Kinetic study of biogas production from anaerobically digested rice straw

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Article Info

Article history:

Received Jun 13, 2024
Revised Nov 25, 2024
Accepted Jan 26, 2025

Keywords:

Anaerobic digestion
Biogas
Gompertz model
Kinetic parameters
Lignocellulose
Pretreatment

ABSTRACT

Rising concern about environmental protection has demanded prompt researchers' attention towards alternative renewable energy sources. Thus, biofuel production with biodegradation of crop straws through anaerobic digestion has attracted the attention of the scientific community. However, the lignocellulosic nature of rice straw poses resistance to its disintegration through anaerobic digestion. Aiming to optimize the concentration of sodium hydroxide pretreatment of rice straw for efficient biogas production this study was conducted. For this purpose, the pretreatment was done on rice straw with different concentrations of sodium hydroxide at about 25 °C temperature for 24 hours before subjecting it to anaerobic digestion for biogas production. The 6% sodium hydroxide pretreated rice straw was observed to be resulting in the highest cumulative biogas production which was found to be 56.3% higher than untreated rice straw. In the kinetic study of biogas production, 6% NaOH pretreated rice straw shows the highest biogas production potential at the highest rate of 15.8496 ml/day with a minimum lag period of 0.6758. The experimental study and kinetic study results represent that 6% NaOH pretreated rice straw has the highest biogas production.

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1. INTRODUCTION

Agriculture biomass such as rice straw, corn cobs, wheat straw, sugarcane bagasse, and cotton stalks is abundantly available in agricultural-based countries such as India. Around 511 million tons of crop residues, were generated in India out of which 145 million tons were found to be surplus crop residues that can be utilized sustainably as renewable energy resources to generate electricity [1]. Wheat and rice are the main staple foods to provide carbohydrates to most of the population in the country resulting in higher biomass production from leftovers such as wheat and rice straw. Wheat straw is mainly used as fodder for buffaloes and cattle. However, the higher silica content present in rice straw makes it unfit for utilization as fodder. Burning of rice straw, in northern states of the country such as Punjab, and Haryana causes greenhouse gas emissions, resulting in air pollution [2]. Thus, declining air quality due to the dispersion of pollutants in the environment is an alarming situation for the Indian Government as it adversely affects human health [3]–[5].

Today, energy requirements can be sustainably fulfilled by replacing fossil fuel with biogas production through anaerobic digestion. However, the lignocellulosic nature of these crop residues poses a hindrance to their biodegradation through anaerobic digestion [6]. The biochemical conversion pathway of sustainable utilization of crop residues can help to reduce dependency on non-renewable energy sources by increasing the renewable energy share in the total energy of the country [7]. The anaerobic digestion, the principal technology of the biochemical conversion process involves four steps to convert organic matter present in crop residue to clean and green energy biogas. The lignocellulosic matrix needs to be disintegrated to have efficient biogas production by different pretreatment techniques. Therefore, various pretreatment techniques involving physical, chemical, and biological were originally adopted to alter the lignocellulosic nature of biomass for bioethanol production. These same pretreatment methods have recently gained attention for biogas production enhancement through anaerobic digestion [8], [9]. Physical pretreatment of rice straw is the preliminary step as it helps to reduce the particle size. The substrate made up of large particle size may result in clogging of the digester thereby adversely affecting its performance. Moreover, microorganisms also face difficulty in attacking large particle sizes as compared to small particle sizes [10]. As a result, other pretreatment techniques such as chemical, and biological were found to be effective in optimum biogas production only after physical pretreatment as seen from the literature survey [11]. Grinding of straw improves digestibility through anaerobic digestion but biogas production enhancement was found to be low. Grinding followed by heating processes resulted in a 20% enhancement in methane production. However, alkaline pretreatment of straw helps to reduce lignin content, leading to saponification and solvation reaction and partial solubilization of hemicellulose [12]. Pretreatment of rice straw with 4% H_2O_2 resulted in 135 m^3 of biogas production [13]. While 4% NaOH pretreatment of corn stover resulted in 125 m^3 of biogas production [14]. Bagasse pretreatment with 4% NaOH was found to be effective as compared to 6% NaOH pretreatment of bagasse [15]. The comparative analysis of wheat straw pretreatment with three different techniques namely; using N-methylmorpholine N-oxide (NMMO), organoslov method, and alkaline pretreatment with NaOH showed that alkaline pretreatment resulted in the highest biogas production [16].

Kinetic study of biogas production from different straws helps to validate the experimental results. Therefore, different models were adopted by the researchers to find the biogas production potential, and production rate. Different kinetic models were discussed for the anaerobic degradation of organic material stating that the first-order kinetic model is best suited for the first stage of hydrolysis but it needs to be modified to take into account hardly degradable material [17]. Kinetic study of liquid effluents like fruit juice effluents and vinasse can be obtained through first-order kinetics [18]. Another kinetic study on biogas production from bananas and cassava using a modified Gompertz equation reported that cassava has higher biogas production than bananas [19]. A kinetic study of biogas production from water hyacinth and sugar mill effluent at 40 °C temperature for the incubation period of 15 days reported good results as compared to 30 °C using the modified Gompertz equation [20]. Three different kinetics models, the Gompertz model, the logistic model, and the Gompertz modified model, were opted to predict the kinetic parameter of biogas production from food waste. It has been reported that the modified Gompertz model was the close-fitting for the experimental study [21]. In another study on kinetic modeling of biogas production from date palm fruits three different models; first-order, Gompertz model, and surface-based models were used to analyze the controlling step. The Gompertz model is best suited to experimental results indicating the bacterial growth rate-limiting step [22]. Various studies available in the literature reported the Gompertz model to be best fitted for the kinetic study of bacterial growth in anaerobic digestion [23], [24]. After reviewing the literature, the effect of rice straw pretreatment with different NaOH concentrations and a kinetic study to validate the experimental results were examined in this study. Compositional analysis, Fourier-transform infrared spectroscopy (FTIR), followed by x-ray diffraction (XRD) was adopted to examine the pretreatment effect on fibrous structure, the chemical structure of rice straw.

2. RESEARCH METHOD

2.1. Material collections and method of pretreatment

A bunch of straw was brought from the village of Sahibzada Ajit Singh Nagar Mohali, District of Punjab. It was then sun-dried to eliminate the moisture. The rice straw was physically reduced to a small size through grinding. The cow dung used as inoculum was collected from the cow shed placed near Chandigarh, chemical pretreatment after physical pretreatment is one of the most effective ways to improve the biodegradation of straw through anaerobic digestion. Therefore, rice straws were pretreated with 2, 4, and 6% (w/v) sodium hydroxide for 24 hours. The pH effect of sodium hydroxide was neutralized by washing soaked straws with tap water. Cow dung was added to straw in a ratio of 1:2 for optimum carbon-to-nitrogen ratio. One-liter digester was used for the experimental study of biogas production in the batch-mode process. The compositional analysis of biomass was carried out using the Soxhlet extraction method [25]. The FTIR spectroscopy was used to observe the pretreatment effect on the chemical bonding present in straw.

The crystalline structure of rice straw was studied using an XRD. The features of rice straw are as represented in Table 1.

Table 1. Features of rice straw

Characteristics	Rice Straw (%)
Moisture content	7.4
Total solids	92.6
Volatile Matter	87.16
Carbon	44.13
Nitrogen	0.813

3. RESULTS AND DISCUSSION

This section delves into the influence of pretreatment processes on both the fibrous structure and the chemical characteristics of the material, with a focus on two key aspects: the effects on the fibrous structure and the impacts on chemical bonding and crystallinity. Specifically, it examines how the pretreatment procedures alter the physical organization and morphology of the fibers, as well as how they influence the molecular and crystalline arrangements within the material. By assessing these two dimensions of structure and chemistry, this section provides a comprehensive understanding of how pretreatment processes can improve or modify material properties, thus setting the stage for subsequent processing or applications.

3.1. Pretreatment effect on the fibrous structure

The fibrous composition of native rice straw constituted by lignin, hemicellulose, and cellulose was found to be 22.4, 29, and 31.2% respectively. The NaOH pretreatment shows significant improvement in the cellulose content of rice straw with a decrease in lignin content proportionally. As seen from Figure 1, lignin to cellulose ratio (L/C) has been decreased from 0.722 for untreated rice straw to 0.215 for 6% NaOH pretreated straw. The cellulose content of straw increased by 9 to 67.7% with an increase in the NaOH pretreatment concentration from 2 to 6%. However, an 18 to 50% decrease in lignin and a 20 to 42% decrease in hemicellulose has been observed with the increase in NaOH pretreatment concentration which is quite comparable with the results obtained by Akhtar *et al*. [26], after micro-alkali-acid pretreatment of rice straw.

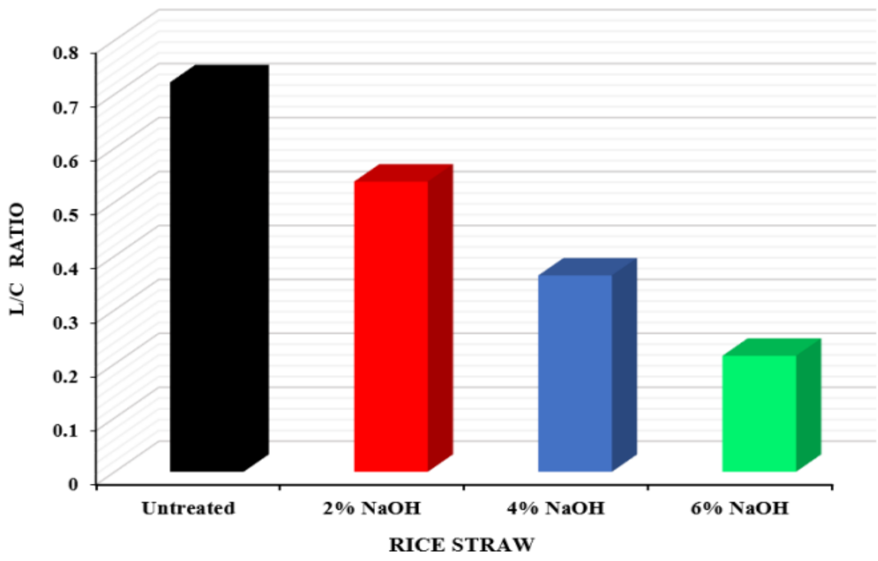

Figure 1. L/C ratio of rice straw

3.2. Pretreatment effect on chemical bonding and crystallinity style

Intrapolymer linkages and interpolymer linkages present in rice straw form multifaceted structures. Lignin, the most complex structure is associated with cellulose, and hemicelluloses by α-ether bonds, glycosidic linkages, and ester bonds. The wide band between 3,300 and 3,450 cm^{-1} forms the backbone of carbohydrates which can be ascribed to the hydroxyl group (OH) present in cellulose and hemicellulose as seen in Figure 2. The enhancement in accessibility of cellulose can be observed from the peaks at 3,440 cm^{-1} signifying that pretreatment affects the hydrogen bonds present in cellulose. The C-H bond stretching in the band at 2914 cm^{-1} represents the splitting of methyl and methylene groups present in cellulose [27]. The aromatic skeletal rings assigned to band 1,512 cm^{-1} present in lignin get weakened after 4% NaOH pretreatment as the intensity of peak reduces as can be seen from Figure 2 [28]. Further, the 899 cm^{-1} band can be attributed to the β-1,4-glycosidic bond linkages present in cellulose and the dissolution of intermolecular hydrogen bonds. However, a small change has been observed in the intensities of peak after 2 and 4% NaOH pretreatment of rice straw in comparison with 6% NaOH pretreatment as seen in Figure 2.

XRD can help to analyze the microstructure of cellulose as the crystalline structure can diffract x-rays in specific patterns. The crystallographic plane (0 0 1) corresponding to the peak at 2θ=18° represents the cellulose I characteristics as observed in Figure 3. The intensity starts to increase after pretreatment as a shift in peak to 22° from 18° has been observed after pretreatment [29]. The crystallinity index of rice straw increases from 54.0% for untreated rice straw to 58.7% for 2% NaOH pretreated rice straw and reaches a maximum of 65.0% for 4% NaOH pretreated rice straw. After this further increase in NaOH pretreatment concentration to 6% resulted in a decrease in the crystallinity index to 63.8%.

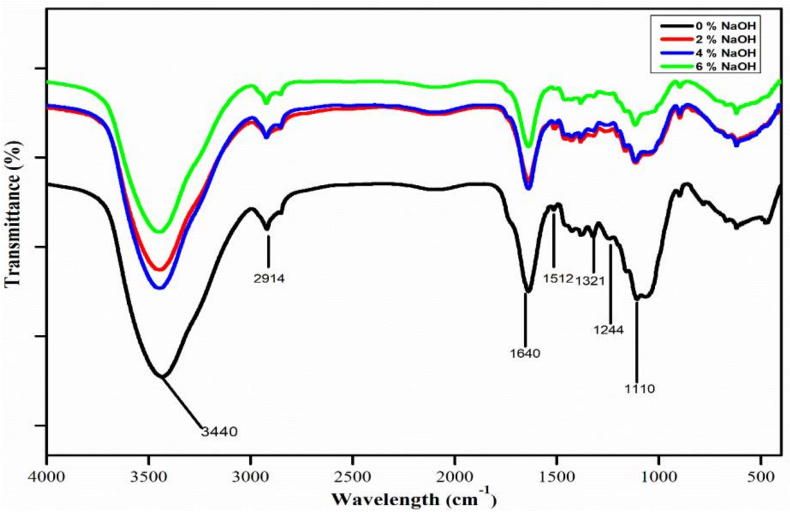

Figure 2. FTIR Spectrum of rice straw

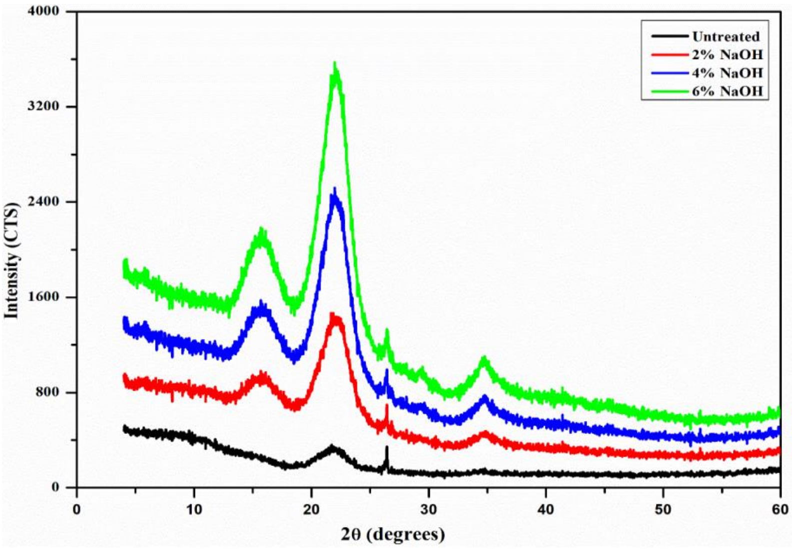

Figure 3. XRD spectra of rice straw

3.3. Production of biogas from rice straw

The cumulative biogas production obtained from anaerobically digested straw for the 45 days of hormone replacement therapy (HRT) at 35+2 °C temperature is shown in Figure 4. It has been observed that the production was less during the initial 3-5 days which may have been due to the high lignin content of rice straw, reduced its digestibility by the microbial attack initially. However, a significant increase in biogas production has been observed between 10-25 days of the period of anaerobic digestion of rice straw. The 6% NaOH pretreatment resulted in 56.3% higher biogas production than the control group while a 38.8 and 10% increase in biogas production was observed after 4 and 2% NaOH pretreatment respectively. 6% NaOH pretreatment gives rise to the maximum production of biogas followed by 4 and 2% NaOH pretreated rice straw as seen in Figure 4.

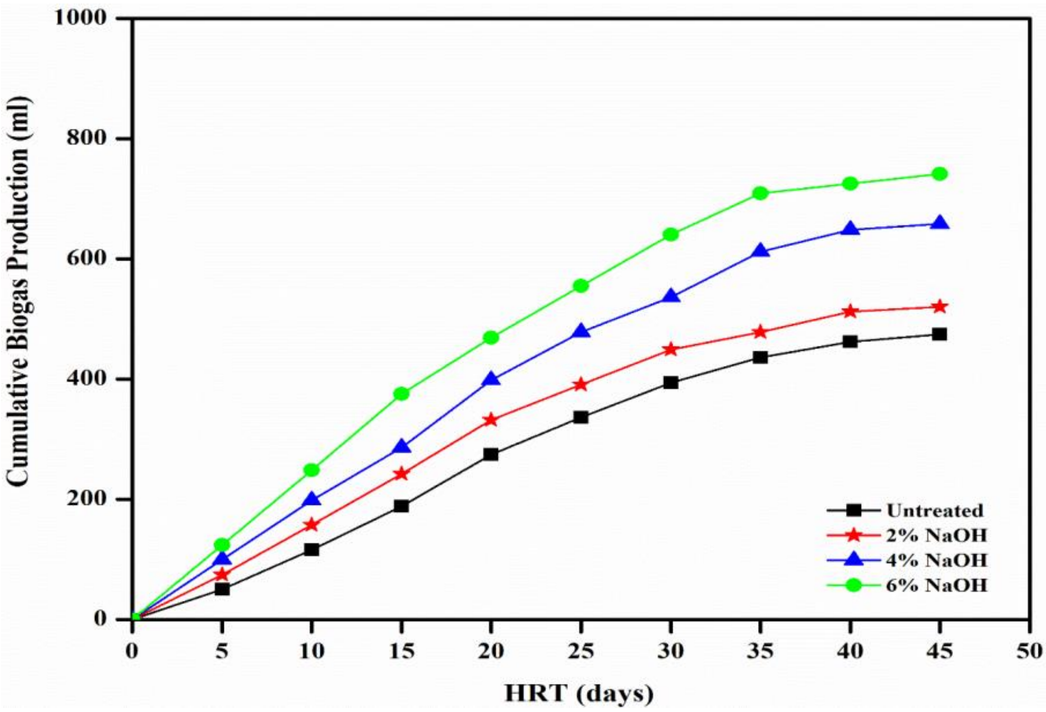

Figure 4. Cumulative production of biogas from rice straw

3.4. Kinetic model fit experimental data

Kinetic models of the experimental data are reported to be an efficient tool for optimizing the co-digestion process and determining the rate of biogas production. The modified Gompertz model applied to bacterial growth fits well with the experimental data obtained for cumulative biogas yield [30]. The modified Gompertz equation corresponding to the methanogenic bacteria growth rate in the digester is (1).

$$Y(t)=A*exp\{-\exp[\mu e\, A(\lambda-t)+1]\} \quad (1)$$

Where the cumulative production of biogas (ml) obtained is represented by Y(t), the production potential of biogas in ml is denoted by A, and the production rate in ml/d is represented by μ, e is a mathematical constant having a value equal to 2.718282, and λ represents the lag phase period, and t represents the period of biogas production (day). Figure 5 represents the experimental data and model data of NaOH pretreated rice straw. It has been observed that the model data fits well with experimental data with a co-efficient of regression (R^2) greater than 0.95 for each pretreatment of rice straw. The kinetic study of biogas production reveals that rice straw after 6% NaOH pretreatment has a maximum biogas production potential of 411.2082 ml at a maximum rate of 15.8490 ml/day with a minimum time lag period of 0.6758 as can be seen from Table 2.

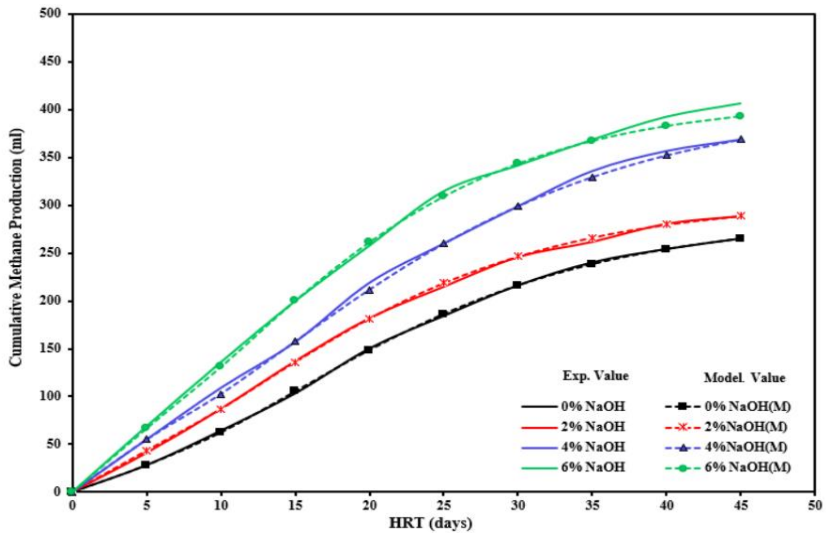

Figure 5. Comparative of experimental and model data for the production of cumulative biogas production

Table 2. Kinetic parameter constants of bagasse

Rice Straw	A (ml)	μ (ml/d)	λ
Untreated	287.2854	10.0349	3.1559
2% NaOH	306.2430	11.2013	1.2429
4% NaOH	408.7547	11.1861	0.9108
6% NaOH	411.2082	15.8490	0.6758

4. CONCLUSION

The pretreatment of rice straw helps to disintegrate the lignin-hemicellulose-cellulose matrix. As in the FTIR spectrum, the cleavage of lignin bonding and new peaks observed after pretreatment can be seen. The increased crystallinity index with chemical pretreatment represented increased cellulose content which was bounded by lignin in untreated rice straw. Further, enhancement in biogas production was observed with increased concentration of sodium hydroxide pretreatment of rice straw. 6% NaOH pretreatment was found to be most effective in biogas production. The kinetic study of biogas production also confirmed the results obtained from the experimental study.

Future research on rice straw pretreatment should focus on optimizing NaOH concentrations, exploring alternative methods, and understanding lignin cleavage mechanisms. Additionally, combining pretreatment techniques, scaling up processes, and evaluating environmental impacts is crucial. Exploring broader applications, such as biofuels and value-added products, will further enhance sustainability and efficiency.

ACKNOWLEDGMENTS

The author is grateful to the SAIF/CIL Lab. of Panjab University, Chandigarh, India where all the testing of straw has been carried out.

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