

**STUDIES ON PRETREATMENTS AND REACTORS
FOR METHANE FERMENTATION FROM
LIGNOCELLULOSIC BIOMASS**

by

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CERTIFICATE

This is to certify that the thesis entitled, “**Studies on Pretreatments and Reactors for Methane Fermentation from Lignocellulosic Biomass**”, being submitted by **Ms. Meena Krishania**, to the Indian Institute of Technology Delhi for the award of the degree of **Doctor of Philosophy**, is a record of *bonafide* research work carried out by her. She has worked under my supervision and guidance and has fulfilled the requirements for the submission of this thesis, which has attained the standard required for a Ph. D. degree of the Institute.

The results contained in this thesis have not been submitted in part or full to any other university or institute for award of any degree or diploma.

Date:

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ABSTRACT

The thesis deals with the studies on “Studies on Pretreatments and Reactors for Methane Fermentation from Lignocellulosic Biomass”. These lignocellulosic biomasses have been considered as main resource to produce bio-energy and bio-products for second generation of bio-fuels production. Lignocellulosic biomass contains high percentages of lignin, which is hard to biodegrade in the biological process of energy conversion. Therefore, pretreatment is required to enhance energy recovery. In this study, four types of pretreatments, i.e., dilute acid, alkali, combination of calcium hydroxide-sodium carbonate, and grinding were applied on wheat straw to enhance the efficiency of methane fermentation. Methane fermentation of untreated and pretreated substrates was carried out at 35 °C temperature in 5 L glass bottle reactors. Cumulative methane production yields of these pretreated substrates were found as 0.125, 0.370, 0.380 and 0.241 m³/kg of VS, respectively, for WS: 2% H₂SO₄, WS: 2% NaOH, WS: 3% Ca(OH)₂ + 3% Na₂CO₃, and WS: PHY treatments compared to that of untreated treatment WS as 0.191 m³/kg of VS. Alkali (2% NaOH on weight/volume ratio basis) and calcium hydroxide with sodium carbonate combination (3% Ca(OH)₂ + 3% Na₂CO₃ on weight/volume ratio basis) pretreatments have been found to improve biogas and methane production yields by 94.0% and 99.0%, respectively in comparison to the untreated wheat straw substrate.

The efficient pretreatment was further optimized by using response surface methodology (RSM) by software Design of Experiments. The RSM was performed to optimize the combinations of catalysts pretreatment with time and temperature for the enhanced production of methane. The experimental results showed that both concentration and time had interactions with temperature, and the interactions had significant effects on the hydrolysis and methanogenesis of pretreated wheat straw. The maximum methane yield was 0.383 m³/kg VS observed. The model of RSM study also supported with the experimental results and showed almost similar methane yield. According to the regression equation obtained by using RSM technique, nearly the theoretical yield was obtained under the following conditions: catalyst concentration 2.89 %, temperature 33.66 °C, incubation time 27.87 h. RSM with the Box-Behnken design has been found very useful tool for identifying the important factors influencing methane

production from pretreated wheat straw and predicting the methane production yield from lignocellulosic substrates.

The optimized pretreated wheat straw with the proper ratio of cattle manure (40:60) was further analyzed in different reactors for field level study. Evaluation of the performance of different semi-continuous reactor configuration in the present study showed that anaerobic digestion of wheat straw as substrate is feasible in FFR and CSTR reactors. With FFR, maximum methane yield of $0.342 \text{ m}^3/\text{kg VS}$ could be obtained at an OLR of $2.2 \text{ kg VS}/\text{m}^3/\text{d}$ and HRT of 90 d. On the other hand, the same process in CSTR reactor was found less efficient at the same substrate concentration which resulted into $0.289 \text{ m}^3/\text{kg VS}$. FFR reactor showed 41 % higher efficiency than control BR and CSTR showed only 10 % increased in methane production efficient compared to control BR. Co-digestion of wheat straw with cattle manure were improved the methane yields in both the reactors. Thus, anaerobic digestion of wheat straw for biogas production was improved the overall energy and the economy of the biorefinery concept in semi-continuous reactor FFR for pretreated straw with cattle manure ratio (40:60).

Furthermore, kinetic study was performed for both batch and semi-continuous reactors. Gompertz model used to analyze the kinetic behavior of anaerobic digestion process in the batch reactor. Kinetic study indicates that Gompertz equation best described the cumulative gas production as a function of the digestion time. The study indicates that the Gompertz equation best describe the cumulative gas production as a function of the digestion time in batch reactors. The biogas yield potential, A was observed maximum for pretreatment substrate WS: 3% $\text{Ca}(\text{OH})_2 + 3\% \text{Na}_2\text{CO}_3$ as $1.1620 \text{ m}^3/\text{kg}$ of VS. Shortest lag phase, B was exhibited by the pretreatment substrate WS: 3% $\text{Ca}(\text{OH})_2 + 3\% \text{Na}_2\text{CO}_3$ as 9.34 days. The biogas production rate, C for pretreatment substrate WS: 3% $\text{Ca}(\text{OH})_2 + 3\% \text{Na}_2\text{CO}_3$ was observed lowest as $0.035 \text{ m}^3/\text{kg}$ of VS/day. Further, the Chen-Hashimoto model best describe the kinetic in the semi-continuous reactors. The best fit equation results in a value of the regression coefficient as 0.998 and 0.996 in semi-continuous reactors FFR and CSTR. The minimum value of retention time to achieve a stable rate of methane production was found as 14 days in both reactors compared to the control reactor (BR).

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