Investigation of Phasic Process of Biogas Yield by Measuring pH, ORP and Electrical Power Changes

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Background & Aims of the Study: Studying the phasic process of the biogas yieldis required to optimize the design and operations; it also helps to lower energy production costs by decreasing the capital investment and operational costs. Here we determine the biogas process by measuring pH, ORP, electrical power and make compatibility to the biogas production trend.

Materials and Methods: In this research, one 1150 ml single chamber reactor is used. Biogas production trend was precisely followed by a probable compatibleness with pH, Oxidation Reduction Potential (ORP), electrical Power at a temperature of $37+ 0.5°C$ with the substrate of cattle manure. The experiment was followed for 120 days approximately.

Results: As a result, the phases of biogas yield could be determined by the measuring of pH, ORP and its compatibility to gas production. In the reactor, hydrolytic, acetogenic and methanogenic phases were occurred in the days 1-7, 8-16 and 17-104, respectively. Also the electrical power at first showed to be produced at high range but by increasing, the production of biogas decreased and then by decreasing the biogas production gradually, it increased slightly.

Conclusion: Our results indicated that the phases of biogas production can be separated completely and by diffracting the phases, the efficiency of biogas production could be increased.

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Background

Investigation on optimized approaches for sustainable energy production is required in facing of increasing competition for energy consumption besides preventing the environmental negative impacts (1). Biogas production through anaerobic digestion of the cattle manure produces renewable energy carriers and prevents the environmental pollution (2). Methane as a compartment of biogas and the product of anaerobic digestion is an energetic compound. Mostly, it is used to produce the electricity in wastewater treatment facilities and power plants (3).

The degradation of an organic matter to biogas is a very complex process. Identified sub processes of degradation are hydrolysis, acetogenesis and methanogenesis (figure 1) (4). The first step is hydrolysis which contains of three parts of the hydrolysis of proteins,

carbohydrates, fats and oil respectively to amino acids, sugars, glycerol and fatty acids (5). The hydrolysis rate depends on the biopolymer, substrate concentration, particle size, pH value and temperature (6).
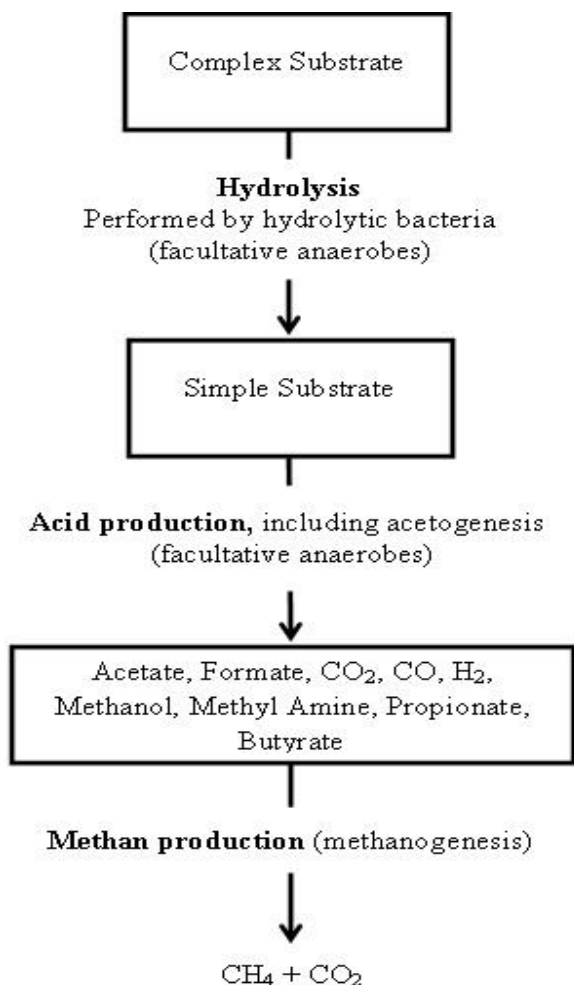

Figure 1) Basic stages of the anaerobic digestion process and production of methane (4).

Acidogenic phase includes the fermentation of amino acids and simple sugar as well as the anaerobic oxidation of long chain fatty acids and alcohols by acid-forming bacteria. Beside carbon dioxide, water and hydrogen gas primarily acetic, propionic, butyric and valeric acid will be accumulated (7).

Acid-forming bacteria are fast-growing type with a minimum doubling time of about 30 minutes. They prefer degradation to acetic acid,

since this step results in the highest energy yield for their growth (4).

Anaerobic oxidation of intermediates such as volatile fatty acids to acetic acid and hydrogen by acetogenic bacteria is called acetogenesis. An accumulation of hydrogen gas has to be avoided due to the inhibition of this sub-process by hydrogen gas. Therefore, hydrogen-utilizing and acetogenic bacteria live in agglomerates close together (8).

Acetogenic bacteria grow rather slowly with a minimum doubling time of 1.5 to 4 days even under optimum conditions such as a low concentration of dissolved hydrogen gas (4).

The last phase is methanogenesis which indicates the methane production by methane bacteria out of acetate and out of hydrogen and carbon dioxide. All methane forming bacteria so far studied utilize hydrogen gas to reduce the carbon dioxide to methane (9). These hydrogen utilizing methane bacteria grow relatively fast with a minimum doubling time of about 6 hours (4). The larger share of the methane (about 70%) is produced by acetoclastic methane bacteria out of acetate (4). Because of the low energy yield of this reaction, acetoclastic bacteria grow very slowly with a minimum doubling time of 2 to 3 days (4). All sub-processes are affected by ambient conditions such as temperature, pH value, alkalinity, inhibitors, trace and toxic elements. Furthermore, all sub-processes are linked to and influenced by each other. Although there are still discussions which step is the rate-limiting step, the degradation of acetic acid to methane is rate limiting (10).

There are many factors affecting the anaerobic digestion processes. pH as one of the effective factors in the production of biogas is an important indicator which should be set between 6.6 and 7.6, at the values of more than 7.6, digestion can continue with less efficiency (11-13).

ORP is an indicator of the capacity of the molecules in the wastewater or sludge to release or gain electrons (oxidation or

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reduction, respectively). Generally, at values greater than +50 mV, aerobic respiration may occur and from +50 to –50 mV, anoxic respiration (denitrification). At values less than –100 mV, not only anaerobic respiration may occur but also we have the production of mixed acids and alcohol fermentation and sulfide removal (14,15). Methane fermentation starts at values less than –200 mV. Usually, in a mixed culture of fermenting organisms which are exist in an anaerobic digester, methane fermentation occurs in values less than -300 mV. This is due to the inability of the methane-forming bacteria to successfully compete with other fermenting organisms at values greater than –300mV (14).

Aims of the study:
In this research, the biogas production was monitored daily. Furthermore the changes of pH, ORP and electrical power through biogas production and their compatibility with biogas production were investigated. The result of this study can be used in designing and operating biogas reactors to optimize the production and capital costs.

Materials & Methods

Substrate preparation
Fresh cattle manure was used as substrate for this research. During the operation of the reactor, no sludge was discharged except for sampling.

Figure 1) The prepared pilot

Experimental set-up and operation
One single chamber reactor which made of one cylindrical housing with the volume of 1150 ml was used. Biogas production trend was precisely followed by its compatibleness with pH and ORP ranges. The reactor was maintained in a warm water bath to support the temperature range at 37+ 0.5˚C.

This experiment was set for 120 days, approximately. Generally, on the base of the biogas production, the reactor performance was defined firstly as the stage 1 between days (1-16) and stage 2 between days (17-120). After that stages were compared with the changes of pH and ORP. Finally on the base of biogas production changes and its compatibility with pH and ORP changes, five phases were determined.

Analytical methods
In the experiment, the biogas volume was documented every day. Totally, 15 samples were taken from the substrate of the reactor and from them pH, ORP and electrical current were determined. In order to measure the volume of the biogas production, a volumetric gas meter model (Behinab G8) was used. It gathered produced bobbles in special container and after its filling, it was discharged subsequently; then a magnetic sensor counted each discharged volume of gas in container. According to the number of emptied container one can measure the time and volume of the produced biogas. It was possible to measure the volume of produced gas on daily basis. Oxidation Reduction Potential (ORP) and pH of the samples were measured by a portable multi test device (AZ 86505) on a weekly basis. Electrical current was measured by the multichannel potentiostat (WMPG100, WonATech, Korea). On the base of the measured voltage (mV), current (mA) and resistance (m Ohmes), the electrical power was determined and used for the analysis.

Results

Table 1 shows a summary of the results of the biogas production, pH and ORP changes in different phases in control.

Figure 2 shows the trend of the biogas production and Figures 3.a and 3.b show the

trend of pH and ORP changes in the biogas process.

Table 1) Summary of the results of biogas production, pH and ORP changes in different phases in control reactor

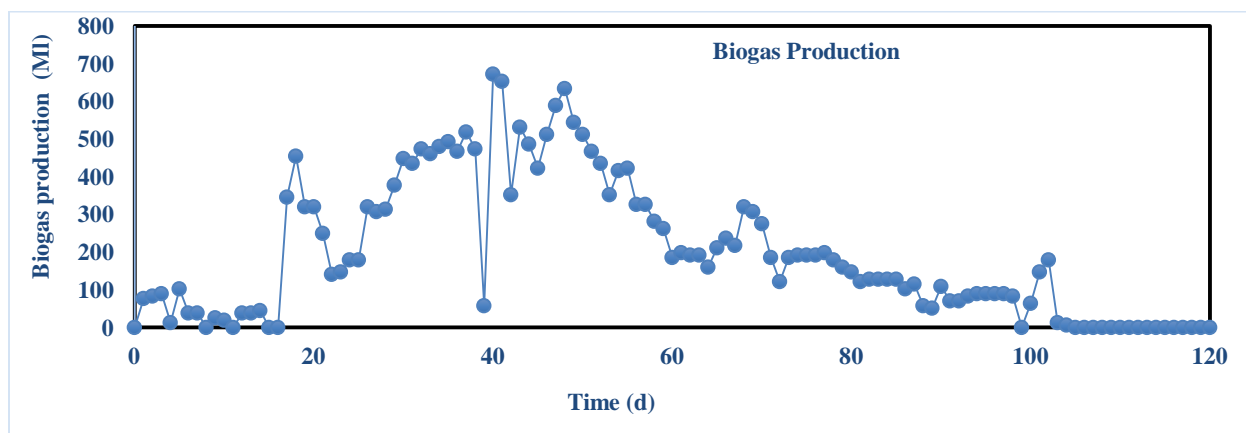| Phase No.	Day	Time (d)	Biogas production (ml)	Mean of pH	Mean of ORP (mV)
1	1-7	7	442	6.75	-218
2	8-16	9	166	6.99	-341
3	17-77	61	20922	7.74	-396
4	78-104	27	2630	7.74	-250
5	105-120	16	0	7.67	-190

Figure 2) Biogas production trend
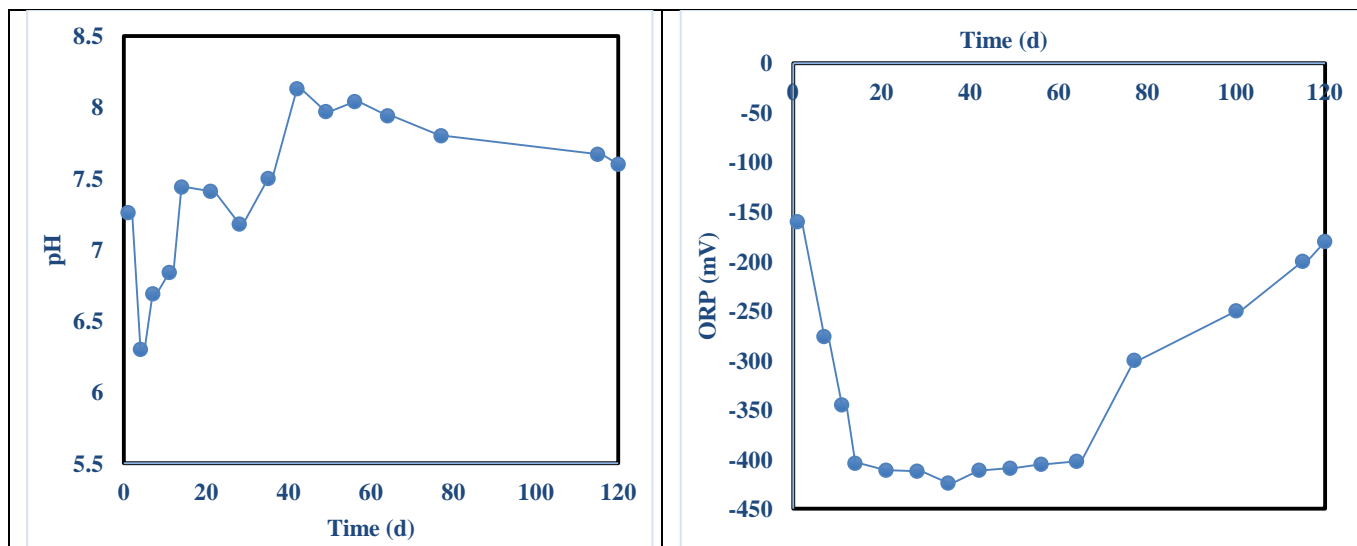
Figure 3) (a) Changes of pH through biogas production, (b) changes of ORP through biogas production

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Archives of Hygiene Sciences   Volume 5, Number 2, Spring 2016
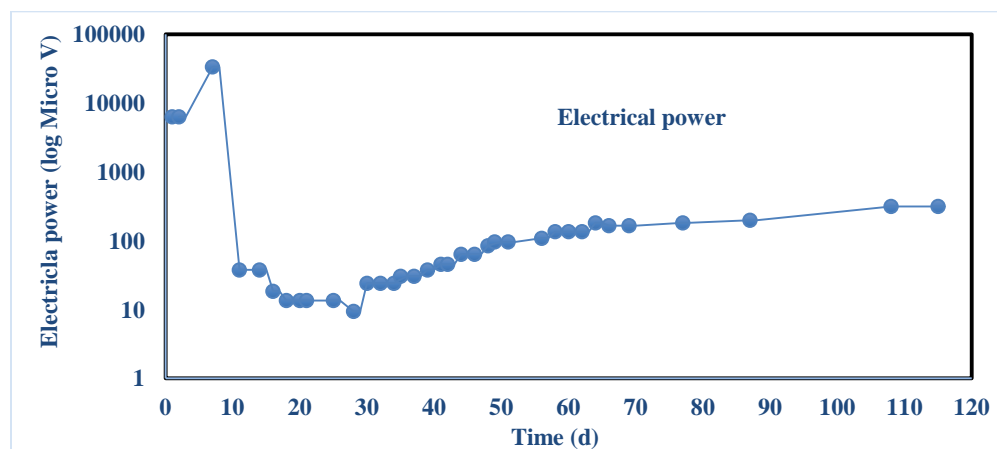
Figure 4) trend of electrical power changes in the reactors

Discussion

The reactor substrate was set to contain total solid of 16 % (16). Volatile solid was measured to be 76% of total solid (16). Also the TKN of the substrate was 1.23% and TOC of that was measured about 28.3%.

The biogas phases are determined on the base of gas production in the reactor. Throughout the 120 days of operation, the biogas production and flux and gas yield rate were measured.

Bousek et al. investigated the impact of strip gas composition on side stream ammonia stripping as a technology aiming at the reduction of high ammonia levels in anaerobic reactors. They found the effect of oxygen contact during air stripping showed a distinct, though lower than perceived, inhibition of anaerobic microflora. Inhibition due to the oxygen exposure was lower than other gas (18). Figure 2 states that there are some bacterial activities and rest which cause risings and fallings in the biogas production and its compatibility with pH and ORP changes. On the base of these risings and fallings each determined continued rising and falling were considered as a phase. On the base of this presumption, it could be determined five operational phases. These phases were happened between the days 0-7, 8-16, 17-77, 78-104, and 105-120 respectively. Ugochuk et

al. investigated the rates production of biogas from various organic wastes and weeds which enabled the determination of an optimal ratio of poultry droppings to domestic wastes. The gas production did not begin until the 7th day and increased steadily at first; then increased sharply until it reached its peak on the 18th day before declining. The total gas produced within the 22 days of experimentation was 1771 cm^3. The maximum volume of gas amounting to 809 cm3 was produced by the sample, containing 50% poultry dropping and 50% weeds (19).

In the phase 1, there is a rising until the day 4 and falling until the day 7. The volume of biogas is 442 ml and pH mean is 6.75 and ORP is -218 mV. These conditions are adapted to the hydrolysis phase of the biogas production (14). Phase 2 is happened through 9 days. The biogas production volume in this phase is 166 ml with the pH=6.99 and ORP=-341 mV. These conditions are mostly adapted to the acidogenic phase of the biogas production (14). Phase 3 is the main phase of the process which 20922 ml of the biogas is produced in this phase. In this phase, pH is 7.74 and ORP is -396 mV. This phase is also adapted to the methanogenic phase (14). There is a sudden change in the ORP values in the phase 4. In the phase 4, the biogas production is 2630 ml and the means of pH and ORP are 7.74 and -250 mV, respectively. Although the mean value of ORP

is to some extend out of the biogas production, still the phase 4 can be considered as the methanogenic phase. There is not the biogas production in phase 5 and pH and ORP values are 7.76 and -190 mV, respectively. On the base of conditions for the biogas production, it seems that the phase 5 is out of the biogas conditions.

Finally, in this research the duration of the hydrolysis was estimated for 7 days. Also, the acetogenic phase was about 9 days and the methanogenic phase lasted for 88 days. More than 97% of gas was produced in the methanogenic phase.

Most of the previous research worked on the duration and the biogas production rate and they did not researched the phases duration separately. Duration of the biogas production in this research is more than the results of Zamalloa et al. 2011. In their research, the biogas production lasted for 75 days but in ours, it was 104 days. Their maximum biogas production rate was 0.12 and ours was 0.55 Lbiogas/Lreactor) (17).

Electrical power is the rate at which the electrical energy is transferred by an electric circuit. As stated, the electrical power is calculated on the base of an electrical voltage, multiple to an amperage or voltage in power 2 divided by resistance in different reactors.

As it is shown, in the reactor 1, there is an increase in the curve from day 1-7 in reactors 1. These changes are happened in the phase of the hydrolysis. After that, a severe decrement is occurred until day 11 and a continued gradually until day 28. Most of the changes are happened in the acidogenic phase. After that a gradual increment is happened until the end of the biogas process.

The Franziska et al. study showed that the biogas production provided an attractive investment opportunity, especially for large farms which led to a boost in the biogas production. The heterogeneous ability of farms to invest in biogas plants could be partly addressed by policies that ease investments for smaller and less competitive farms by providing additional subsidies for smaller plants. On average, biogas farms could not increase their profitability. The main reason for this effect can be seen in the fact that a significant share of the value added is transferred via increased rental prices to land owners (20).

Study of Reddy et al. showed that the renewable energy based, decentralized energy systems proved to be a viable option for sustainable power production especially in rural areas. The results based on experimental analysis showed that the power deterioration of 32% on raw biogas (21).

Conclusion

In this study, the biogas production through anaerobic digestion was studied. On the base of the results, the phases of the biogas yield can be determined by the measuring of pH, ORP and its compatibility to gas production.

In the researched reactor, the hydrolytic phase was occurred in the days 1-7 and at this time the mean value of pH and ORP were 6.75 and -218 mV, respectively. Less than 2% of total gas was produced in this phase. The acidogenic phase was happened between days 8-16.The mean value of pH and ORP were 6.99 and -341 mV, respectively and less than 1% of gas was produced in this phase.

Finally, the methanogenic phase was occurred between days 17-104. More than 97% of biogas was produced in this phase and the mean value of pH and ORP were 7.74 and -396 mV, respectively.

In the reactor that most of the produced electrical power was occurred in the hydrolytic phase which states hydrolytic bacteria produced more electrical power and after that the values are low which shows in the acidogenic and methanogenic phases the bacteria consumes energy to produce biogas instead of electrical power.

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Archives of Hygiene Sciences

Volume 5, Number 2, Spring 2016

134

Footnotes

Conflict of Interest: The authors declared no conflict of interest.

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Archives of Hygiene Sciences

Volume 5, Number 2, Spring 2016

135