Application of response surface methodology (RSM) for optimizing methane yield of oxidative pretreated *Xyris capensis*

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Abstract: This study investigated the application of Response Surface Methodology (RSM) for optimizing and predicting methane yield from oxidative pretreated *Xyris capensis*. Input process parameters of retention time, temperature, and pretreatment condition were considered, with methane yield as the response. The results show that all three process parameters selected significantly influence methane yield, and analysis of variance (ANOVA) indicates that the RSM model is significant for the study. A correlation coefficient (R^2) of 0.9071 was recorded, which implies that the model has 91% prediction accuracy. Interactive influence of temperature and retention time, pretreatment and retention time, and pretreatment and temperature were significant to methane release. Optimum conditions for methane release from RSM model are 14 days retention time, 25 °C temperature, and pretreatment condition of 85% H_2O_2 and 15% H_2SO_4 with daily optimum methane yield of 32.65 $mLCH_4$ /gVS_{added}. This study shows that RSM is suitable for methane yield optimization and prediction during the anaerobic digestion of oxidative pretreated lignocellulose substrates.

Keywords: *Xyris capensis*, anaerobic digestion, methane, optimization, RSM

1 Introduction

Renewable energy is clean energy generated from non-depleted origins that can be replenished and lower greenhouse gases. Either directly or indirectly, renewable energy relies on the sun. Biomass, an example of renewable energy, stores energy from the sun to produce another form of energy. It is energy from living organisms like agricultural residues, wood, grass, manure, etc. Renewable energy in the form of biofuels can be generated from biomass through biological, chemical, and thermal waste-to-energy technologies [1,2]. Anaerobic digestion is a biological process that converts organic feedstocks into biogas during the activities of microorganisms and without oxygen. The process can release methane-rich biogas that can be used for heating, power, and electricity generation and can be injected into the grid after purification [3]. Renewable energy generation through anaerobic digestion is a bright technique due to the low initial investment cost and energy requirement [4].

Lignocellulose feedstocks are second-generation materials that can be used to generate biogas and other biofuels. Attention has been shifted to these feedstocks due to their availability, and it does not compete with food supply and agricultural land. Lignocellulose feedstocks can be obtained from agriculture residues, forest wastes, grasses, livestock wastes, etc. [5,6]. It is made up of lignin, hemicellulose, and cellulose, and these compositions are intertwined with very strong bonds, making them recalcitrant [7]. This characteristic of lignocellulose feedstocks hinders the hydrolysis stage of anaerobic digestion with longer retention time and low biogas and methane yields. Therefore, there is a need to introduce a pretreatment technique to break down the lignin content that resists the microorganisms from accessing the cellulose that is digested to produce methane. Several pretreatments, such as physical/mechanical, chemical, thermal, biological, nanoparticle additives, and combined pretreatments, have been experimented with on lignocellulose materials and were reported to enhance methane yield and lower the retention period [7]. Oxidative pretreatment employs oxidizing agents like H_2O_2, $FeCl_3$, and oxygen or air to disintegrate the lignin and hemicellulose portion of lignocellulose materials to improve the hydrolysis of organic contents during anaerobic digestion [8]. Oxidative pretreatment aims to disintegrate hemicelluloses partially and delignification of the feedstock [9].

Biogas production process parameters have been identified to influence the methane yield significantly. The optimization of methane needs an accurate selection of these parameters to achieve the optimization target. Developing a suitable and reliable optimization model that can forecast and optimize methane yield accurately without going through the experimental process is

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challenging due to its non-linearities. Identifying statistical models that can forecast the optimum parameters that can be replicated on an industrial scale would enable us to determine and understand the depth dynamic of the process by simple and general-comparable data optimization [1]. Response Surface Methodology (RSM) statistical model combines statistical and mathematical methods, and it has been reported to be suitable for optimizing process and reactions that require experimental design. It has been experimented with in drug research [10], biodiesel synthesis [11], and biogas production [4]. Nevertheless, it is difficult to conclude that it applies to all optimization processes as reported that it is unsuitable for some optimization experiments [12]. Therefore, this study aims to statistically optimize the methane yield of *Xyris capensis* using response surface methodology and pretreatment technique.

2 Materials and methods

2.1 Substrate collection

Xyris capensis grass was sourced locally, chopped into smaller sizes (4 – 8 mm), and kept in well-ventilated conditions for further use. Stabled inoculum from an existing anaerobic digester was collected and used for this study. Both feedstock and inoculum were analyzed in the laboratory for physicochemical properties following the Association of Official Analytical Chemists (AOAC) standard procedure [13]. The substrate and inoculum were stored in the laboratory at room temperature for the experimental setup.

2.2 Pretreatment

Oxidative pretreatment was carried out using Piranha solution, and the solution was prepared as reported by Shrivash et al. [14] with slight modification. 75 g of ice cube was put in a 500 mL beaker, and H_2O_2 and H_2SO_4 were added, as shown in Table 1. The mixture was stirred continuously to form a homogenous solution. The chopped *Xyris capensis* was then soaked in the prepared solutions in a ratio of 1: 10 of solid to liquid. The beaker with its contents was then placed on a magnetic stirrer for two hours at 200 rpm set at 90 °C. After the treatment exposure time, 10% of NaOH was added to stop further oxidation of the substrate, and warm distilled water was added as an anti-solvent to prevent further reaction. The pretreated *Xyris capensis* was filtered and washed with water until a neutral pH of 7 was achieved. The pretreated substrate was then dried in an oven set at 60 °C for 6 hours and stored in zip-lock bags for laboratory analysis and anaerobic digestion.

Table 1. Oxidative pretreatment conditions of Xyris capensis

Treatment	H_2O_2 concentration (%)	H_2SO_4 concentration (%)
A	100	0
B	95	5
C	85	15
D	75	25
E	Control	Control

2.3 Anaerobic digestion

The Biomethane potential of oxidative pretreated and untreated *Xyris capensis* was studied on a laboratory-scale using Automatic Methane Potential Test System II (AMPTS II) at mesophilic temperature (37 ± 2 °C) [15]. 500 ml reactor bottles were charged with 400 g of stable inoculum. Equation 1 was used to calculate the quantity of substrate added to each digester as prescribed by VDI 4630 [15]. The mass of substrate added was determined using volatile solids (VS) of the substrate and inoculum (2: 1). The experiment was duplicated twice, and two digesters with only inoculum were run parallel. The gas released from the parallel digester was deducted from other digesters with both substrate and inoculum. AMPTS II software was supplied with the following information before the commencement of the experiment. Flush gas for carbon dioxide removal was maintained at 10%, stirring time was put at 60 sec and 60 sec off time, and the mixer speed at 80%. Methane yield was predicted to be 60% [16], and a headspace of 100 ml was maintained for all digesters. The anaerobic condition was set in the digester when nitrogen gas purged oxygen off the system before connecting the silicon pipes to the digester. Sodium hydroxide (3M NaOH) was used to remove the carbon oxide from the gas produced. Silicon pipes from the digesters were linked directly to the carbon dioxide removal unit that contains a 75 mL NaOH solution, and another silicon pipe was connected from the carbon dioxide removal unit to the third unit, where the volume of biomethane released was recorded. The process was stopped after 24 days when it was observed that the daily gas yield was less than 1% of the total yield.

$$M_s = \frac{M_i C_i}{2C_S} \quad (1)$$

Where: M_s = Mass of the substrate (g), M_i = Mass of inoculums (g), C_s = Concentration of substrate (%), C_i = Concentration of inoculum (%) [15].

2.4 RSM parameters and analysis

RSM was used to investigate the process parameters optimization, and central composite design (CCD) was utilized to create experiment runs. Design Expert 13.0 was used, and retention time (A), temperature (B), and pretreatment (C) were the process parameters considered. Using the results from some initial experiments, the independent variables were set between -1 and +1 across all levels. The total number of experimental runs for the three factors (F) is 30, as determined by equation 2, and the response is presented in equation 3. Analysis of variance (ANOVA) was used to forecast a second-order polynomial regression and results [17].

$$F = 2^b + 2b + 6 \quad (2)$$

Where b is the factor's number (b = 4), and 6 is the constant value.

$$X = \gamma_o + \epsilon\gamma_{ii}Z_1 + \gamma_o + \epsilon\gamma_{ij} Z_i Z_j \quad (3)$$

Where: X = the measured response, γ_o = the intercept term, γ_{ii} = quadratic coefficient,

γ_{ij} = interaction coefficient, Z_i and Z_j are the coded independent variables.

Table 2. Observed and RSM predicted methane yield.

Run	A	B	C	Methane Yield (mL CH_4/ g VS_{added}) Observed	RSM Predicted
1	2	29	C	14.21	13.28
2	10	28	D	15.88	14.770
3	9	22	A	18.82	18.31
4	13	24	C	8.45	8.13
5	2	23	B	32.65	30.18
6	7	24	C	12.48	12.32
7	13	24	D	8.58	8.36
8	15	24	A	6.47	6.46
9	9	26	E	12.03	11.48
10	7	20	B	30.23	31.25
11	7	23	E	12.66	12.51
12	26	21	A	6.18	6.19
13	4	24	C	13.33	15.57
14	16	26	C	10.22	9.22
15	5	26	D	11.73	11.85
16	9	28	D	13.29	15.13
17	6	29	B	16.85	19.60
18	8	26	A	19.12	16.76
19	5	24	C	14.93	14.43
20	15	23	E	7.12	7.96
21	8	28	B	20.81	18.05
22	11	31	D	10.84	11.00
23	16	31	A	7.35	7.30
24	10	28	B	21.60	17.46
25	12	27	B	7.38	14.35
26	8	22	E	13.99	13.51
27	2	24	C	13.71	14.36
28	19	27	C	5.58	5.26
29	10	25	C	12.09	11.02
30	4	25	A	20.29	22.87

3 Results and Discussion

The experimental and RSM predicted methane yield for 30 runs is presented in Table 2. It can be observed from the table that all the process parameters selected had a significant influence on methane yield. For example, the methane yield was not the same when the temperature and pretreatment method was the same, but variation in retention time (runs 6 & 9, and 21 & 24). Variation in methane released was also observed when temperature varied, but retention time and pretreatment were the same (runs 1 & 27). Likewise, pretreatment's influence was noticed at the same temperature and retention time (runs 4 & 7). This result agreed with the previous studies that indicated that temperature, retention time, and pretreatment techniques significantly influence the methane released from lignocellulose feedstocks [16].

3.1 Interactive relationship of process variables on methane yield

The ANOVA results for methane production from the model suggested quadratic equation for all the responses are presented in Table 3. It can be observed that the model is highly significant because of the P-value of 0.0057. The model F-value of 5.14 indicate significance, and there is a tendency of just 0.57% that an F-value this big could be experienced because of noise. The value of P below 0.0500 shows the significance of the model terms, and it was discovered that no model term is significant ($P < 0.05$) in this case [18]. P-values above 0.100 implies that the model terms are insignificant, and in this case, reduction of the model may enhance the model. The coefficient of correlation (R^2) determined the model's accuracy, and the R^2 value of 0.9071 (91%) was observed from this model. This shows that the model provides an accuracy of 91% in predicting the methane released from *Xyris capensis* pretreated with oxidizing agents. This value is lower than what some authors reported [4] but higher than what was observed by other authors in related studies [19]. R^2 within the range of 0.75 and 1 has been adjudged to be an excellent predictive ability of a model [12], this shows that the result from this study is satisfactory. Reasonable agreement exists between the predicted R^2 and adjusted R^2 because the variation between the two values is less than 0.2. Adequate precision defines the signal-to-noise ratio, which measures the prediction range and its associated errors. For signal-to-noise ratio, a ratio higher than 4 is recommended [20], and 9.3628 was observed in this investigation which shows a satisfactory signal. Therefore, this model can be used to boycott the design space. The final regression model of ANOVA can be presented with second-order polynomial equation 4 that can be used to forecast the methane yield. Equation 4 can forecast the response for the selected factor's level, -1 and +1 coded levels for low and high levels, respectively, by default. The relative influence can be ascertained with this equation when the coefficient of the selected factors is related.

$$Methane = 8.97 - 6.26A + 11.30B + 0.5302C - 6.30AB + 0.8964AC - 6.20BC - 0.2352A^2 - 2.53B^2 + 0.0617C^2 \quad (4)$$

Table 3. ANOVA for methane generated from oxidative pretreated *Xyris capensis.*

Source	**Sum of squares**	**df**	**Mean Square**	**F-value**	**P-value**	
Model	1127.76	19	59.36	5.14	0.0057	Significant
A – Time	7.22	1	7.22	0.6252	0.4457	
B – Temp.	12.13	1	12.13	1.05	0.3297	
C – pretreatment	0.0779	1	0.0779	0.0067	0.9362	
AB	1.08	1	1.08	0.0936	0.7659	
AC	0.1490	1	0.1490	0.0129	0.9118	
BC	3.35	1	3.35	0.2900	0.6020	
A^2	0.0035	1	0.0035	0.0003	0.9865	
B^2	2.12	1	2.12	0.1837	0.6773	
C^2	0.0016	1	0.0016	0.0001	0.9910	
Residual	115.56	10	11.56			
Cor. Total	1243.31	29				
Std. Dev.	3.40		R^2	0.9071		
Mean	13.96		Adjusted R^2	0.7305		
C.V. %	24.35		Predicted R^2	0.9230		
PRESS	2390.90		Adeq. Precision	9.3628		

3.2 Analysis of methane yield residual plot.

Fig. 1 presents the perturbation plot of the methane yield, and this shows the relationship of all the input variables at the center of the response, methane yield. The impact of individually selected process parameters from the identified reference point was also ascertained from the perturbation plot, while other parameters were held constant. In this investigation, the reference point was selected in the middle of the design space, representing the zero-coded level for each feature. In retention time (A), the methane yield kept increasing until day 14, when the yield started declining. This could be a result of the reduced available feedstock for the consumption of methanogenic bacteria and declining methane release. This agrees with what was earlier observed in previous study that at a particular point of the digestion process, the methane yield will begin to decline due to insufficient feedstock for microbial activities [18]. Temperature (B) can be observed to significantly influence the methane yield, as shown in Fig. 1. It can be observed that when the temperature begins to rise, the quantity of methane released keeps increasing linearly until a point when a further increase in temperature results in a decline in methane yield. This can be linked to the strength of methanogenic bacteria to thrive well when the temperature is around 25 °C. Therefore, a temperature rise beyond this level will reduce the methane yield. At the point indicated in this Figure, the methanogenic bacteria are saturated, and a rise in temperature will be harmful, which will lower their activities. This result agrees with reports from previous studies on the reaction of methanogenic bacteria to temperature changes [12]. The effect of oxidative treatment (C) shows a very slight influence on methane produced. It can be inferred that methane released was enhanced with 85% H_2O_2 and 15% H_2SO_4. This indicates that H_2SO_4 less than 15% was unable to remove/redistribute the lignin content of the feedstock, and H_2SO_4 above 15% will produce inhibitory compounds or there will be a loss of some hemicellulose and cellulose portions. This result corroborates previously reported that pretreatment techniques can improve the methane yield if the appropriate conditions are selected [19].

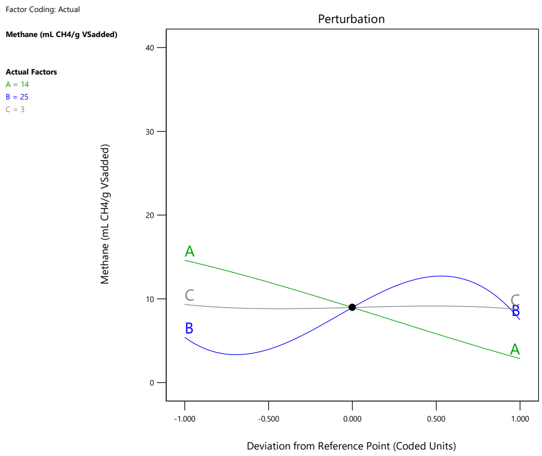
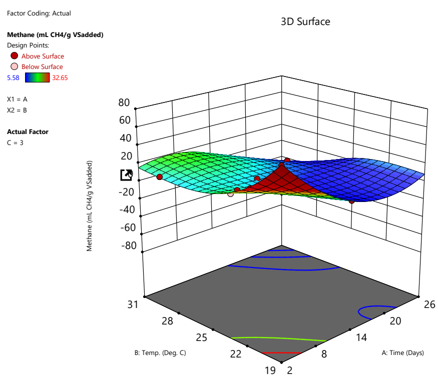


Fig. 1: Perturbation analysis plot of anaerobic digestion of oxidative pretreated *Xyris capensis*.

3.3 Response surface plots

To investigate the synergetic effect between the selected input variables and methane released, three-dimensional (3D) plots were produced with the model. Fig. 2 presents the 3D plot where one parameter is kept constant at the optimum condition, and the other two parameters are varied within the experimental range. Fig. 2A presents the interactive relationship between temperature and retention time on methane yield while the other parameter (pretreatment condition) was constant. It can be noticed that the methane production started to increase at the initial stage and then started to decline with further increases in temperature and time. Temperature and retention time are two important process parameters for methane generation. The temperature of the system significantly influences the performance of the methanogenic bacteria, and there is a particular range that further increases this parameter and makes the bacteria uncomfortable and less productive. It has been reported that there are three conditions for methane production which are psychrophilic (around 25 °C), mesophilic (35 – 37 °C), and thermophilic (53 – 60 °C) [21]. An increase in retention time is inversely proportional to the feedstock availability in the digester. With time the bacteria could be noticed to have less feedstock to feed on, reducing the methane yield as shown in Fig. 2A. Fig. 2B illustrated the interactive relationship between pretreatment and retention time while the temperature was kept constant. It could be noticed that pretreatment has a marginal influence on the methane released compared to retention time. This could be traced to the linear increase in the percentage of H_2SO_4 used during the pretreatment process. The optimum methane yield was reported when 85% H_2SO_4 was combined with 15% H_2SO_4 (treatment C). This can be traced to the strength of H_2O_2 to have less influence on the lignin content of the substrate until the percentage of H_2SO_4 was increased to 15%. After 15% H_2SO_4, there is a tendency there will be the release inhibitory compounds, which will hinder the release of methane, especially when 75% H_2O_2 is combined with 25% H_2SO_4. This result corroborated what was earlier noticed that pretreatment above a particular condition will result in methane reduction [7].

Fig. 2C showed the interactive effects of pretreatment and temperature while the retention time was constant. It could be noticed from this plot these two parameters have the least interactive effect. Pretreatments enhance the accessibility of the microbes, and when the temperature of the process favors the activities of the methanogenic bacteria, it can result in a high biodegradability rate. This degradability may improve the hydrolysis stage, leading to overaccumulation of the process's volatile fatty acids (VFAs) and altering the process's pH. Overaccumulation of VFAs will influence the pH and make the process harmful to methanogenic bacteria that are sensitive to changes in pH. It has been observed that methanogenic bacteria thrive well at neutral pH (6 – 8) during anaerobic digestion, and values outside this range will affect the methane yield negatively [22]. Both the pretreatment can alter the pH of the process through a hydrolysis process that can under or over-produce the VFAs. This interactive effect on methane yield was noticed in Fig. 2C, and it could be inferred that the hydrolysis stage of the process was satisfactory.



(A)

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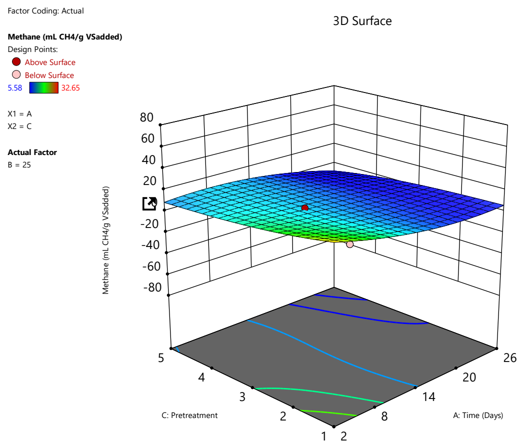
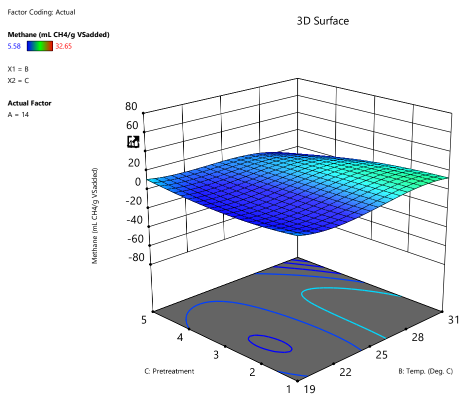


(B)



(C)

Fig. 2. 3D surface plot for (A) temperature and time, (B) pretreatment and time, and pretreatment and temperature

3.4 Desirability analysis for optimization

The RSM model can be employed for single or multi-objective optimization by applying desirability analysis, an important tool for optimization. Higher desirability is achieved when the parameters are set such that the desirability is closer to 1. The values around 1 have been judged to be the best conditions, and the co-occurrent actual function is a geometric means of all outputs. For this study, the maximum process parameters were set with the aim of maximizing the methane yield. Fig. 3A shows the ramp plot presenting the optimum input process parameters and the forecasted methane yield. It can be observed that it presents an approximate retention time and temperature of 15 days and 25 °C, with treatment C (85% H_2O_2 and 15% H_2SO_4) to produce an optimum daily methane yield of 32.65.37 mL CH_4/ gVS_{added}. The desirability plot of the optimization for the objective function is illustrated in Fig. 3B. The desirability is an objective function that is between zero (0) out of the boundaries to one (1) at the goal [17]. The maximum desirability function was located within the numerical optimization. The desirability function relies on the closeness of the lower and higher limits set relative to the real optimum conditions. From this study, it can be observed that the desirability value is 1, which is the best desirability performance. Therefore, the optimum condition recorded from this investigation can be used to set up another experiment for further verification.

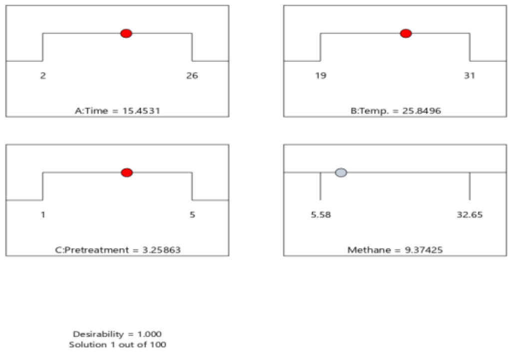
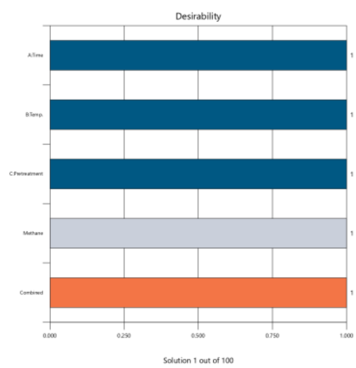


Fig. 3A. Ramp plot for desirability analysis.



(B)

Fig. 3B. Bar chart for desirability analysis

4 Conclusion

This study has shown that retention time, temperature, and oxidative pretreatment conditions significantly influenced the methane yield of *Xyris capensis*. The interactive impacts of retention time and temperature, pretreatment and retention time, and pretreatment and temperature were observed to affect methane yield significantly. The RSM model coefficient of correlation (R^2) value of 0.9071 was recorded, showing a valuable model for predicting and optimizing methane yield from the statistical and mathematical evolution in anaerobic digestion of oxidative pretreated feedstocks. The optimum conditions for methane yield from RSM were 14 days retention time, 25 °C temperature, and 85% H_2O_2 and 15% H_2SO_4 treatment conditions with a response methane value of 32.65 mL CH_4 /g VS_{added}. This model can be applied commercially to optimize the methane yield of pretreated lignocellulose feedstocks to save time and cost.

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