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Research paper



Effect of Fe_2O_3 as Catalyst on Biogas Production from Dry Banana Leaves

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Abstract

Anaerobic digestion (AD) of dry banana leaves to produce biogas and the biogas production patterns under the influence of additives has been studied in present work. The impact of different dosage of Fe_2O_3 catalyst along with urea added by 2% based on dry weight of banana leaves added in sewage water inoculums for production of biogas were observed for 50 days of retention time. Simultaneous scrubbing arrangement was arranged to purify the raw biogas to enrich the methane content in the upgraded biogas. The results revealed that sewage water (S) with urea reached the peak CH_4 concentration in biogas (64.72%) during 38 days, as compared to S+Urea+15 mg Fe_2O_3 (67.25%) in 30 days and S+Urea+25 mg Fe_2O_3 (65.15%) in 34 days. Addition of Fe_2O_3 indicated a reduction of lag phase in CH_4 generation and attains the peak CH_4 concentration at a faster rate. Purification of the raw biogas with 1 N NaOH solution has shown a drastic enrichment in CH_4 content by absorption of CO_2. The peak CH_4 content after purification was found to be 83.24, 86.02 and 84.25% for S+Urea, S+Urea+15 mg Fe_2O_3 and S+Urea+25 mg Fe_2O_3 inoculums respectively.

Keywords: *Banana leaves; biogas; methane; microbes; urea.*

1. Introduction

The increasing energy demand is a vital element for economic expansion of a developing country that needs to be addressed to sustain the growth rate. In most of the cases fossil fuel is used as the source of energy which is depleting the conventional reserves of energy at a faster rate that insists the researchers for development and dissemination of renewable energy resources to consider as a substitute [1,2]. Presently numerous researches are going on to find suitable alternative sources of energy to overcome the energy demand and simultaneously reduce the green house emissions to the environment [3]. Biomass is one of the indispensable renewable energy assets in the field of sustainable renewable energy. Biogas can be produced from biomass such as algae, wastes from agriculture, garden waste, food wastes and municipality solid wastes by biological process. Anaerobic digestion (AD) is a biological degradation process, which can be broadly segmented into four stages namely: hydrolysis, acidogenesis, acetogenesis and methanogenesis. During hydrolysis the feedstock is broken down into simpler sugar by enzymes, followed by acidogenesis where acidogenic bacteria or acid forming bacteria utilize the products such as amino acids, fatty acids and monomeric sugars for their growth leading to formation of volatile fatty acids like butyric acid, valeric acid, and propionic acid in company with carbon dioxide (CO_2), water (H_2O) and hydrogen (H_2) as bi-products. In next step acetogenic bacteria use volatile fatty acids for their growth and decompose them into acetic acid as well as CO_2 and H_2. Lastly, in methanogenesis phase methanogens convert hydrogen and acetic acid produced by acid formers to methane and CO_2. Biogas is primarily composed of 50-75% methane (CH_4) and 25-50% CO_2 produced from AD of organic matter. Biogas can be used for the production of electricity, cooking purpose, steam generation and heating in rural as well as urban areas [4]. Sorathia et al. investigated on impact of different factors such as temperature and pH within the digester affecting the rate of biogas production and found that raise in pH and temperature during AD reduced the rate of biogas production [5]. Meabe et.al investigated the performance of AD under mesophilic and thermophilic conditions and concluded that mesophilic range of operating temperature gives enhanced biogas generation [6]. Tian et al. investigated that biogas production from agricultural waste; can reduce environmental pollution caused by natural decay of such wastes [7]. The rate of biogas production depends upon both influential factors within the reactor and composition of the biomass used. Thus, prior to AD, pretreatment is highly essential in reduction of the compositional and structural disablements of lignocellulosic biomass. This in turn helps in easy microbial breakdown of polymeric chains of cellulose and hemicellulose leading to increased rate of organic degradation and biogas generation. Liu and Ge sequentially studied the consequence of urea dosage in AD and found that, with addition of 2% urea by dry weight of the giant reed grass yields 18% higher methane [8]. Abdelsalam et al. studied the impact of nanoparticles (NPs) dosage in AD process. They observed that NPs reduces the lag phase and stimulates rate of biogas production [9]. Wang et.al investigated four representative NPs during AD of waste activated sludge for methane production and found that low concentration of non-zero valent ions (nZVI) and ferric oxide enhanced the amount of microbes and enzymes activity whereas higher concentration of silver and magnesium oxide NPs inhibited growth of the microbes [10].

Kamdem et al. studied the production of biogas from different morphological part of the banana tree in 50 ml of culture volume of each sample. They concluded that leaf blades generated less biogas than other samples, while biogas produced from leaf blades is richest in CH_4 (78%) [11]. Jena et.al investigated CH_4 content in the generated biogas from banana leaves taking different sample quantities (25 g, 50 g, 75 g) and found that 50 g sample gave

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highest CH_4 production indicating the optimized substrate to effluent ratio [12].
The purpose of this study is to perform an experiment to investigate the impact of different amount of Fe_2O_3 catalyst on biogas production from semi-dried banana leaves in urea added sewage water. Simultaneously biogas purification was performed using NaOH solution to absorb CO_2 content from the raw biogas.

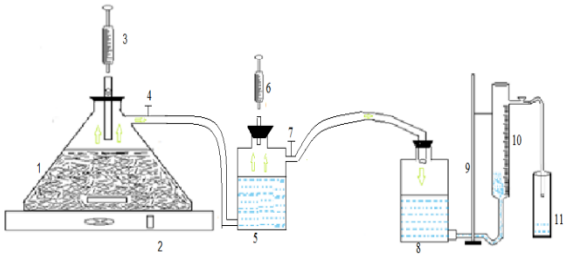
2. Materials and Methods

2.1 Raw Materials

Banana leaves were collected from a local plantation farm, thoroughly washed in water and the leaf blades were sundried. Then the leaf blades were chopped into smaller pieces before being grinded to smaller sized particles (2-3 mm). Sewage water was chosen to prepare microbial inoculants, which was collected from the local municipality wastewater treatment plant and filtered to separate inorganic substances like plastic, stones, sand etc. In this experimentation 1*N* NaOH solution was chosen as absorbent for purification of the raw biogas. The composition of produced biogas was determined by a gas chromatograph (Chromatography and Instruments Company, India), assisted with a thermal conductivity detector using nitrogen gas as carrier gas. An air tight gas syringe (VICI, US) was used to collect gas sample in each 4 days interval to measure the concentration of biogas compositions. Three consecutive samples of gas was taken from each inoculums and readings were obtained from the gas chromatograph and the mean value was considered for analysis.

2.2 Procedure

A batch experiment was conducted with a sample of 500 ml of sewage water (S) poured into 3 reactors each of capacity 1 L, sealed with a rubber stopper as shown in Fig. 1.



1. Reactor
2. Magnetic stirrer
3. Syringe
4. Stopper valve
5. Solution vessel
6. Syringe
7. Stopper valve
8. Water vessel
9. Stand
10. Burette
11. Drainage container

Fig. 1: Schematic layout of biogas generation setup.

The pH of all the 3 inoculums was measured using pH meter and maintained in the range of 7.5±0.2 by using 1 *N* NaOH solution. 2% of urea based upon the dry weight of the banana leaves was added to all reactors and stirred at 130 rpm for 30 minutes.
In one reactor 15 mg of Fe_2O_3 catalyst was added and the mixture (S + Urea +15 mg Fe_2O_3) was stirred for an hour with the help of magnetic stirrer. Then in next reactor, 25 mg of Fe_2O_3 catalyst was added (S+ Urea +25 mg Fe_2O_3) and stirred properly for an hour. Then 50 g of the ground banana leave sample (2-3 mm size) was added to all reactors and stirred properly for an hour. Lastly, all the reactors were tightly sealed after placing the stopper in the reactor.
The outlet of each reactor is connected through plastic hose to the bottom of a 500 ml vessel containing 1*N* NaOH solution as absorbent, where the produced raw biogas was bubbled for purification. The initial pH of 1 *N* NaOH solution was found to be 11.94±03. Two sampling points are present in the reactor setup, to take raw and purified biogas respectively as shown in Fig. 1. The gas accumulated in the solution vessel moves to the water vessel and under pressure displaces water level in the measuring burette to be balanced with atmospheric pressure, indicating the amount of gas produced on daily basis.

3. Results and Discussion

The deviation of biogas generation with respect to time under varying dosage of Fe_2O_3 catalysts with urea added sewage water inoculums is presented in this work. The digesters were kept under observation for 50 days and the impact of additives on biogas production and CH_4 content in the produced biogas were analyzed.

3.1 Variation of CH_4 Content in Biogas

The variations of CH_4 content with respect to time for different inoculums are illustrated in the Fig. 2. Based on the experimental results, it is evident that for all the inoculums, the methane gas composition in the produced biogas was low during the initial phase of the observation. Methane production showed an initial lag phase of 4-5 days for Fe_2O_3 added inoculums while S+Urea have showed a lag period of 10-12 days. This may be due to proper nutrient balance and increased buffer capacity with presence of additives that enhanced the bacterial activity and helped to reaches the highest peak of CH_4 content in the range of 30-34 days. The favorable growth of methanogen bacteria due to presence of urea along with proper stirring which facilitate effective activity of bacteria inside all the reactors. Fe_2O_3 as catalyst with urea added sewage reached the peak value of CH_4 content earlier as compared to S+ Urea inoculums, indicating positive impact of Fe_2O_3 on hydrolysis and acidogenesis. Fe_2O_3 is a semi-conductive mineral which serve as electron donors and acceptors that accelerates the methane production reaction [10]. Then the percentage of CH_4 showed steady decline in the rate of biogas generation after certain days, which may be attributed to increase in ammonia concentration with accumulation of other toxic compounds and decrease in pH value leading to buildup of volatile fatty acids in the inoculums which hindered the bacterial growth and caused a fall in fermentation rate [12,13]. It was found that the methane concentration reached the peak value for S+Urea+15 mg Fe_2O_3 which recorded to be 67.25% in 30 days compared to 65.15% in 34 days for S+Urea+25 mg Fe_2O_3 and that for S+Urea solution it is found to be 64.72% in 38 days.

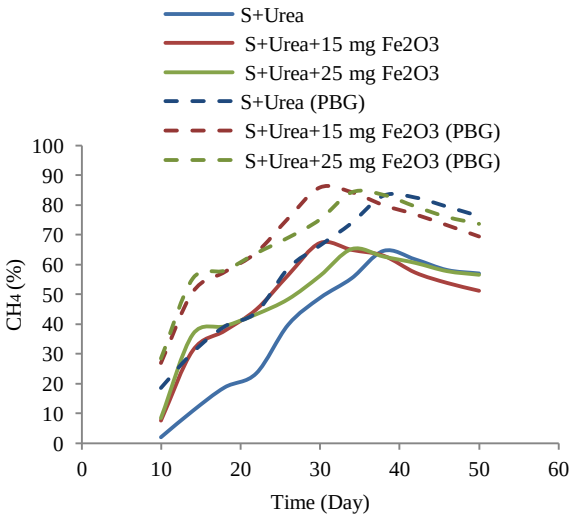


Fig. 2: Variation of CH_4 content with respect to time.

Fig. 2 represents the impact of NaOH solution on purification of biogas in terms of enriched CH_4 content. The graphical representation indicates that purified biogas (PBG) shows enriched CH_4 content. The bubbling effect of biogas in NaOH solution plays a huge role in CO_2 absorption. The reaction of CO_2 with NaOH solution could be expressed as:

$$H_2O + CO_2 \rightarrow 2H^+ + CO_3^- \quad (1)$$

$$2H^+ + NaOH + CO_3^- \rightarrow NaCO_3 + H_2O \quad (2)$$

The highest CH_4 content of 86.02% was achieved in PBG for S+Urea+15 mg Fe_2O_3 inoculums in 30 days. S+Urea+25 mg Fe_2O_3 effluent have shown 84.25% of CH_4 content in PBG at 34 days retention time, while for S+Urea inoculums reached a peak of CH_4 content up to 83.24% in 38 days of retention time. The final pH of 1 mole NaOH solution used for purification for all samples was found to be in the range 8. 32 to 8.65.

3.2. Effect of Fe_2O_3 Catalyst on Volume of Biogas Production

The daily biogas generation and cumulative biogas generation are shown in Fig. 3 and 4 respectively. Addition of Fe_2O_3 clearly indicates its stimulating effects on biogas production as observed from Figure 3. The average production of biogas is found to be 30.6 ml and 31.4 ml for S+Urea+15 mg Fe_2O_3 and S+Urea+25 mg Fe_2O_3 respectively as compared to 18.2 ml for S+Urea during the first five days of retention time. Inoculums with Fe_2O_3 additives given more than 90 ml per day of biogas from day 25-36, while inoculums without Fe_2O_3 additives given more than 57 ml per day of biogas from day 31-41.

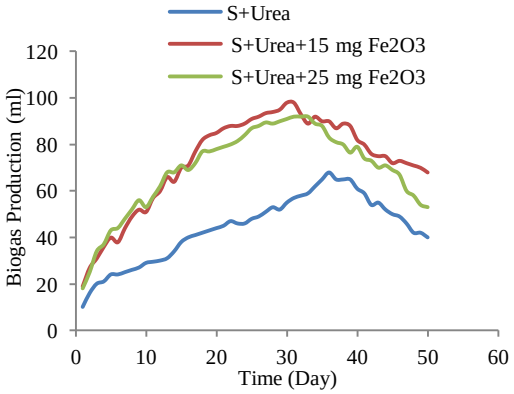


Fig. 3: Variation in daily volume of biogas production with time.

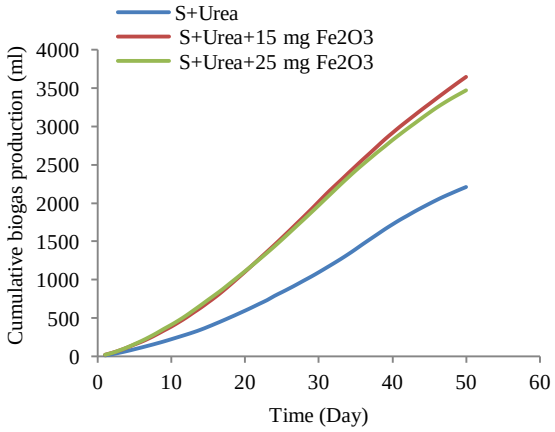


Fig. 4: Variation of cumulative biogas production with time.

Furthermore, the highest daily methane yield was achieved by S+Urea+15 mg Fe_2O_3 which yielded around 98 ml biogas by 30 days, while for S+Urea+25 mg Fe_2O_3 inoculums highest biogas yield was found to be 92 ml from 31-33 days. It can be noticed from Fig. 4 that, cumulative methane production curves illustrates that by addition of Fe_2O_3 cumulative biogas production reached 3648.5 and 3471 ml for S+Urea+15 mg Fe_2O_3 and S+Urea+25 mg Fe_2O_3 respectively indicating a significant increase in biogas volume by 1.65 and 1.57 times the volume produced by S+Urea (2209.5 ml).

3.3. Variation of CO_2 Content in Biogas

The variations of CO_2 with time for different additives are illustrated in the Fig. 5. Based on the experimental results, it is evident that for all the inoculums, a similar trend was observed for the rate of change of concentration of CO_2 gas in the reactors.

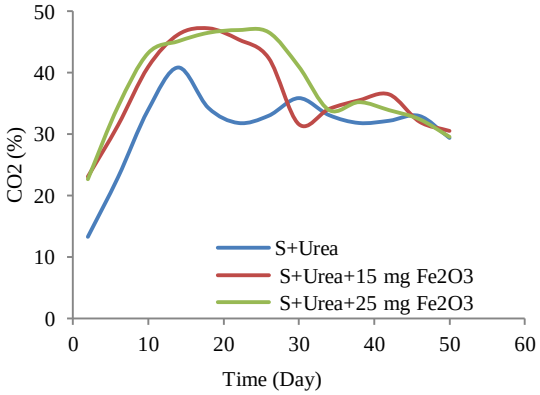


Fig. 5: Variation of concentration of CO_2 in biogas.

CO_2 was more in initial phase as the long chain polymeric molecules are converted to smaller ones and then converted to volatile fatty acids with generation of CO_2. Therefore, a steep rise in CO_2 was observed in all reactors. Different amount of Fe_2O_3 catalyst has shown slightly high concentration of CO_2 throughout the retention time (days) as compared to S+Urea inoculums. After 14-18days, concentration of CO_2 in the produced biogas starts a decrease trend in all inoculums, may be due to impact of methanogens which reduces CO_2 and H_2 to produce CH_4.

4. Conclusions

Biogas production from dry banana leaves and its purification using NaOH solution were performed in the current study, the following conclusions are drawn.

- Fe_2O_3 addition as catalyst in urea added sewage water increased the production rate of methane in biogas due to catalytic effect of ferrous ions, which increased the bacterial inter action with the substrate.
- Addition of ferrous additives decreased not only the lag phase but also the time to accomplish the maximum biogas and volume of methane generation in daily basis.
- Fe_2O_3 with a dosage of 15 mg/L observed to be efficient in enhancing the biogas and methane production, which reached the highest concentration of 67.25% in 30 days followed by 65.15% for S+Urea+25 mg Fe_2O_3 and 64.72 for S+Urea.
- The cumulative CH_4 production reached to 2209.5, 3648.5 and 3471 ml for S+Urea, S+Urea+15 mg Fe_2O_3 and S+Urea+25 mg Fe_2O_3 respectively in 50 days of retention time.

- Nearly 100% CO_2 removal was achieved by bubbling of raw biogas through 1 mole NaOH solution during the 50 days of retention time.
- In purified biogas the peak CH_4 content was found to be 83.24, 86.02 and 84.25% for S+Urea, S+Urea+15 mg Fe_2O_3 and S+Urea+25 mg Fe_2O_3 inoculums respectively.

Fe_2O_3 can be considered as suitable catalyst to reduce the lag phase of biogas production during AD of banana leaves. However, impacts of catalysts in large scale production needs experimentation with proper design of the reactor and controlling the influential factors of AD process in desired level.

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