Optimization of Biogas Production from Anaerobic Fermentation of Corn Stalk by Combination Alkali Pretreatment

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Abstract. In order to explore the influence of alkali concentration, solid-liquid ratio, pretreatment time and component ratio on biogas production from corn stalk anaerobic fermentation in the pretreatment process of combined alkali, four factors and five levels of quadratic orthogonal rotary combination design experiment were used to optimize the technological conditions for biogas production from corn stalk anaerobic fermentation by combined alkali pretreatment, and corresponding mathematical model is established. The results showed that the regression equation was significant and the fitting condition was good. The four factors affected the biogas production of corn stalk in the order of composition ratio, treatment time, alkali concentration and solid-liquid ratio. The optimum combination of process parameters was as follows: alkali concentration was 6%, solid-liquid ratio was 1:5, treatment time was 4.5 days, component ratio was 1:1.25. Under the optimum conditions, the production of biogas from corn stalk anaerobic fermentation was the highest.

1. Introduction

Because of the complex structure of lignin, cellulose and hemicellulose in crop straw plant fibers, it is difficult to be degraded effectively either in anaerobic fermentation or in other applications. How to destroy the complex chemical structure of straw and improve its bioavailability and conversion rate has become an urgent problem to be solved [1, 2]. Pretreatment of straw material is one of the main ways to improve the stability of anaerobic fermentation and the biogas production. Therefore, it is necessary to carry out research work on straw pretreatment. The pretreatment methods of straw material mainly include physical method, chemical method and biological method [3]. Compared with other treatment methods, chemical pretreatment has the advantages of convenience, rapidity, low cost, simple operation, obvious treatment effect and short treatment time [4]. William E. Kaar’s [5] pretreatment of corn straw with hydrated lime can effectively improve the sugar yield of enzymatic hydrolysis. R. Uma Rani [6] investigated the effect of combined alkaline and dispersive pretreatment on sludge disintegration. The results showed that alkali treatment was an effective method to promote biodegradation, which laid a foundation for improving biogas production. Jiang Wu [7] et al. soaked straw with NaOH solution, and found that the biogas production increased significantly. Xueping Guo [8] et al. studied the effect of Ca(OH)₂ pretreatment on biogas production from rice straw by anaerobic fermentation. The results showed that under the optimized pretreatment conditions, the pretreatment could significantly promote the start-up of fermentation and shorten the fermentation time. According to the related research, NaOH...
has strong causticity and high requirement for equipment because of its strong alkali, and the alkalinity of NaOH solution decreases rapidly in the pretreatment process of straw raw materials, while Ca\(^{2+}\) in Ca(OH)\(_2\) has a certain promoting effect on fermentation. It can combine with organic substances in straw during the treatment process and provide continuous alkalinity in the subsequent fermentation process. Bioas production is promoted step by step, and the price is low, so it can be reused. Attempts to combine the two can make up for each other's shortcomings and reduce the solid loss of the substrate. Previous studies mostly focused on single pretreatment methods, but few on combined pretreatment methods of several alkali agents [9, 10, 11, 12]. Based on the chemical characteristics of NaOH and Ca(OH)\(_2\), the effects of combined alkali on the anaerobic fermentation pretreatment of corn straw and its biogas production performance were investigated in order to provide a theoretical reference for further improving the effect of alkali pretreatment and reducing the production cost.

2. Materials and Methods

2.1. Test materials
Corn stalk: from the experimental base of Shenyang Agricultural University. Combination alkali: Ca(OH)\(_2\) and NaOH combination alkali; Inoculated sludge: from a farmer's biogas digester in the suburb of Shenyang, the pH value is 7.4. The indices of corn stalk and inoculated sludge were determined, and the contents of each component were shown in Table 1. A self-made small anaerobic fermentation equipment was used in this study.

**Table 1. Index content of corn stalk and vaccinal sludge (%)**

| Ingredients       | TS     | VS      | Lignin | Cellulose | Hemicellulose |
|-------------------|--------|---------|--------|-----------|---------------|
| Corn straw        | 93.17  | 90.15   | 15.32  | 22.54     | 22.25         |
| Inoculated sludge | 15.43  | 12.14   | -      | -         | -             |

2.2. Test scheme and data analysis

2.2.1. Experimental design. Using quadratic regression orthogonal rotary combination design method, the alkali concentration, solid-liquid ratio, treatment time and component ratio (Ca (OH)\(_2\) and NaOH mass ratio) were selected as test factors, and the process conditions of corn stalk alkali pretreatment were optimized with biogas yield as test index, i.e. response value, and the corresponding mathematical model was established. The test factors and levels are coded as shown in Table 2.

**Table 2. Experimental factors and levels (The implementation of 1/2)**

| Factor                  | Horizontal encoding | Alkali concentration \(X_1\) | Solid liquid ratio \(X_2\) | Processing time \(X_3\) | Component ratio \(X_4\) |
|-------------------------|---------------------|------------------------------|--------------------------|------------------------|------------------------|
| Upper asterisk arm      | +1.682              | 6                            | 1:9                      | 10                     | 1:2                    |
| Lower level             | +1                  | 5.2                          | 1:7.38                   | 8.5                    | 1:1.645                |
| Zero level              | 0                   | 4                            | 1:5                      | 6.5                    | 1:1.125                |
| Upper level             | -1                  | 2.8                          | 1:2.62                   | 4.5                    | 1:0.605                |
| Lower asterisk arm      | -1.682              | 2                            | 1:1                      | 3                      | 4:1                    |
| \(\Delta j\)            | 1.8                 | 1.8                          | 2.38                     | 2                      | 1:0.52                 |
2.2.2. Data analysis. Excel, DPS and MATLAB software were used to analyze the test data.

3. Results and analysis

3.1. Establishment of mathematical regression model

The quadratic regression orthogonal rotation combination design was used to design the experimental scheme. The experimental results were shown in Table 3.

| Test number | \(X_1\) | \(X_2\) | \(X_3\) | \(X_4\) | \(Y/\text{mL}\) |
|-------------|--------|--------|--------|--------|-------------|
| 1           | 1      | 1      | 1      | 1      | 22400       |
| 2           | 1      | 1      | -1     | -1     | 18500       |
| 3           | 1      | -1     | 1      | -1     | 22700       |
| 4           | 1      | -1     | -1     | 1      | 21100       |
| 5           | -1     | 1      | 1      | -1     | 18200       |
| 6           | -1     | 1      | -1     | 1      | 23600       |
| 7           | -1     | -1     | 1      | 1      | 21400       |
| 8           | -1     | -1     | -1     | -1     | 15100       |
| 9           | -1.682 | 0      | 0      | 0      | 22700       |
| 10          | 1.682  | 0      | 0      | 0      | 25700       |
| 11          | 0      | -1.682 | 0      | 0      | 19200       |
| 12          | 0      | 1.682  | 0      | 0      | 22300       |
| 13          | 0      | 0      | -1.682 | 0      | 21800       |
| 14          | 0      | 0      | 1.682  | 0      | 25600       |
| 15          | 0      | 0      | 0      | -1.682 | 15500       |
| 16          | 0      | 0      | 0      | 1.682  | 16500       |
| 17          | 0      | 0      | 0      | 0      | 25500       |
| 18          | 0      | 0      | 0      | 0      | 25300       |
| 19          | 0      | 0      | 0      | 0      | 26300       |
| 20          | 0      | 0      | 0      | 0      | 25400       |
| 21          | 0      | 0      | 0      | 0      | 24000       |
| 22          | 0      | 0      | 0      | 0      | 25700       |
| 23          | 0      | 0      | 0      | 0      | 26300       |

Based on the results of Table 3, the regression coefficients of each factor are calculated, and the mathematical regression models of biogas production and alkali concentration, solid-liquid ratio, pretreatment time and component distribution ratio are established. Regression equation see formula 1.

\[
Y = 25350.52988 + 838.06843X_1 + 557.48986X_2 + 936.58558X_3 + 1148.27268X_4 - 248.90063X_1X_2 + 65979X_2X_3 - 425.67732X_2X_3 - 3148.0385X_4 + 1025.0000X_1X_2 + 575.0000X_1X_3 + 1175.0000X_1X_4
\]  

(1)

The F test was used to test the significance of the regression relationship, the significance of the regression coefficient and the dissimilarity of the regression model. The results of variance analysis of the regression model are shown in Table 4.
Table 4. Variance analysis of the regression equation

| Source of variation | Sum of squares | Freedom | Mean square | Partial correlation | Ratio F | P-numerical value |
|---------------------|----------------|---------|-------------|---------------------|---------|------------------|
| X₁                  | 6976007.8242   | 1       | 6976007.8242 | 0.6267              | 5.1741  | 0.0439           |
| X₂                  | 3086895.5828   | 1       | 3086895.5828 | 0.4717              | 2.2895  | 0.1584           |
| X₃                  | 8712502.6724   | 1       | 8712502.6724 | 0.6685              | 6.4620  | 0.0274           |
| X₄                  | 13095981.7413  | 1       | 13095981.7413 | 0.7405              | 9.7132  | 0.0098           |
| X₁²                 | 715871.5474    | 1       | 715871.5474  | -0.2495             | 0.5310  | 0.4814           |
| X₂²                 | 24924445.9686  | 1       | 24924445.9686| -0.8354             | 18.4863 | 0.0013           |
| X₃²                 | 2093843.0754   | 1       | 2093843.0754 | -0.4032             | 1.5530  | 0.2386           |
| X₄²                 | 114515198.5861 | 1       | 114515198.5861| -0.9560             | 84.9352 | 0.0001           |
| X₁X₂                | 6112727.4579   | 1       | 6112727.4579 | -0.6014             | 4.5338  | 0.0567           |
| X₁X₃                | 1923636.4219   | 1       | 1923636.4219 | 0.3890              | 1.4267  | 0.2574           |
| X₁X₄                | 8032727.5160   | 1       | 8032727.5160 | -0.6533             | 5.9578  | 0.0328           |

X₂X₃ Linear correlation with preceding factor X₁X₄
X₂X₄ Linear correlation with preceding factor X₁X₃
X₃X₄ Linear correlation with preceding factor X₁X₂
Regression 259827332.5688 11 23620666.5972 F₂=17.51929 0.0001
Surplus 14830928.3008 11 1348266.2092
Loss of imitation 11210928.3008 5 2242185.6602 F₁=3.71633 0.0325
Error 3620000.0000 6 603333.3333
The sum 274658260.8696 22

The significance of regression relationship was tested according to F value. Firstly, the validity of the experiment was tested. The table F₂ = regression mean square/residual mean square = 17.51929 > F0.01 (11, 11) = 4.46 showed that there were significant differences in the effect of anaerobic fermentation of corn straw among different treatments. Therefore, the level of the experimental factors in the regression model was reasonable. Secondly, the dissimilarity test showed that F₁ = dissimilarity mean square/error mean square = 3.71633 < F0.05 (5, 6) = 4.39, that is, the dissimilarity of regression equation did not exceed 5%. This indicated that the fitting degree of the regression equation was higher. The experimental factors selected by the regression model could reflect the effect of pretreatment conditions on anaerobic fermentation biogas production of corn straw in the experiment, that is, the regression equation obtained in this experiment was meaningful. Through P value analysis, the significance of regression coefficient can be concluded that the proportion of components has a significant effect on the anaerobic fermentation biogas production of corn straw, and the alkali concentration and treatment time have a significant impact on the anaerobic fermentation biogas production of corn straw. The interaction effect between alkali concentration and component ratio is very significant, but the interaction effect between other factors is not significant. Formula 2 is the simplified regression equation after eliminating the insignificant terms at the significant level of α=0.05.

\[
Y=25350.52988+838.06843X₁+936.58558X₃+1148.27268X₄-248.90063X₁²-3148.03835X₄²-1175.00000X₁X₄
\]  
(2)
Through software analysis and the above regression equation analysis results, in combination with
the previous single factor test and the test results in this chapter, the influence of each factor on the
biogas yield of straw is: component ratio, treatment time, alkali concentration and solid-liquid ratio.

3.2. Influence of various factors on biogas production by anaerobic fermentation of corn stalk
Other factors were fixed at zero level to study the effects of $X_1$ (alkali concentration), $X$ (solid-liquid
ratio), $X_3$ (treatment time) and $X_4$ (component ratio) on the biogas production of anaerobic fermentation
of corn stalk.

The influence of alkali concentration. Concentration of alkali ($X_1$) effect on the biogas production
rate is relatively gentle increase trend, namely with the increase of concentration of alkali, corn stalk
anaerobic fermentation biogas production has steadily increased, this shows that for biogas production
of anaerobic fermentation, increased concentration of alkali more benefit to the improvement of biogas
production.

The influence of solid-liquid ratio. The influence of solid-liquid ratio ($X_2$) on biogas production first
increases and then decreases, and the extreme point is at the position where the solid-liquid ratio is zero.
This shows that the increase of solid-liquid ratio in a certain range is conducive to the improvement of
biogas production, and if the solid-liquid ratio is too large, it will lead to the reduction of biogas
production.

The influence of treatment time. The effects of treatment time $X_3$ and alkali concentration $X_1$ on
anaerobic fermentation biogas production of corn stalk are similar, and the trend of increasing biogas
production is not very big.

The influence of component ratio. The effects of component ratio $X_4$ and solid-liquid ratio $X_2$ on
anaerobic fermentation biogas production of corn straw are similar. The extreme point is at the zero
level of component ratio. That is, with the increase of component ratio, the biogas production of
anaerobic fermentation of corn straw increases first and then decreases. This also shows that the increase
of component ratio in a certain range is beneficial to the increase of biogas production. If the component
ratio is too large, the biogas production will be reduced.

3.3. Effects of interaction on biogas production by anaerobic fermentation of corn stalk
Regression equation analysis showed that only the interaction effect between alkali concentration ($X_1$)
and component ratio ($X_4$) reached significant level, and the interaction effect between alkali
centration and component ratio reached significant level, while the interaction effect between other
factors had no significant effect on biogas production, so only the interaction effect with significant
effect was analysed. When $X_2$ and $X_3$ are fixed at 0 level, see formula 3.

$$Y=25350.52988+838.06843X_1+1148.27268X_4-248.90063X_1^2-3148.03835X_4^2-1175.00000X_1X_4$$  \(3\)

The response surface curves and contours are shown in Figure 1.

From Figure 1, it can be seen that the biogas production increases slowly with the increase of alkali
concentration, while increases first and then decreases with the increase of component ratio. When alkali
concentration and group allocation ratio change from both ends to their respective zero levels at the
same time, the slope of response surface is gentle and the contour line is sparse, which indicates that the
sensitivity of the change of biogas production with the interaction effect decreases at this time; when
alkali concentration and group allocation ratio both tend to low level and high level at the same time, or
tend to relative changes at both ends, the slope of response surface is steeper and the contour line is
sparse. Dense, indicating that the sensitivity of biogas production changes increases at this time.
3.4. Optimal conditions combination and model verification

The results of quadratic regression orthogonal rotation test were analyzed. It was concluded that the horizontal coding values of each factor were X₁ = 1.682, X₂ = 0, X₃ = -1 and X₄ = 0 when the biogas production of anaerobic fermentation of maize straw reached the highest value. The optimal pretreatment conditions for four factors were alkali concentration 6%, solid-liquid ratio 1:5, treatment time 4.5 d, and component ratio 1:1.125. Under these conditions, the biogas production of anaerobic fermentation of corn stalk can reach 28335 mL.

In order to verify the accuracy of the predicted value of the model, the anaerobic fermentation biogas production test of corn straw was carried out by using the combination of the above predicted optimum conditions. Under the combination of these conditions, the final biogas production measured was 28199 mL. The relative error between the experimental value and the predicted value of the selected experimental group was less than 0.5%, which indicated that the optimized combination parameters of the optimum conditions were accurate and reliable. The regression model between the combination of various factors and biogas production fits well.

4. Conclusion

(1) Mathematical regression model between test results and test factors was established. Get the regression equation. Based on the response surface and contour lines of the interaction effect between $Y = 25350.52988 + 838.06843X₁ + 557.48986X₂ + 936.58558X₃ + 1148.27268X₄ - 248.90063X₁² - 1468.65979X₂² - 425.67732X₃² - 3148.03835X₄² - 1025.00000X₁X₂ - 575.00000X₁X₃ - 1175.00000X₁X₄.

Through the analysis and verification of the model, it is concluded that the model is accurate and reliable; the model can provide some reference for predicting the actual pretreatment process combination.

(2) The effects of four factors on biogas production of straw are in turn: component ratio, treatment time, alkali concentration and solid-liquid ratio.

(3) The optimum combination of alkali pretreatment was obtained as follows: alkali concentration was 6%, solid-liquid ratio was 1:5, treatment time was 4.5 days, component ratio was 1:1.125. Under these conditions, the biogas production of anaerobic fermentation reached 28335 mL, which is the maximum value.
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