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Influence of catalyst (Yeast) on the Biomethanization of Selected Organic Waste Materials

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ABSTRACT: Yeast catalyzed the rate of biomethanization of waste materials and rate at which it alter the reaction rate has been determined. It was observed that addition of yeast improved the quality and quantity of biogas generated and also fastened the acid and methane forming stages during biomethanization. The volumes of biogas in the catalyzed process was found to be 6550 cm^3 for cow dung, 5640 cm^3 for millet husk, 3240 cm^3 for rice husk ,1000 cm^3 for saw dust and 800 cm^3 for the paper waste, as against 5430 cm^3, 5230 cm^3, 2110 cm^3, 950 cm^3 and 590 cm^3 respectively for the uncatalyzed biomethanization process.

INTRODUCTION

Organic waste materials can be converted into gas or biogas which is composed of different gasses by microorganisms under anaerobic condition (Arianne, 1981). The organic waste contains complex organic compounds such as cellulose, protein, starch, tannins, etc. The complex compounds are first broken down into simpler water soluble substances such as glucose, fructose, fatty acids and amino acids which are easily acted upon by some of the methanogens in the digester. Like any chemical reaction biomethanization could be influenced by factors that usually affect the rate of chemical reaction such as temperature, concentration, surface area and catalyst (Akpan, 1995).

Kinetics is the study of the rate (how fast) a reaction progresses. The rate of a reaction is a physical property of a reaction and is measured by the change in some reaction quantities such as volume, mass or concentration per unit time. The most common method used to calculate the rate of reaction is to measure the change in concentration of the reactant(s) in mol dm^{-3} s^{-1}. The rate becomes: - (change in concentration of reactant in mol dm^{-3}) per unit time (in seconds). The rate of a reaction may be represented by a mathematical equation related to the chemical equation for a reaction. e.g. for the hydrolysis of haloalkanes,

If S_N1, mechanism is followed, the most important reaction, or **the rate- determining step**, is the breaking of the carbon–halogen bond. For example in the equation (1),

$$(CH_3)_3C\text{-}X \rightarrow (CH_3)_3C^{\oplus} + X^{\ominus} \quad (1)$$

The rate equation for this reaction is written as;

$$\text{Rate} = k[(CH_3)_3C\text{-}X] \quad (2)$$

Where k = the rate constant for the reaction and $[(CH_3)_3CX]$ = the concentration, in mol dm^{-3}, of the haloalkanes.

If reaction is S_N2; the rate-determining step here is the displacement of the halogen atom with a hydroxyl group,

$$CH_3CH_2X + {}^{-}OH \rightarrow CH_3CH_2OH + X^{-} \quad (3)$$

The rate equation here is,

$$\text{Rate } r_A = k[CH_3CH_2X][{}^{-}OH] \quad (4)$$

Generally for the equation;

$$mA + nB \rightarrow \text{products.}$$

$$r_A = k[A]^m[B]^n \quad (5)$$

Where [A] and [B] are the concentrations of the various reactants and m,n = the number of molecules of each of the reactant involved in the rate determining step also known as the order of each of reactant. The biodigestion process can be considered like any chemical reaction where the substrates are the reactants that undergo transformation to biogas under the influence of microorganisms.

Mathematical models (a simplified mathematical description of the operations of a biogas plant) provide a way of doing this (Checchi *et al,* 1990).

The actual mechanism in the plant, with many types of bacteria contributing in biogas production is somewhat complex and difficult

to define. So any model used must be gross over simplification of reality on ground. The most effective ones seem the simplest, mainly because they define clearly two or three parameters by which a plant design or feed stock can be assessed. A good model should roughly predict how much gas a designer could get each day, given that, a particular design uses a particular feed stock under defined conditions (Checchi *et al,* 1990).

To be able to grow and perform metabolic functions microbes require an appropriate mixture of the required nutrients, suitable temperatures and hydrogen ions concentration within a tolerable range. The gas obtained can be a product of one pathway or the other and at different rates based on the conditions.

There are various kinetic models employed for this purpose. The Monod model was adopted to describe the kinetics of anaerobic digestion of organic waste. It has the advantage that the kinetic parameters (i.e. the microorganism's maximum specific growth rates and half-velocity constants) have deterministic connotation that describes the microbial processes and predict conditions when maximum biological activity occurs and when activity will cease.

Catalysis: Catalyst is a compound that increases the rate of a reaction by providing an alternative reaction mechanism for a chemical process. This alternative mechanism has lower activation energy, (E_A) so that more molecules will have energy greater or equal to E_A and so more collisions will be effective, so the rate constant is higher and the rate of reaction is increased. Catalysts can be homogeneous, heterogeneous or enzymatic in nature (Atkin and Paula, 2002).

Studies on the methane and non methane producing bacteria from the rumen and other environment have shown that the need for the supply of some catalyst either organic or inorganic is the medium of for optimal growth and activity of the bacteria (Guit *et al,* 1988).have reported improved growth of methanogens supllied with an appropriate mixture of Ni^{2+}, Co^{2+} and Mo^{6+} . Machido *et al,* 1996 *reported* the enhancement of biogas production from cowdung by the addition of inorganic catalyst. This paper reports on the study on the effect of enzymetic catalyst on bioconversion of various organic wastes.

Homogeneous catalysts: These are catalysts, which are in the same phase as the reactants e.g. catalysts that are soluble in the same solvents as the reactants. With these sorts of catalysts there is direct action between the catalyst and reactant. For example, crown ethers are good examples of this type of catalyst. They form complexes with ionic compounds to be dissolved in organic solvents so they can carry out reactions there e.g. Oxidation-using potassium per mangnate (VII) (Atkins and Paula, 2002).

Heterogeneous catalysts: These are catalysts, that are in a different phase to the reactants e.g. a solid catalyst in a reaction between gases or a solid catalyst in a reaction, occurring in solution.

With this type of catalysis, the reactants have to be either absorbed or adsorbed .The reaction proper can then occur in/on the solid catalysts (Atkins and Paula, 2002).

Enzymatic Catalyst: These are biological catalysts, which are often reaction specific. They have large, complex 3-D structures, which provide sites for only certain molecules to interact with them. They may also require a certain level of pH, moisture or other external factors (Atkins and Paula, 2002).

The following equations are used to investigate the effect of enzymatic catalyst, which is reported to proceed in two stages (Sharma, 1981). The stages involved are as follows;

a) The formation of catalyst – substrate complex as in equation (10)

$$E + S \rightleftharpoons ES \quad (10)$$

Where E is the quantity of the catalyst used, S is the substrate and ES is the complex formed between the enzyme and the substrate.

$$ES \xrightarrow{k} products + E \quad (11)$$

Let Θ be the fraction of the enzyme molecules that are involved in complex formation. The rate of formation of complex v will be proportional to the concentration of free

enzyme i.e. $(1- \Theta)$ $[E]_0$ and also to the concentration of the substrates [S],

Thus $v \propto (1- \Theta)[E]_0[S]$ (12)

Where $[E]_0$ is the concentration of the total enzyme used. The rate of the backward reaction v^1 is proportional to concentration of the complex, $\Theta [E]_0$

i.e $V^1 \propto \Theta[E]_0$ (13)

Equations 12 and 13 can be written as;

$V = k(1-\Theta)[E]_0[S]$ (14)

$V^1 = k^1\Theta[E]_0$ (15)

Since at equilibrium the rates of forward and backward reactions are equal,

$V=V^1$ (16)

$k(1-\Theta)[E]_0[S] = k^1\Theta[E]_0$ (17)

$$\frac{\Theta}{1-\Theta} = \frac{k[S]}{k^1} \quad (18)$$

Where k and k^1 are the rate constants for the forward and reverse reactions respectively,

Since = $\frac{k}{k^1} = A$ (19)

Where A is the equilibrium constant,

It is therefore assumed that the equilibrium constant is equal to one (unity). The value of the equilibrium constant estimated from equation (19) was used to obtain equation (20)

$$\Theta = \frac{A[S]}{1+A[S]} \quad (20)$$

From which the fraction of the enzyme involved in forming complex with the substrate was evaluated. Since the quantity of enzyme required in forming complex with the substrate was evaluated, then the rate at which the complex decomposed into biogas with simultaneous regeneration of the enzyme can also be evaluated using;

$$r = \frac{dp}{dt} = K[ES] = -\frac{kA[E]_0[S]}{1+A[S]} \quad (21)$$

Where [ES] is the concentration of the enzyme – substrate complex, $[E]_0$ is the initial concentration of the enzymatic catalyst, [S] is the concentration of the substrate and k is the rate constant.

In this paper the kinetics of biomethanization was followed using the effects of enzymatic catalyst.

MATERIALS AND METHODS

Materials: The raw materials used in this investigation as substrates were cow dung, millet husk, rice husk, saw dust and paper wastes all of which are agricultural waste materials. All the waste materials were obtained at different locations around Sokoto metropolis. The paper waste was a mixture of various types of papers, such as pure white, newspapers, cardboard, tissue and packaging papers of different types. The cow dung was collected fresh and sun dried for ten days before use.

The millet husk was collected from Shama village near the main campus of Usmanu Danfodiyo University Sokoto. The rice husk was collected from a rice mill near the animals market while the sawdust was obtained from the wood market (Timber shade) both in Sokoto.

Treatment of Samples: All the samples were air-dried before drying in an oven at 110^0C for 24 hours. The dried samples were grounded using wooden pestle and mortar, and stored in black polythene bags until required (Garba, 1999).

Fabrication of Digesters: The digesters were made up from four-litre capacity metallic cylindrical gallons. A hole was bored on the top and a polyvinyl chloride (PVC) tube of 50 cm length and 0.8 cm diameter was inserted. The PVC tube was glued using araldite and firmly waxed to ensure air tightness.

Preparation of slurry: The slurry was prepared from the stored samples by taking, 400g, in separate beakers and adding 2000 cm^3 of water to the substrate to obtain a ratio of 1:5 w/w and mixed thoroughly and transferred into the digester. For each substrate two sets of digesters were made. Set A and B. each set consisting of three digesters. To Set A digesters of each type of substrate, 3.00g of yeast was added, while to set B no yeast was added. Each digester was sealed before the end of the PVC tube from the digester was connected to the inlet of a Buckner flask containing 100g of silica gel, which served as drying agent. The digesters were then jacketed in polyurethane foam to minimise the temperature fluctuations in the digester. For each set up another PVC tube of the same dimension was connected to the outlet of the Buckner flask and the other end of the tube was connected to an inverted 1000 cm^3 capacity measuring cylinders which was filled with

water in sodium chloride was added. The downward displacement of water in each measuring cylinder was taken as a measure of the volume of biogas produced for each digester, and the volume of daily biogas production for each digester was recorded separately. To each set of digesters a control was done in no yeast was added.

RESULTS AND DISCUSSION

The total mean biogas yield as obtained from the replicate data for the retention period of nine weeks, were recorded in Table 1.

Table 1: Volumes of biogas produced (cm^3) for the catalyzed and uncatalyzed substrates.

Substrates	Uncatalyzed.	Catalysed.
Cow dung	5430 ± 50	6550 ± 25
Millet husk	5230 ± 30	5640 ± 24
Rice husk	2110 ± 32	3240 ± 30
Saw dust	950 ± 30	1000 ± 31
Paper waste.	590 ± 45	800 ± 35

Effects of enzymatic catalyst of biogas production rates: From the results reported in Table: 1, it is evident that there is a profound effect of the enzymatic catalyst on the total volume of biogas recorded. The results have shown that there are increases in the volumes of biogas produced from all the substrates under investigation. The results in Table 2 indicated that the bioconversion of the substrates started earlier when catalysed, in other words the lag time was greatly reduced. Cow dung started gas production on the first day, millet husk on the second day, rice husk on the third day, saw dust on the fifth day and paper waste started gas production only on the seventh day of the retention period. These when compared to the uncatalyzed process (Figure 2) show reduction in the lag time. Equation (20) for the reaction of enzymes was applied to analyse the effects of catalyst. The equation proved that only a fraction of the enzyme added was used in the actual formation of complex with the substrate. The remaining free enzyme, which did not take part in the complex formation, is referred to as the free enzyme. This shows that not all the quantity of yeast added was involved in complex formation with the substrate. When a catalyst is added to a chemical reaction the catalyst can either be completely involved in forming complex or some quantity of it will remain as free catalyst. It is always better to have excess catalyst than to have shortage because concentration of catalysts is proportional to the rate of catalyst – substrate complex formation (Sharma,. 1981).

Table 2: Daily catalyzed biogas yield in the first two weeks of the retention period (cm^3)

Days	Cow dung	Millet husk	Rice husk	Saw dust	Paper waste
1	5	0	0	0	0
2	10	6	0	0	0
3	50	40	30	0	0
4	100	80	60	0	0
5	160	120	80	5	0
6	200	150	100	10	0
7	250	200	130	40	5
8	270	250	170	60	8
9	300	270	190	80	10
10	350	290	200	80	30
11	380	300	240	100	40
12	400	350	260	120	50
13	410	380	270	140	100
14	450	400	300	150	150

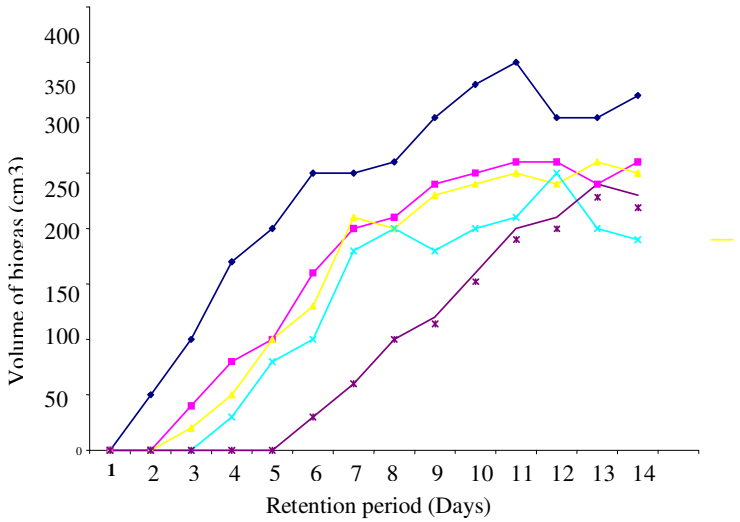

Figure 2: Daily uncatalyzed biogas production in the first two weeks of the retention period.

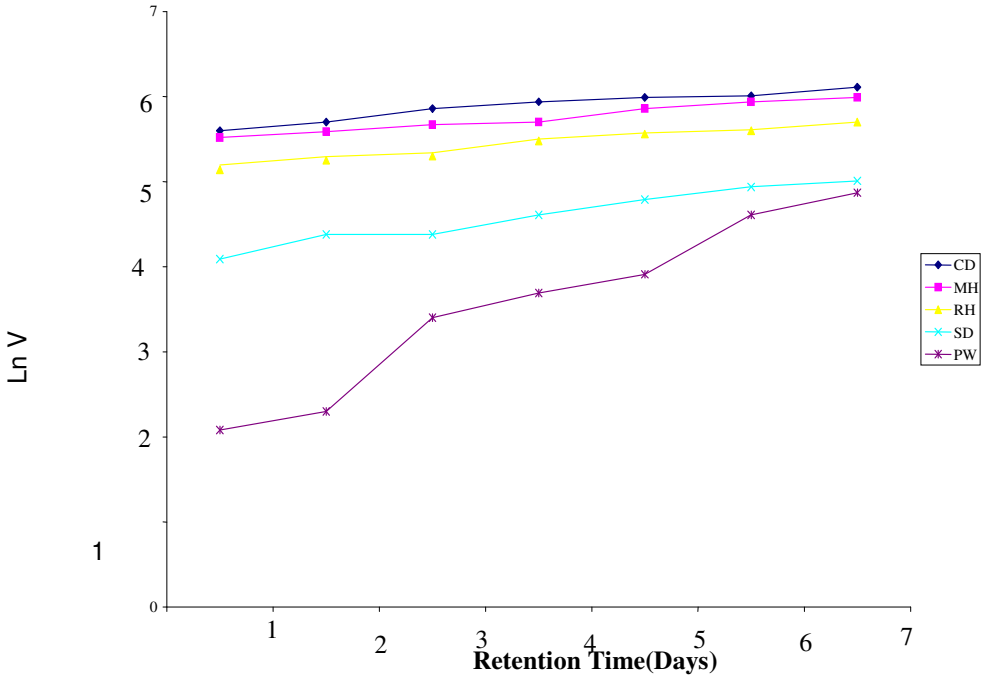

Figure3: plots of Ln V against time for the uncatalyzed bioconversion of the substrates

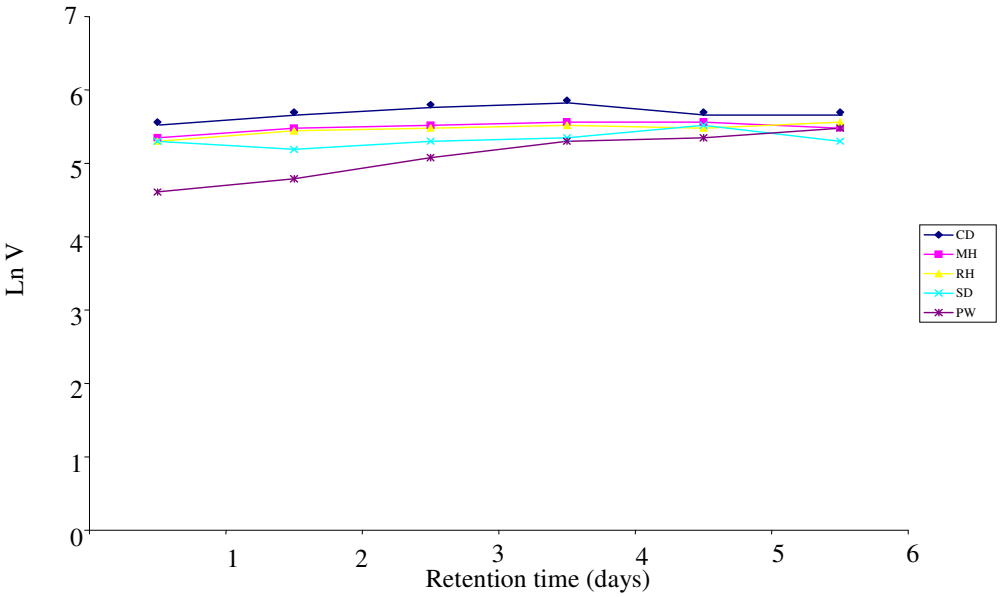

Figure 4: Plots of Ln V against time for the catalysed fermentation

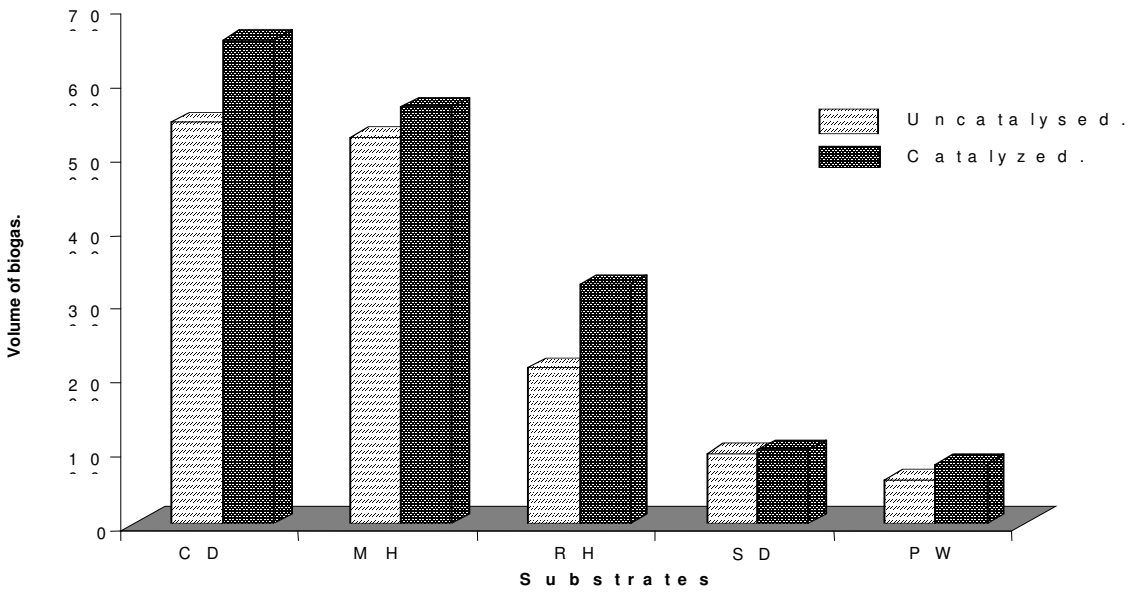

Figure 5: Cumulative volumes of biogas produced for both the catalyzed and uncatalyzed slurries.

Thus; $\Theta = \frac{A[S]}{1+A[S]}$

Where Θ = fraction of enzyme involved in complex formation.

A = Equilibrium constant assumed to be = 1
[S] = Concentration of the substrate (in case taken to be (400g/2000cm^3) and that is equal to 0.2g/cm^3
For the catalyzed reaction:

$$\Theta = \frac{1(0.2)}{1+1(0.2)}$$

$$\Theta = \frac{0.2}{1.2} = 0.167\text{g}$$

The free enzyme remaining after the first day is therefore:
3.00 – 0.167g = 2.833g
The rate of the catalyzed reaction can be evaluated using equation 21:

$$\mathbf{r} = \frac{kAE_0[S]}{1+A[S]}$$

Where k is rate constant determined from the graph of Ln V against time for the catalyzed fermentation of cow dung (Figure 4)

$$\mathbf{r} = \frac{0.5 \times 1 \times 3.0 \times 0.2}{1+1 \times 0.2} = \frac{0.30}{0.40} = 0.75 \text{ g day}^{-1}$$

Therefore the catalyst contributed to the conversion of 0.75g on the day of the commencement of biogas production, and the subsequent day the rate depends on the actual daily concentration of the slurry.
The rate at which the reaction occurred due to the enzymatic action was found to be 0.75g on the day the biogas production commenced as estimated using equation (20). This meant that the addition of enzymes (yeast) contribute towards converting 0.75g of the substrate into biogas on the day biogas production commenced, and for the subsequent days, the amount of substrate that can be converted into biogas due to enzyme depends on the actual daily concentration of the slurry (i.e. the amount remaining after previous conversion).
The plots Ln V against time for both the catalysed and the uncatalyzed reactions are shown in Figure 3 and Figure 4 respectively. The graphs are fairly straight indicating that the first order kinetics was followed during the second week of the retention period.
Conclusion: From the results of the investigations carried out, it could be concluded that bioconversion like any chemical reaction can be enhanced by the addition of catalyst. The nature of the catalyst used also allows for another conclusion that the biocoversion process is a biochemical reaction which depends on the activities of micro organisms. We can also conclude that only a fraction of the added catalyst was actually involved in the formation of complex with the substrates while the bulk remained as free catalyst in the digesters. Since the plots of Ln V against time for the catalysed reaction are straight line graphs it could be concluded that the catalytic biomethanization of all the substrates follow the first order kinetic model.

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