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***Research paper***



# Effect of Different Catalysts on the Production Rate of Biogas from Banana Leaves

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## Abstract

In this study, the effect of metal oxide nanoparticles (NPs) such as titanium oxide ($TiO_2$) and aluminum oxide ($Al_2O_3$) mixed with urea (2% by dry mass of the leaves) added to 500 ml of sewage water samples on production of biogas and was compared with the results of pure sewage water as base effluent. The observations revealed that sewage water with urea alone (S+U) showed better performance in the production of biogas and methane content than pure sewage water and NPs mixed inoculums. Maximum methane yield content was found in case of S+U effluent as recorded to be 65.28% in 38 days. While methane content of pure sewage was found to be 54.46 % in 46 days and in case of $TiO_2$ added effluent methane yield was found to be 59.18 % in 38 days and in case of $Al_2O_3$ added effluent it was recorded to be 54.88% in 42 days.

***Keywords***: *Anaerobic digestion; biogas; methane; microbes; nanoparticles.*

## 1. Introduction

Increasing population and industrialization of the world have led to sharp rise for demand of fuels. India being a rapidly developing economy is a major consumer of fossil fuels, as 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]. Non-Conventional sources of energy can curb the increasing demand of fossil fuels and help towards sustainable development of the economy. Thus, renewable sources of energy are being given immense attention these days to curb the rising demand of energy. One of such renewable alternatives is the use of biogas. Owing to easy and cheap availability of raw materials, use of biogas in rural areas is highly recommended. Moreover, the cost of installation as well as maintenance is also less compared to other renewable sources like wind, solar, tidal etc. Biogas can be produced from biomass by biological process, which includes algae, trees or wastes from agriculture, food wastes and municipality solid wastes.

Anaerobic digestion (AD) can be broadly categorized into four processes namely: hydrolysis, acidogenesis, acetogenesis and methanogenesis. Hydrolysis is the first step that involves breaking down of solids (particulate and colloidal wastes). The hydrolytic microbes produce extracellular enzymes, which decompose complex organic polymers into simple monomers (volatile acids and alcohols). In acidogenesis where acidogenic bacteria or acid forming bacteria utilize the simple monomers 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 along with $CO_2$, 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 and hydrogen. Lastly in methanogenesis involves the production of methane and carbon dioxide by the utilization of acetic acid [4]. Biogas is primarily composed of 50-75% methane ($CH_4$) and 25-50% carbon dioxide ($CO_2$) generated from AD of organic matter in the absence of oxygen. Biogas can be used for the production of electricity, cooking purpose, steam generation and heating in rural as well as urban areas [5,6].

Meabe et.al investigated the performance of AD under mesophilic and thermophilic conditions and concluded that mesophilic conditions are more effective for microbe growth, resulting in higher biogas generation [7]. Tian et al. investigated that biogas production from agricultural waste; can reduce environmental pollution caused by natural decay of such wastes [8]. Again, pretreatment of the substrate used 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 studied the impact of urea addition in reacting medium of AD and observed, with addition of 2% urea by dry mass of the giant reed yields 18% higher $CH_4$ content in the generated biogas [9]. Gopinath et al. examined the consequence of urea in pineapple pulp waste, which gives 19% higher biogas production as compared to the control, and in addition to that, they found out that with addition of various metal ions enhanced the biogas production [10]. Feng et al. concluded from their experimentation that with dosage of trace elements like cobalt (Co), nickel (Ni) increased the rate of biogas production [11]. Abdelsalam et al. studied the consequence of nano-particles (NPs) addition in AD and concluded that, presence of NPs in reacting medium decreased the lag phase in turn enhances the rate of biogas production [12]. Use of additives could improve the production and performance of biogas significantly. The suitability of an additive depends on the type of substrate used for the generation of biogas [13]. Wang et.al investigated four

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representative nanoparticles during anaerobic digestion 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 [14]. India ranks second in the world after china for the production of vegetable and fruits and wastes from these products are produced in large amount. Biomass rich in ligno-cellulose like agricultural and crops residuals are considered as an abundant organic resource. Ligno-cellulosic biomass generally consists of three major kinds of polymers namely lignin, cellulose and hemicellulose. Banana being the second most cultivated fruits in India [15]. Previously researchers already experimented on different parts of banana tree to produce biogas. Kalia and Sonakya achieved reasonably higher $CH_4$ content in generated biogas at mesophilic condition using dry banana stems and fresh cattle dung effluent [16]. 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%) [17]. 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 highest $CH_4$ production indicating the optimized substrate to effluent ratio [15].

The purpose of this study is to perform an experiment to evaluate the impact of metal-oxides ($TiO_2$ and $Al_2O_3$) and compared their results with sludge added with urea and pure sewage for the production of biogas using anaerobic digestion process using waste banana leaves.

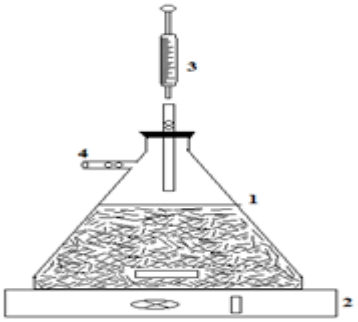
## 2. Materials and Methods

### 2.1 Raw Materials

Banana leaves were collected from a local plantation farm and thoroughly washed in water for the experimental analysis and these leaf blades were sundried. Furthermore, these were chopped into smaller pieces before being ground to smaller sized particles (2 to 4 mm). For microbial inoculants, sewage water from the local municipality wastewater treatment plant was collected and filtered to separate inorganic substances like plastic, stones, sand, gravel etc.

### 2.2 Procedure

A batch experiment was conducted with a sample of 500 ml of sewage water poured into four reactors each of capacity 1 L, sealed with a rubber stopper and a gas outlet as shown in Fig. 1. pH of all the four inoculums were measured using pH meter and maintained in the range between 7- 7.5 by using 1 *N* NaOH solution.




1. Reactor 3. Syringe
2. Magnetic stirrer 4. Gas purge

**Fig. 1:** Block diagram of biogas reactor.

2% of urea by dry weight of the banana leaves was added to three reactors and stirred for 30 minutes. From these three reactors, 15 mg $L^{-1}$ of $TiO_2$ was added to one reactor and 15 mg $L^{-1}$ of $Al_2O_3$ were added in one reactor (urea added effluent) and mixture was stirred for an hour with the help of magnetic stirrer. Then in each digester, 50 grams of the ground banana leaves sample was mixed thoroughly and stirred. All the reactors were tightly sealed after placing the stopper in the reactors, and were made vacuum to remove the oxygen content using vacuum pump. All processes were done at mesophilic temperature of 35˚C [18]. 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 were taken from each effluent and readings were obtained from the gas chromatograph and the mean value was considered for analysis.

## 3. Results and Discussion

The variation of biogas production with respect to time (days) for different NPs, pure sewage (S) and sewage water with urea (S+U) are illustrated, which depicts the favorable states for biogas generation. The digesters were kept under observation for 54 days.

### 3.1 Concentration of Methane in Produced Biogas

The variations of $CH_4$ with time for different blends are illustrated in Fig. 2. A comparative study of $CH_4$ content in the produced biogas was done to study the effect of $TiO_2$ as catalyst with urea inoculums (S+U+$TiO_2$), $Al_2O_3$ as catalyst with urea added inoculums (S+U+ $Al_2O_3$), S+U effluent and pure sewage.

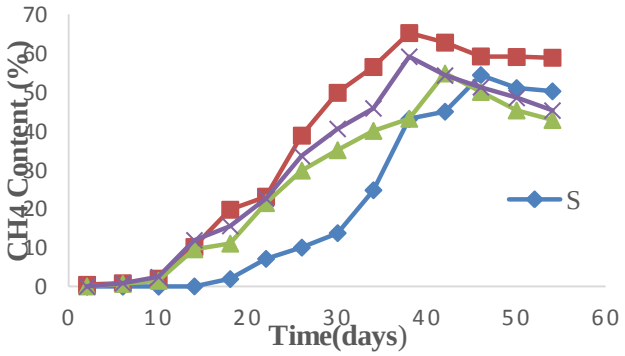



**Fig.2:** Variation of $CH_4$ content with respect to time.

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 (3-5 days) for all the inoculums expect pure sewage water as it has showed a lag phase of 18 days. Methane percentage increases in the range from 14-22 days gradually for all the blends except pure sewage water, which increased in the range of 22-34 days. This may be due to proper nutrient balance and increased buffer capacity with presence of additives that reaches to highest peak of $CH_4$ content in the range of 38-46 days, because of the favorable growth of methanogen bacteria along with proper stirring which facilitate effective activity of bacteria inside all the reactors. Then the percentage of $CH_4$ showed steady decline in the rate of biogas generation after certain days, which can be attributed to increase in ammonia concentration with accumulation of other toxic compounds which hindered the microbe growth and might resulted a drop in fermentation rate [19]. Pure sewage sludge showed lowest methane yield might be due to absence of urea that provides a nitrogen enriched medium for the growth of bacteria.

From the experimentation, it was found that the methane yield was maximum in case of S+U reaching 65.28 % in 38 days compared to S+U+$TiO_2$ which is recorded to be 59.18 % in 38 days, for $Al_2O_3$ was found to be 54.88 % in 42 days and that for pure sewage solution it is found to be 54.46 % in 46 days.

### 3.2 Concentration of Carbon Dioxide in Produced Biogas

The variations of $CO_2$ with time (days) for different additives are illustrated in Fig. 3. As observed from the experimental results, it is noticed that for all the inoculums, a similar trend was observed for the rate of change of concentration of $CO_2$ gas in the reactors. $CO_2$ 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. A comparative study of $CO_2$ was done for different effluents tested for biogas production. Pure sewage has shown higher content of $CO_2$ throughout the retention time, indicating slow conversion rate of $CO_2$ into $CH_4$ as compared to the effluents with additives.

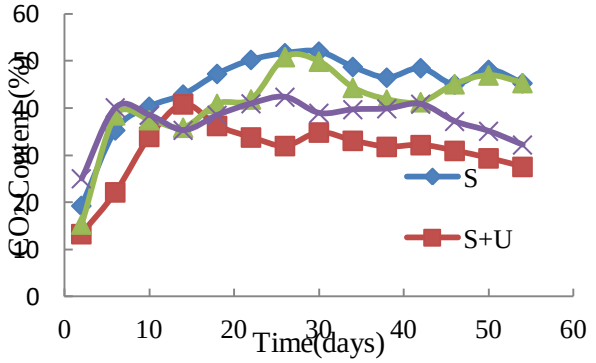



**Fig.3:** Variation of $CO_2$ content with respect to time.

### 3.3 Components of Generated Biogas

Calorific value (CV) of any gaseous fuel mostly depends upon its combustible gas constituent. The components of the biogas are prejudiced by temperature, microbe growth and pH value. Presence of methanogenic bacteria will increase the methane content while lower bacterial activity increases hydrogen content. In the present experimentation, the biogas generated from different reactors was analyzed by a gas chromatograph to record their constituents. The constituents of generated biogas with different additives and their respective CV were presented in Table 1. CV of biogas from S+U is found to be highest 23.61 MJ $Nm^{-3}$ followed by biogas generated from $TiO_2$ added inoculums 21.34 MJ $Nm^{-3}$, $Al_2O_3$ added inoculums 19.77 MJ $Nm^{-3}$ and that of pure sewage water 19.64 MJ $Nm^{-3}$.

**Table 1:** Constituents and calorific values of produced biogas.

| Compositions | S | S+U | S+U+$TiO_2$ | S+U+$Al_2O_3$ |
|---|---|---|---|---|
| $CH_4$ | 54.46 | 65.28 | 59.18 | 54.88 |
| $CO_2$ | 45.05 | 31.82 | 39.91 | 41.31 |
| $H_2$ | 0.002 | 0.064 | 0.001 | 0.002 |
| CO | 0.268 | 0.835 | 0.358 | 0.131 |
| CV (MJ $Nm^{-3}$) | 19.64 | 23.61 | 21.34 | 19.77 |

## 4. Conclusions

According to the results of this study, it is concluded that $CH_4$ content increases in case of S+U with increase in retention time compared to metal oxides NPs ($TiO_2$ and $Al_2O_3$) added effluents and pure sewage water. Production rate of methane increases in S+U effluent due to increase in nitrogen content leading to improved bacterial growth. Highest methane yield was found to be 65.28% in 38 days with calorific value 23.61 MJ $Nm^{-3}$ for S+U effluent. Methane content in pure sewage water was found to be 54.46 % in 46 days with CV 19.64 MJ $Nm^{-3}$. Addition of metal oxide NPs ($TiO_2$ and $Al_2O_3$) shows reduction in lag phase of $CH_4$ formation as compared to pure sewage water.

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