 denote the quandratic terms while AB, AC, and BC are the products terms. Equation 2 was used to predict the yield of furfural at different conditions of the parameters.

Predicted and actual yield relationship
Figure 1 shows the relationships between the predicted and actual responses. The Figure presented the design expert parity plot of the predicted furfural yield against their respective actual responses for the evaluation and optimization of process parameters of furfural from microalgae.

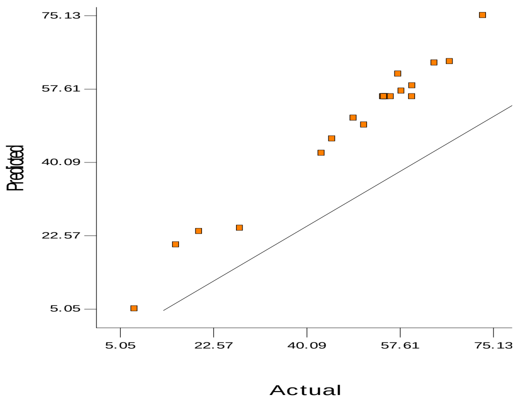

Fig. 1: Correlation between actual (experimental) and predicted yield of furfural production from microalgae

As shown in Fig. 1, the data points were well distributed close to the regression line, which suggested an excellent relationship between the predicted and experimental (actual) values of the response. That there was no outlier among the data point suggests inappropriate underlying assumptions of this analysis. The approximate distribution of data points along a straight line in both Fig. 1 showed a good correlation between the actual (experimental) and predicted values. The data points as shown in the Fig. 1 are well distributed close to the regression which revealed that, the model developed is highly significant and adequate to represent the actual relationship between input variables and output response.

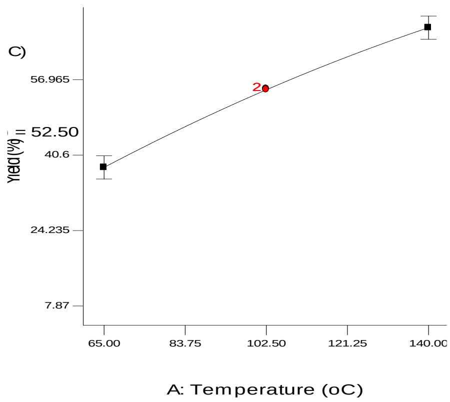

Fig. 2a: One factor plot: Temperature vs.Yield

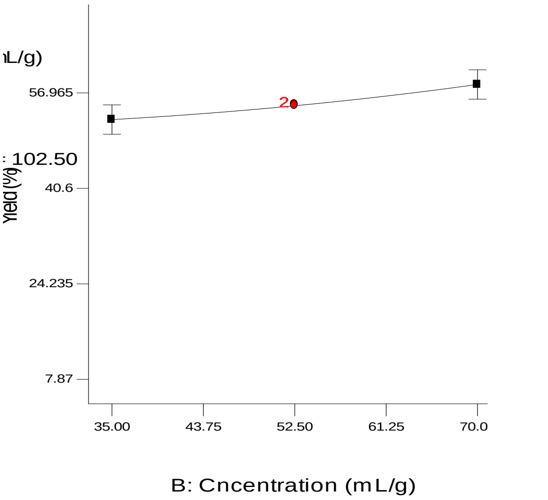

Fig. 2b: one factor plot: Concentration vs.Yield

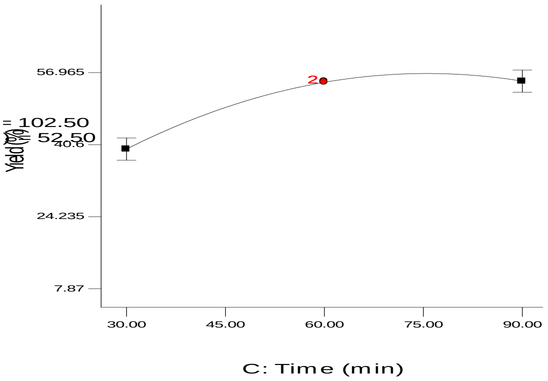

Fig. 2c: One factor plot: Time vs. Yield

It can be seen from the Fig.2a, furfural yield increases with increase in temperature. This is in agreement with the result of Wenjuan*et al.* (2016) who recorded 61.06% yield of furfural from corncob. However, at higher temperature, it was observed that furfural yield begins to decrease, these trends may be due that at high temperature, furfural cannot be recovered from the reactor due to its degradation, because, as temperature increases, furfural degradation rate also increase which agreed with the Wang *et al*. (2015). Also at high temperature, much of the furfural produced cannot be recovered, because at high temperature, furfural in the reactor react with intermediate such as formic acid or other furfural monomer and were instantly converted to more polymers.

Also the effect of concentration on furfural yield can be observed from Fig. 2b that at high concentration, furfural degradation is accelerated rapidly thereby leading to loss of furfural yield. It was noticed also that initially acid concentration increase with increase in furfural yield but subsequent increase in acid concentration does not increase furfural yield ,this may occur because at high concentration, it's difficult to separate furfural produced in liquid phase using standard laboratory separation methods, this result is in accordance with that of Shafeeq*et al.* (2015). He established that the factors upon which furfural yield depends are acid/solid volume ratio, temperature and reaction time hence it can be said that furfural yield remained constant despite increase in acid concentration in that acids to biomass ratio has reached its optimum and furfural yield may not increase despite increase in acids concentrations as shown in figure 2b.

The effect of time on furfural yield is illustrated in Fig. 4c. Increase in furfural yield was observed with increase in reaction time from 30 – 90 min, keeping all other factors constant. This observation is in harmony with the result of Shaukat*et al.* (2012) who also reported that increase in % yield of furfural increase with time. After certain time, It was observed that increase in time leads to decrease in furfural yield, this could probably be that greater extent of pentosans in the microalgae must have been be already be converted to furfural and that after a long period of reaction, there might be formation of side reaction as reaction continues thereby leading to furfural degradation and reduction in yield,this also correspond to the result of Ayse*et al.* (2013).

Figures 3a, 3b and 3c below shows the 3D-Surface diagram of significant model term interactions among the variables varied and the response yield. The 3D response surface plots generally illustrate the effects of the independent variables and their interactive effects on the responses. The 3D plots shown in Fig. 3a and 3b and 3c illustrate the effect of temperature and concentration on the reaction time and furfural yield responses, respectively.

The effects of temperature and acid concentration on furfural yield for furfural production from microalgae are depicted in Fig. 3a. As the temperature and concentration of acid vary (either increasing or decreasing), the yield of furfural changes. As shown in the same Fig. 3a for instance, at a temperature of 140^0C (x-axis) and acid concentration of 70 mL/g (z-axis), the corresponding furfural yield on y-axis is 69.08%. Thus, several plots for other runs of varying parameters against furfural yield in the same graph resulted to the 3D surface plots as shown

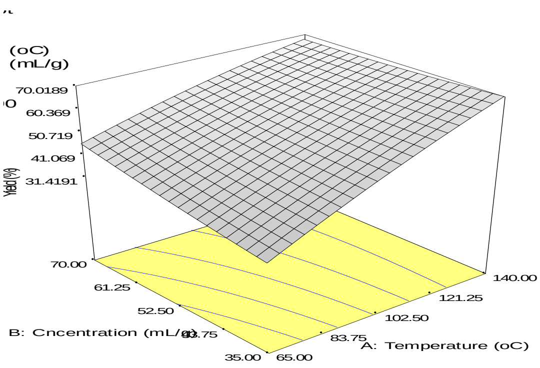

Fig. 3a: 3D Plot of furfural yield against concentration versus temperature

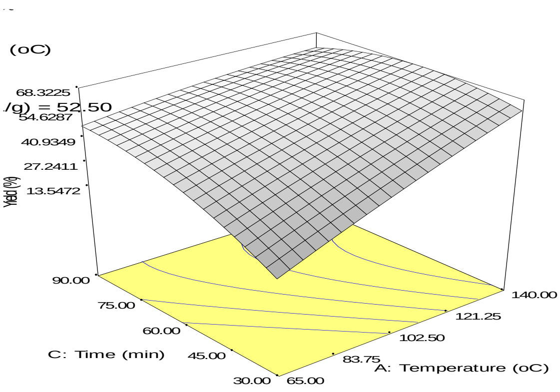

Fig. 3b:3D Plot of furfural yield against reaction time versus temperature

The effects of temperature and reaction time on furfural yield for furfural production from microalgae are depicted in Fig 3b. As the temperature and reaction time vary (either increasing or decreasing), the yield of furfural changes. As shown in the same figure for instance, at a temperature of 140^0C (x-axis) and reaction time of 90 minutes (z-axis), the corresponding furfural yield on y-axis is 60.43%. Thus, several plots for other runs of varying parameters against furfural yield in the same graph resulted to the 3D surface plots as shown in Figure 3b. Also, the variations in furfural yield showed that the interactions between the variable parameters are significant, as evidenced from the elliptical nature of the plot.

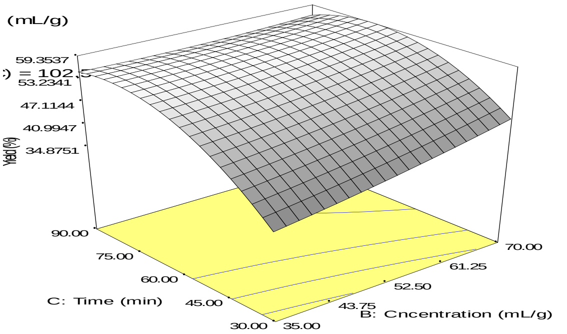

Fig. 3c:3D Plot of furfural yield against reaction time versus concentration

The effects of acid concentration and reaction time on furfural yield for furfural production from microalgae are depicted in Fig. 3c. As the acid concentration and reaction time vary (either increasing or decreasing), the yield of furfural changes. As shown in the same figure for instance, at an acid concentration of 70 mL/g (x-axis) and reaction time of 90 min (z-axis), the corresponding furfural yield on y-axis is 59.45.43%. Thus, several plots for other runs of varying parameters against furfural yield in the same graph resulted to the 3D surface plots as shown in Fig. 3c. Also, the variations in furfural yield showed that the interactions between the variable parameters are significant, as evidenced from the elliptical nature of the contours plot.

Optimization of process parameters for furfural production from microalgae

Having carried out statistical analysis on the input response, optimization was done by setting goals, constraint for the investigated parameters and response. The yield of furfural was maximized while other factors (reaction temperature, reaction time and acid concentration) were set in range as shown in Table 6. A numbers (10) optimized solutions were generated and five (5) out of these solutions were selected and validated to see how well the model predict the magnitude of the response (furfural).The validated experiment is shown in Table 7.

Table 6:Factors optimized, goal and constraint for CCD of furfural yield from microalgae

Factors	Goals	Lower limit	Upper limit
A	Is in range	65	140
B	Is in range	35	70
C	Is in range	30	90
Furfural yield (%)	Maximized	7.87	73.33

A= Temperature (ºC), B=Concentration of $1MH_2SO_4$(mL/g) and C= Time (min)

Table 7:Validation experiment of optimized solution

S/N	Temp. (ºC)	Concentration of $1MH_2SO_4$(mL/g)	Time (min)	Predicted yield	Experimental (Actual) Yield	Desirability
1	140	35.00	65.29	69.32	67.10	0.939
2	140	35.06	64.97	69.31	67.00	0.939
3	140	38.23	63.52	69.16	66.00	0.936
4	140	41.21	62.10	69.04	65.56	0.934
5	140	70.00	53.49	68.99	65.00	0.934

The results of the validated experiment as shown in Table 7 and the predicted and actual value are in closed range suggesting that the quadratic model is adequate and successfully predicted the yield of furfural from microalgae.

Conclusion

From the crude fibre analysis carried out on microalgae, it was observed that feedstock had higher hemicellulose contents (58.14%) compared to agricultural feedstocks such as corn cob, rice husk and sugarcane bagasse, hence it is a suitable raw material for production of furfural after which the acid hydrolysis of microalgae biomass into furfural via hydrolysis and distillation was investigated. Response Surface Methodology (Central Composite design) was successfully applied to study the key process parameters (i.e., A=Temperature B=Concentration of $1MH_2SO_4$ and C= Reaction time) for the production of this platform chemical (furfural) where the key process parameters were set as independent variables, whereas furfural yield was set as a response factor. ANOVA result revealed that all terms of both regression equations (2) were significant except B^2 term (Concentration of $1MH_2SO_4$) which has negligible effect on the yield of furfural which might be that the ratio of catalyst to feedstock ration have reach a maxima and increasing the catalyst will keep the yield constant. From the results, the optimal conditions for furfural production from microalgae were determined to be: 140°C, 35.06 mL/g and reaction time of 64.97 min with predicted furfural yield of 69.31% and validated yield of 67.00%. Higher catalyst loading and reaction temperature enhanced the production of furfural from microalgae however, the polymerization of by- products were observed to be accelerated. Therefore, optimization of reaction condition would be helpful to facilitate the furfural production. The factors upon which the yield of furfural depends are largely Temperature and Reaction Time.

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