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Mesophilic Process and Kinetics Studies of Selected Biomolecules as Potential Enhancers of Biomethanization of Cow Dung in an Anaerobic Tubular Batch Reactor

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Abstract

Mesophilic biogas production and substrate decomposition is one of the significant limiting steps in biogas generation. The rate of generation and quality often affect the viability of biogas systems. This study assessed the potential for biogas process catalysis using powdered *Sorghum bicolor L.*, *Zea mays*, and *Pennisetum glaucum*. The kinetics and biogas generation processes were studied. Experiments were conducted in 1 m^3 tubular batch reactors, where batches were dosed with various organic biomolecules. Results show that the use of *P. glaucum L.* and *S. bicolor L.* reduced the biogas retention times significantly. Biogas generation commenced after the first day for digesters fed with *S. bicolor L.* and *P. glaucum L.* while one with *Z. mays* and control occurred on day two. The rate of biomethanation and methane content were enhanced. *S. bicolor L.* led to the highest methane content. Findings reveal that locally available organic biomolecules improved biogas quality and quantity.

Keywords

Mesophilic, Kinetics, Biomolecules, Biomethanation, Reaction Rates, Anaerobic

1. Introduction

Biogas is a clean and environment-friendly fuel produced through the anaerobic digestion of organic wastes such as cow-dung, vegetable wastes, municipal solid waste and industrial wastewater [1]. It is increasingly becoming important in domestic and industry as fuel due to its costs and cleanliness. The main component of the gas is methane, carbon dioxide, hydrogen, nitrogen, and hydrogen sulphide [2].

The methane content in biogas constitutes the fuel; it is thus desirable that biogas is of high methane content. To achieve such high methane content highly effective anaerobic digestion through hydrolysis of substrates is critical. More often than not, the hydrolysis process tends to be inefficient due to the general stableness of substrates by enzymes or bacteria. Further, the biogas production process is a biochemical process that is affected by changes in temperature, nutrients, C:N ratio, trace elements as well as inhibitory substances such as ammonia [3].

Like any other production process, biogas production can be enhanced or catalyzed through the use of trace elements like iron and its oxides, process optimization, and the use of catalysts, both organic and inorganic [4].

1.1. Anaerobic Digestions and Its Bacteria

Generally, several species of micro-organism are involved in the production of biogas and anaerobic digestion as shown in **Figure 1**. These can be classified into four trophic groups and stages:

1) Stage 1: Hydrolysis by hydrolytic and fermentive bacteria—they remove oxygen and create anaerobic conditions. In addition, they hydrolyze and ferment organic materials. They include obligate and facultative anaerobes

2) Stage 2: Acidogenesis by syntrophic hydrogen producing bacteria—the oxides NADH by reducing hydrogen ions to hydrogen. Further, they break down acids that have 2 carbon atoms or more to produce carbon dioxide, hydrogen, and acetate. They include the obligate proton reducing bacteria

3) Stage 3: Acetogenesis by acetogenic bacteria—the oxidize hydrogen by reducing carbon dioxide, which is used by the methanogens to produce methane.

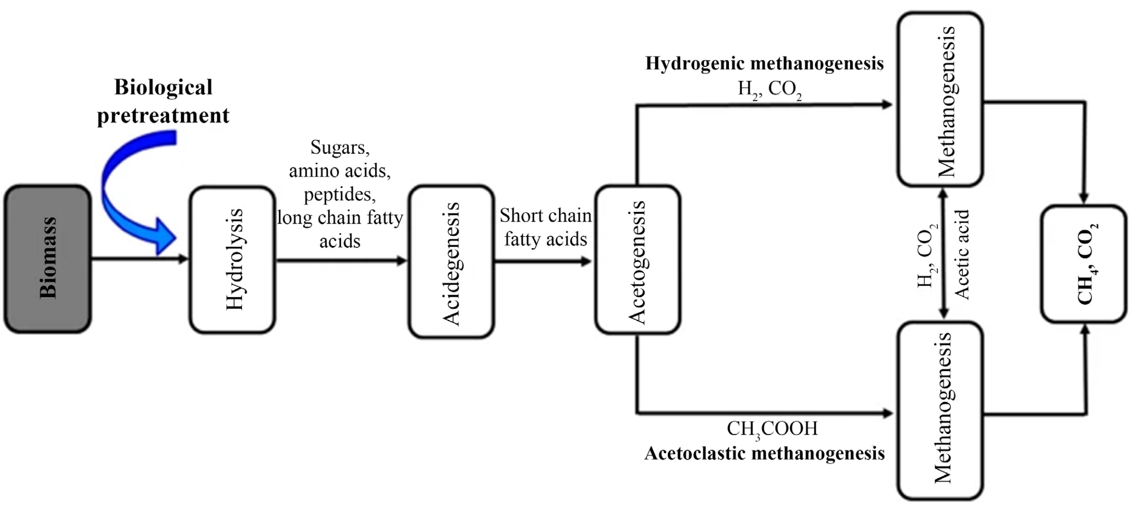

Figure 1. Biological stages of anaerobic digestion [5].

Removal of hydrogen enables the obligate hydrogen producing bacteria to continue their function.

4) The last group of bacteria is the methanogenic bacteria—it converts carbon dioxide, acetate, and hydrogen into methane. This is achieved by the oxidation of hydrogen through the reduction of carbon dioxide.

1.2. Biomethanation

Biomethanation is a chemical reaction where the substrates undergo biodegradation to biogas mediated by anaerobic microorganisms. Catalysts can be defined as substances that enable a chemical reaction to proceed at a usually faster rate or under different conditions (as at a lower temperature) than otherwise possible [6].

Catalysts hasten biomethanation; a biochemical process that can be loosely described as synthetic biology. The process initiation is the formation of catalyst-substrate to form a complex which can be broken further [7].

The complex formation with substrate can be presented using Equation (1);

$$A + F \Longrightarrow AF \quad (1)$$

when a catalyst is added to a reaction vessel some of it participates in the reaction in a reversible process. If φ represents the catalyst, the rate of formation, V, of the catalyst substrate complex is directly proportional to the amount of catalyst remaining at any time x, $(1 - \varphi)$ and feedstock concentration $[F]$, implying that;

$$V \alpha (1-\varphi)[A]_0 [F] \quad (2)$$

where $[A]_0$ is the total catalyst added to the reaction, if the rate of the forward and backward reaction is equal which happens at equilibrium amount of catalyst φ at any time, t, can be calculated using Equation (3);

$$\varnothing = \frac{A[S]}{(1+A)[S]} \quad (3)$$

using the laws of thermodynamics on first order and second order reaction kinetics, the rate of the catalyzed reaction can be evaluated using Equation (4):

$$r = \frac{kAEo[F]}{1+A[F]} \quad (4)$$

where k is the rate constant determined by plotting a graph of $\ln(V)$ against the retention time for the catalyzed process.

1.3. Biogas Catalysis

Biogas production kinetics is the study of the rate (how fast) a reaction progresses. This is a physical property of a reaction and is measured by the change in biogas volume, mass, or concentration per unit time. The rate of a reaction may be represented by a mathematical equation related to the chemical equation for a reaction. Subsequently, methane production is enhanced or catalyzed by the introduction of substances that directly impact one or more of the aforementioned bacteria.

Food crops, waste materials, chemicals, and nuts have been reported to increase the rate of biogas production, and this can be attributed to the high nutrient levels in the cereals as well as the high C:N ratio. *S. bicolor L.*, *Zea mays*, and *P. glaucum* find wide application in fermentation processes and need to be widely used in fermented food products. This attribute makes them good candidates for biomethanation process enhancement. The growth of microorganisms in digesters follows an exponential curve which has a direct influence on biogas generation. High microbe population and pretreatment increase the biogas yields [8].

The actual implementation of particularly milling or size reduction of up to 0.2mm (flour like additives as catalysts has not been fully investigated both in terms of quantities utilized and type of the material employed. This work thus contributes to the understanding and local utilization of powdered lignocellulosic materials as catalysts for enhanced biogas production.

2. Materials and Methods

Raw materials used in the study included; cow dung, water, powdered grain powders as potential biogas production enhancers; *S. bicolor L.*, *P. glaucum L.*, and *Z. mays*. All the waste materials were obtained from local markets in Juja Subcounty, Kenya. The cow dung was collected fresh from the university farm and mixed with water at a ratio of 1:1 to give slurry with a concentration of 0.5 $kg \cdot L^{-1}$. The resultant mixture (slurry) was further treated with inoculum at the ratio of 400:1.

A series of batch reactors were used for the experiments. The bio-digesters used in the study were made of UV treated polyethylene material with a capacity of 1 m^3. Gas outlets were connected to a drying media, loaded with silica gel and anhydrous sodium hydroxide. The system was integrated with a digital flow meter for cumulative biogas generation recording. Volume readings in m^3 with the accuracy of 0.001 were read out every day at 10.00 am.

A gas sample was collected on each consecutive 3rd day for compositional analysis using conventional gas samplers in replicates after the drying stage. The gas was flared at the end of each experiment before being released into the environment.

The slurry was monitored for variations in pH, total dissolved solids (TDS), temperature, and electrical conductivity using a conductivity meter (model EC500). The quality of biogas was determined using a gas chromatograph coupled with a thermal conductivity detector (TCD) detector model (Schimadzu). The experiments were conducted in batches and a control experiment was included in all sets of experiments. Experiments were conducted in triplicates. All sample collection and tests were conducted using standard procedures [9].

Data was cleaned and analyzed using statistical tests such as T-test, ANOVA, and Excel. The process kinetics was studied by calculating the catalyzed and uncatalyzed reaction rates, substrate converted on commencement of the biodegradation as well as amounts of catalysts remaining after day one as described by [10].

3. Results and Discussion

The biogas production for both catalyzed and uncatalyzed reactions was monitored; the cumulative gas volumes are presented in Figure 2. The data reveals that the biogas production forms a sigmoidal or exponential curve same as the exponential growth curve for microbes in anaerobic digesters. The results show that *S. bicolor L.* and *P. glaucum L.* have the highest biogas yields for all days monitored.

The profiles for *Z. mays* and uncatalyzed reactions are not significantly different. *S. bicolor L* shows high biogas yields, whereas *P. glaucum L.* has the highest cumulative yields of 12,086 liters compared to *S. bicolor L.* with 11,720 liters (Figure 3). *S. bicolor L.* has the highest yield from the 1st to the 5th, 13th, 14th, and 15th day.

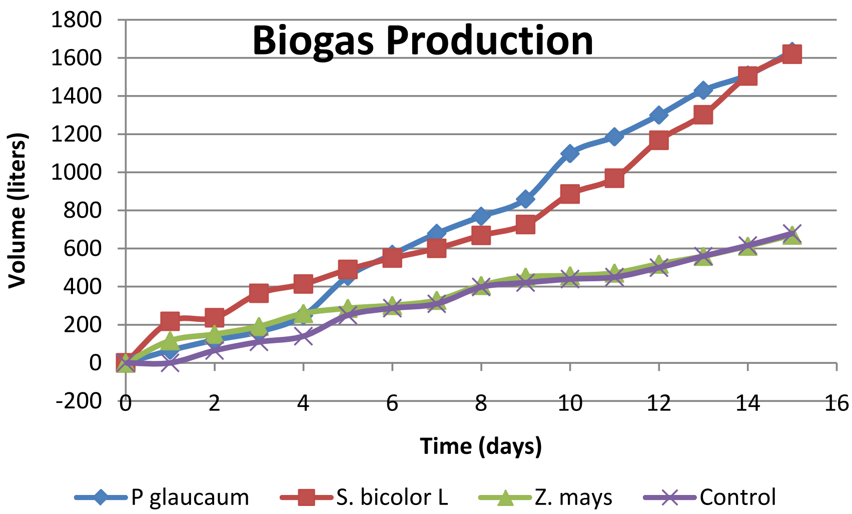

Figure 2. Cumulative Biogas yields for catalyzed and uncatalyzed biogas processes.

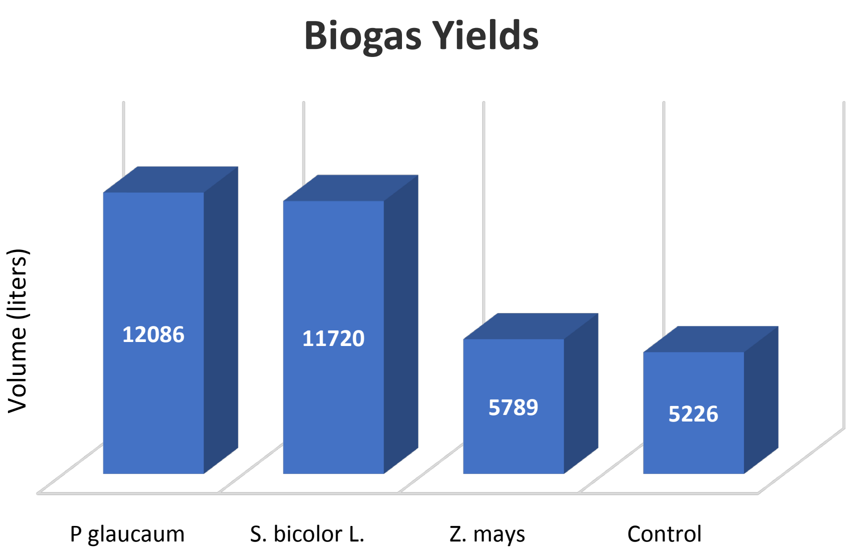

Figure 3. Total biogas produced for both the catalyzed and uncatalyzed processes.

The daily biogas yield was monitored; results are presented in **Figure 4**. The daily production reveals wide variations between days; the highest yields were recorded 5th, 10th, 12th, and 14th in days which can be attributed to ambient environmental temperatures and effects inside the anaerobic reactors.

To study the reaction kinetics, plots of Ln *V* of daily yields versus retention times (days were plotted and are presented in **Figure 5** and **Figure 6**.

The plots reveal that there were wide variations between days which can be attributed to biochemical process variations.

Reaction rates for both catalyzed and uncatalyzed reactions were calculated. The reaction rates ranged between 0.15 - 0.56 for catalyzed processes whereas for the uncatalyzed processes was 0.08 as presented in **Table 1**. Data revealed that the biomolecules had a catalytic effect by enhancing the biogas production process. S showed the highest rate of 0.56 which is significantly different from the rates for the uncatalyzed reactions. In terms of catalytic effects; the catalysts can be ranked as follows *S. bicolor L.* > *P. glaucum* > *Z. mays.* There was a significant difference between the reaction processes, uncatalyzed processes and those rates for *S. bicolor L.* > *P. glaucum* > *Z. mays.*

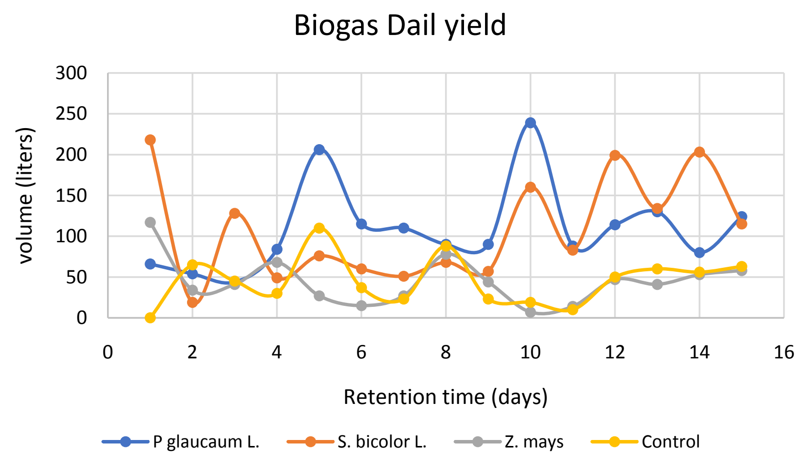

Figure 4. Daily Biogas Production for catalyzed and uncatalyzed biogas processes.

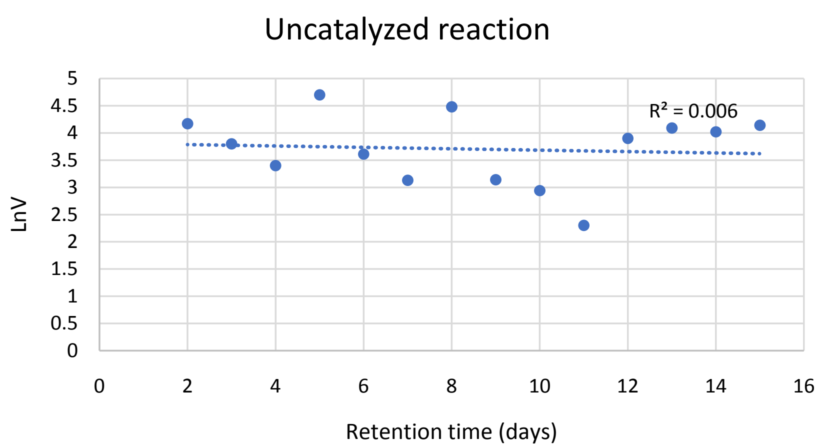

Figure 5. Plots of Ln *V* against time for uncatalyzed bioconversion of the substrates.

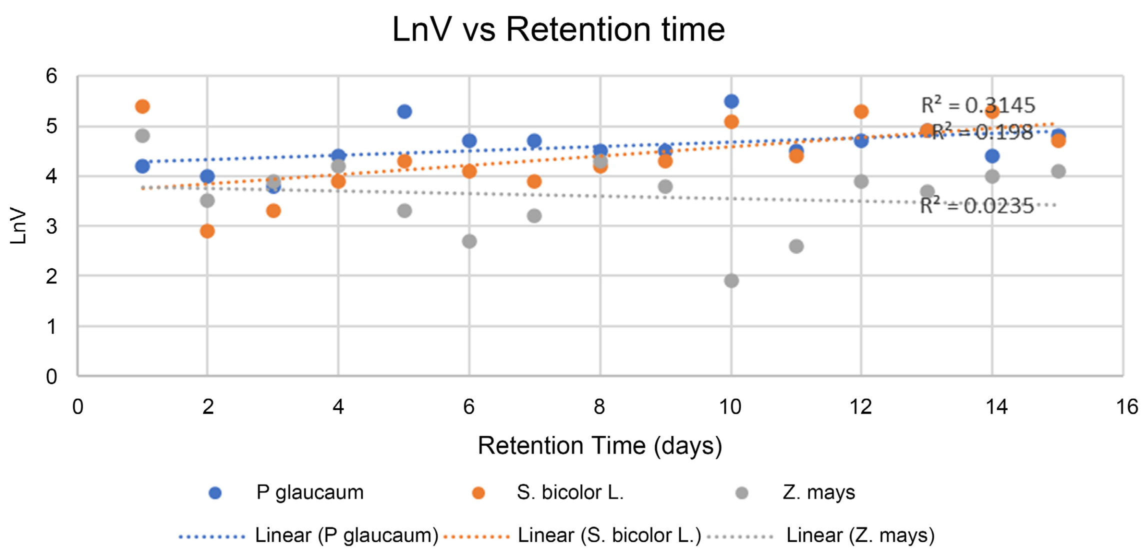

Figure 6. Plots of Ln *V* against time for catalyzed bioconversion of the substrates.

Table 1. Reaction rates for catalyzed and uncatalyzed biogas processes (n = 3).

Catalyst	R^2	Reaction rates
S. bicolor L.	0.314	0.56
P. glaucum	0.198	0.44
Z. mays	0.024	0.15
Control (uncatalyzed)	0.007	0.08

Table 2. Biomethanation reaction kinetics for catalyzed biogas processes (n = 3).

Catalyst	Catalyst remaining after day 1 (Kg)	Substrate converted by catalyst on day 1
S. bicolor L.	0.67 ± 0.1	0.37 ± 0.6
P. glaucum	0.69 ± 0.3	0.15 ± 0.02
Z. mays	0.9 ± 0.3	0.13 ± 0.01

The amounts of catalysts consumed during the commencement of process; day 1 and the substrate converted to biogas are presented in Table 2.

Data revealed that catalyst consumption ranged between 0.67 ± 0.1 to 0.9 ± 0.3 whereas the highest consumption was found to e of *S. bicolor L.* The substrate converted ranged from 0.37 ± 0.6 to 0.13 ± 0.01. Biogas composition revealed that *S. bicolor L.* led to the highest methane content with a mean of 61.2 ± 5.5 and 56.4 ± 4.2, 52.2 ± 5.1 and 49.3 ± 2.3 for *P. glaucum*, *Z. mays*, and uncatalyzed process respectively as shown in Table 3.

Results of the study indicate that biodegradable wastes bioconversion like any chemical process can be enhanced via catalyst mediated reactions. It further proved that the biogas quality and quantity can be manipulated using biomolecules with the potential to amend the bioconversion process.

Table 3. Biogas compositional data for catalyzed and uncatalyzed biogas processes (n = 3).

Gas	*S. bicolor L.*	*P. glaucum*	*Z. mays*	Control (uncatalyzed)
CH_4	61.2 ± 5.5	56.4 ± 4.2	52.2 ± 5.1	49.3 ± 2.3
CO_2	27.3 ± 4.3	28.8 ± 5.2	24.2 ±2.2	35.7 ± 2.2
N_2	6.4 ± 0.4	6.4 ± 1.2	7.7 ± 1.5	8.2 ± 2.7
O_2	3.1 ± 0.5	6.1 ± 1.1	7.1 ± 1.1	4.3 ± 3.4

From the foregoing, it is noted that *S. bicolor L.* has the highest biogas production followed by *P. glaucum* and *Z. mays*. The impact of such catalyzation will however need to be investigated now on large-scale digesters to determine the optimal ratio, due to the unstratified mixing in long tubular bio-digesters.

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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