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EFFECT OF CARBON TO NITROGEN RATIO ON BIOGAS PRODUCTION

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ABSTRACT: *Various parameters such as concentration of slurry, pH, moisture, total solids, temperature, and C/N ratio are among the main parameters affecting biogas production. The carbon and nitrogen contents of various biogas feedstocks were determined using standard methods and the volume of biogas produced by the substrates were measured using the graduated gas cylinder. The results show that carbon to nitrogen ratio affects the volume of the generated biogas. The production of biogas depends to a large extent, on the choice of feedstock and its carbon to nitrogen ratio.*

KEYWORDS: *Biogas, C/N Ratio, Feedstocks, Concentration, Temperature, Ph.*

INTRODUCTION

Biogas is produced by the anaerobic digestion of biodegradable material such as manure, sewage, plant material, and crops residues amongst others (Cuellar et al, 2008). It can be made from most waste materials regardless of the composition and over a large range of moisture contents, with limited feedstock preparation (Deublein et al, 2008 & NNFCC, 2012). Waste feedstocks for biogas production may be solid, slurries, and both concentrated and dilute liquids. In fact, biogas is also made from the left over organic material from both ethanol and biodiesel production. The yield of biogas from any substrate is highly dependent on the C/N ratio of the material, concentration, pH, temperature (Ponsa et al, 2008 & National Non-Food Crops Centre, 2011).

Some biogas plants are processing residual sludge from wastewater treatment plants (Himanen et al, 2011). Other facilities are processing wastes from chicken processing, juice processing, brewing, and dairy production. However, the range of potential waste feedstocks is much broader including: municipal wastewater, residual sludge, food waste, food processing wastewater, dairy manure, poultry manure, aquaculture wastewater, seafood processing wastewater, yard wastes, and municipal solid wastes (Nakasaki, 2009 & Richards et al,1994). Food processing wastewaters may come from citrus processing, dairy processing, vegetable canning, potato processing, breweries, and sugar production (Sezun et al, 2011).

Biogas comprises primarily methane (CH_4) and carbon dioxide (CO_2) and may have small amounts of hydrogen sulphide (H_2S), moisture and some other gases. The gases methane, hydrogen, and carbon monoxide (CO) produced, can be combusted or oxidized with oxygen (Ryckebosch et al, 2011 & Garba et al, 1998). This energy released allows biogas to be used as a fuel. Biogas can be used as a fuel in any country for any heating purpose, such as cooking. It can also be used in anaerobic digesters where it is typically used in a gas engine to convert the energy in the gas into electricity and heat (Biomethane fueled vehicles, 2009). Biogas can be compressed, much like natural gas, and used to power motor vehicles. In the UK, for example, biogas is estimated to have the potential to replace around 17% of vehicle fuel (State Energy Conservation Office, Texas, 2009). It is a renewable fuel so it qualifies for renewable energy subsidies in some parts of the world. It can also be cleaned and upgraded to natural gas standards when it becomes bio methane. The objective of this work is to find out the extent of the effect of C/N ratios of substrates on biogas yields.

THEORY

Many microorganisms affect anaerobic digestion, including acetic acid-forming bacteria (acetogens) and methane-forming bacteria (methanogens). These organisms promote a number of chemical processes in converting the biomass to biogas (NNFCC, 2012).
There are four key biological and chemical stages of anaerobic digestion:

1. Hydrolysis
2. Acidogenesis
3. Acetogenesis
4. Methanogenesis

In most cases, biomass is made up of large organic polymers. For the bacteria in anaerobic digesters to access the energy potential of the material, these chains must first be broken down into their smaller constituent parts. These constituent parts, such as sugars, are readily available to other bacteria. The process of breaking these chains and dissolving the smaller molecules into solution is called hydrolysis. Therefore, hydrolysis of these high-molecular-weight polymeric components is the necessary first step in anaerobic digestion (Sleat et al, 2006). Through hydrolysis the complex organic molecules are broken down into simple sugars, amino acids, and fatty acids.

Acetate and hydrogen produced in the first stages can be used directly by methanogens. Other molecules, such as volatile fatty acids (VFAs) with a chain length greater than that of acetate must first be catabolised into compounds that can be directly used by methanogens (Boone et al, 2006).

The biological process of acidogenesis results in further breakdown of the remaining components by acidogenic (fermentative) bacteria. Here, VFAs are created, along with ammonia, carbon dioxide, and hydrogen sulfide, as well as other byproducts (Hanreich et al,2011). The third stage of anaerobic digestion is acetogenesis. Here, simple molecules created through the acidogenesis phase are further digested by acetogens to produce largely acetic acid, as well as carbon dioxide and hydrogen (Ferry, 1997).

The terminal stage of anaerobic digestion is the biological process of methanogenesis. Here, methanogens use the intermediate products of the preceding stages and convert them into methane, carbon dioxide, and water. These components make up the majority of the biogas emitted from the system. Methanogenesis is sensitive to both high and low pHs and occurs between pH 6.5 and pH 8 (Martin, 2007).

Methane Formation

The methane producing bacteria decompose further the compounds with a low molecular weight. For example, in order to form methane and carbon dioxide, the methane producing bacteria utilises hydrogen, carbon dioxide and acetic acid. The bacteria exists under natural conditions under water, in ruminant stomaches and in marshes, where anaerobic conditions are present. These microorganisms are very sensitive to environmental variations since they are obligatory anaerobic. The methanogenic bacteria are included in the archeabacter genus in contrast to acidogenic and acetogenic bacteria. There are three types of methanogenic bacteria involved in the metane producing process;

- Methanosarcina genus (spherically shaped)
- Methanothrix bacteria (long and tubular)
- Bacteria that catabolise furfural and sulfates (short and curved rods) (Kossmann et al, 2007)

The equations below illustrate that various products, by-products and intermediates products that are formed in the digestion process of an anaerobic production of methane. The acids produced are processed by methanogenic bacteria to generate methane, which is described in the following equations (Kossmann et al, 2007).

$$\underset{\text{Acetic acid}}{CH_3COOH} \rightarrow \underset{\text{methane}}{CH_4} + \underset{\text{carbon dioxide}}{CO_2}$$

$$\underset{\text{Ethanol}}{2CH_3CH_2OH} + \underset{\text{Carbon dioxide}}{CO_2} \rightarrow \underset{\text{Methane}}{CH_4} + \underset{\text{Acetic acid}}{2CH_3COOH}$$

$$\underset{\text{Carbon dioxide}}{CO_2} + \underset{\text{Hydrogen}}{4H_2} \rightarrow \underset{\text{Methane}}{CH_4} + \underset{\text{Water}}{2H_2O}$$

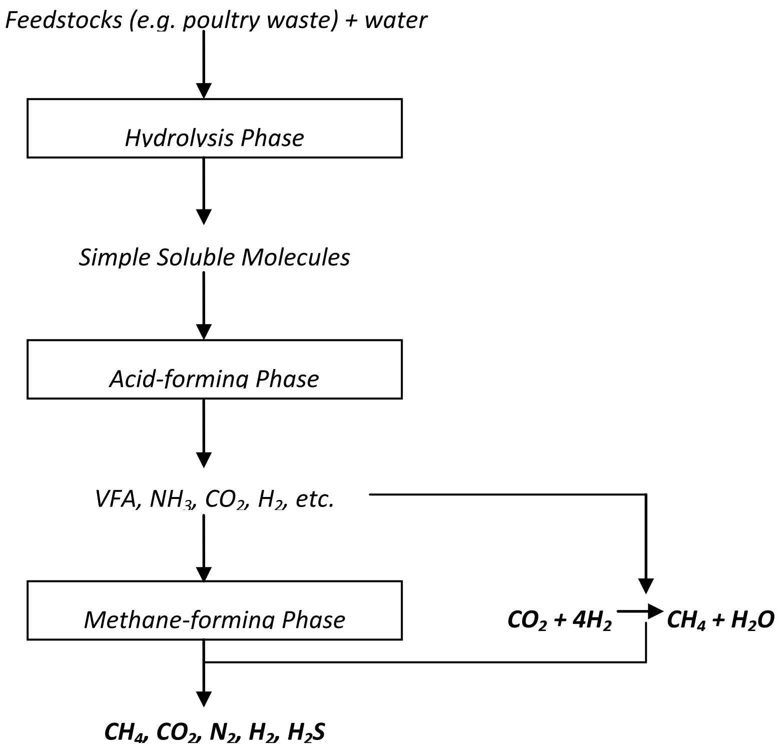

Figure 1: Flow Diagram of Biogas Process

Factors Affecting Biogas Production

Various factors such as biogas potential of feedstock, design of digester, innoculum, nature of substrate, pH, temperature, loading rate, hydraulic retention time (HRT), C : N ratio, volatile fatty acids (VFA), etc. influence the biogas production.

Meher et al (1990), reported that the performance of floating dome biogas plant was better than the fixed dome biogas plant, showing an increase in biogas production by 11.3 per cent, which was statistically significant. Furthermore, the observed reduction in biogas yield was due to the loss of gas from the slurry-balancing chambers of fixed dome plant. Dhevagi et al (1992), used different feedstocks like cow dung, buffalo dung, dry animal waste, stray cattle dung, goat waste, and poultry droppings for their biomethanation potential and observed that poultry droppings showed higher gas production. Earlier, Yeole and Ranade(1992) compared the rates of biogas yield from pig dung-fed and cattle dung-fed digesters and reported that the biogas yield was higher in the former. They attributed this higher biogas yield to the presence of native microflora in the dung. Shivraj and Seenayya(1994)

reported that digesters fed with 8 per cent TS of poultry waste gave better biogas yield, and attributed the lower yield of biogas at higher TS levels to high ammonia content of the slurry.
For increased gas yield, a pH between 7.0 and 7.2 is optimum, though the gas production was satisfactory between pH 6.6 and 7.6 as well. Sahota and Ajit Singh(1991) reported that the gas production was significantly affected when the pH of the slurry decreased to 5.0. They observed that apart from the decreased methanogenic activity due to lower pH, the population of

cellulolytic bacteria, amylolytic organisms, and proteolytic organisms reduced by 4 and 2 log order, respectively. Nagamani and Ramasamy(1998) observed that though there was higher production of biogas at 55°C, the process was unstable due to higher production of volatile fatty acids and that specific microbial consortia was needed for biomethanation of cattle waste at 55°C.

In the case of C : N ratio, 25–30 : 1 is optimum for biogas production (Maishanu et al, 1991). Yeole and Ranade (1992) reported that HRT of 14 days was optimum for biogas production from cow dung. Gadre et al (1990), investigated the optimum retention time for the production of biogas from cattle dung and reported that 15 days HRT was the best for maximum production of biogas from cow dung. They further observed that shorter HRT resulted in accumulation of VFA, whereas at HRT longer than 15 days, the digester components were not fully utilized. Ranade et al (1990), studied the influence of different TS content of biogas production and reported that the optimum production was observed at 8 per cent TS. However, the methane content of the gas produced did not vary significantly with varying levels of TS. Hence, they suggested that high TS content of 14% cattle dung (2 : 1 dilution) can be followed in areas during the time of water scarcity rather than discontinuing the feeding of the digester.

MATERIALS AND METHODS

Anaerobic digestion of different organic wastes for biogas production at 33-42 ^{0}C

Methods

50 g of sun dried cow excreta was placed at temperature range of 33 – 42^{o}C inside clean 250 ml flat bottom conical flask that was dried in oven. To the substrate in the flask, 270 ml of distilled water was added and stirred to form slurry. The flask was covered with two holed rubber cork. Thermometer was fitted airtight in one hole of the rubber corks, while the other hole was placed the gas delivery glass tubing. Rubber hose was fitted on the glass tube to pass the biogas produced in the conical flasks into an inverted 250 ml graduated gas jar cylinder filled with water. The gas cylinder was held in position in a trough of water by a retort stand. The set-up was replicated for all the substrates in Table 1. Biogas production led to downward displacement of water in the gas measuring cylinders. The results of the cumulative yields of biogas from some substrates are shown in Fig. 2.

Determination of nitrogen and carbon contents of some feedstocks

Nitrogen Content

Nitrate nitrogen (N) is an important plant nutrient which promotes foliar growth and increases yield. In the Palin test, nitrate sample was extracted using 1M ammonium chloride at a sample to water ratio of 1:2 (Method of Soil Analysis, 1979). The extracted nitrate was reduced to nitrite during extraction stage and then reacted to form a red azo-dye. The intensity of the red colour produced is proportional to the nitrate level in the sample and was determined by using a Palintest photometer.

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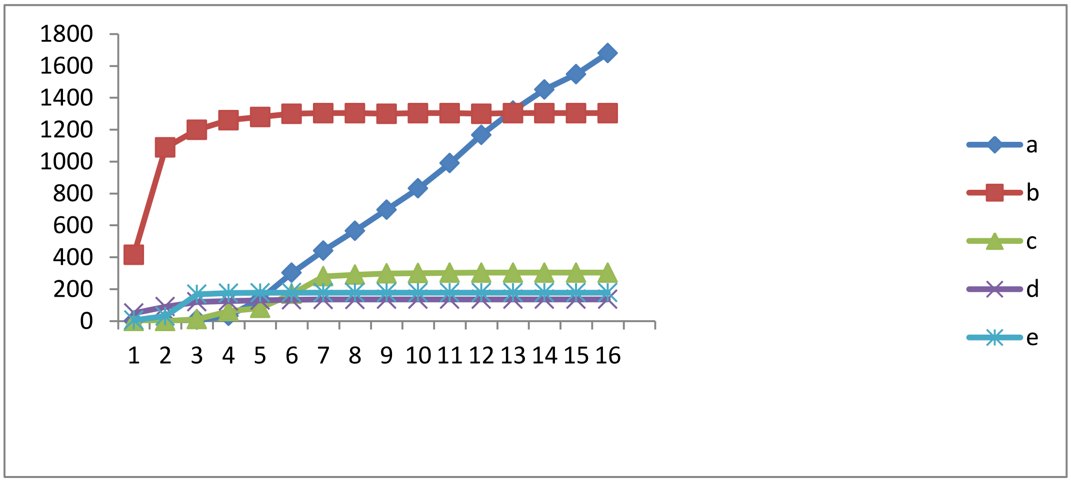
Test Procedure:
A round glass test tube was filled to the 10 ml mark with the extract. One Nitricol N tablet was crushed and mixed with sample to dissolve and the solution allowed to stand for 10 minutes to develop full colour. A wave length of 570 nm was selected on photometer. The photometer reading was taken (%T). The nitrate calibration chart was used to find the nitrate nitrogen concentration in the sample.

Carbon Content
The Carbon content was estimated approximately by assuming it to be 58% of the volatile solids (organic matter) according to (Tinsely and Nowakowski,1959).

RESULTS



Key:

a=Cow dung

b=Poultry droppings
c=Rice husks

d=Neem tree leaves
e=Sugar cane bagasse

Fig 2: Comparative cumulative yields of biogas (cm^3) from 50 g of five different organic wastes at 33-41^{o}C.

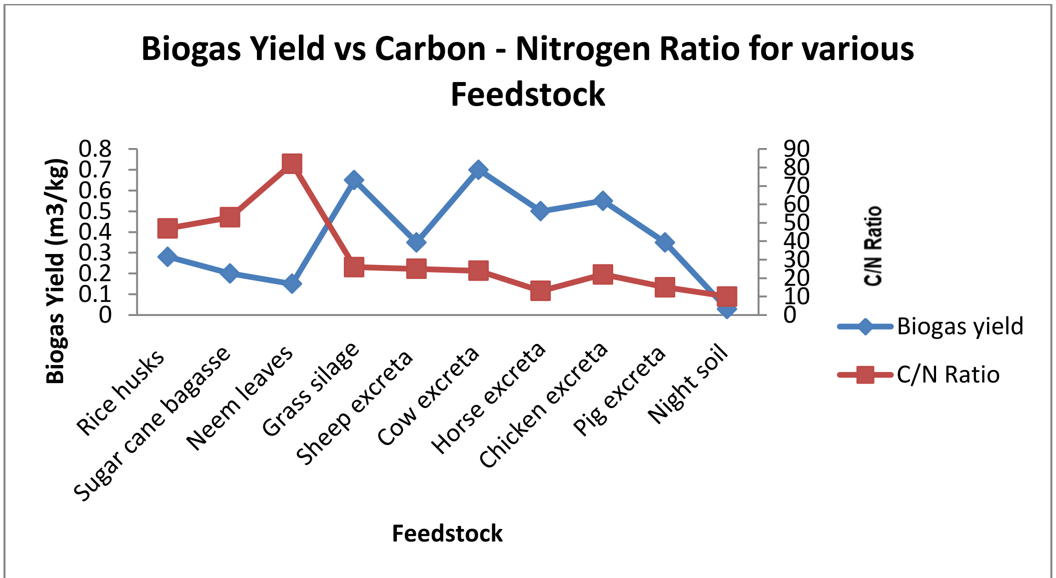


Fig. 3: Correlation of biogas yields of substrates with C/N ratios

Table 1: Carbon to Nitrogen Ratio of Some Wastes

Feedstock	Carbon content of Feedstock by weights %	Biogas Yields m^3/kg of Volatile Solids	Nitrogen content of feedstock by weight %	Carbon Nitrogen Ratio (C/N)
Rice husks	46.23	0.28	0.98	47:1
Sugar cane	45.23	0.20	0.75	53:1
bagasse	53.27	0.15	0.65	82:1
Neem leaves	14.00	0.65	0.54	26:1
Grass silage	14.60	0.35	0.58	25:1
Sheep excreta	10.00	0.70	0.42	24:1
Cow excreta	15.80	0.50	1.20	13:1
Horse excreta	48.72	0.55	2.19	22:1
Chicken excreta	36.12	0.35	2.40	15:1
Pig excreta	60.00	0.028	6.00	10:1
Night soil				

DISCUSSIONS

The results of the comparative studies of cumulative yields of biogas from cow dung, clean poultry droppings, rice husks, neem tree leaves and sugar cane bagasse at the temperature of 33-42^{O}C are given in Figure1. The results showed that cow dung gave the highest cumulative yield of biogas followed by the poultry droppings. Rice husks gave about 25% of the yield of poultry droppings while neem tree leaves and sugar cane bagasse gave 10% and 15% of poultry droppings yield respectively. The study revealed that neem tree leaves and sugar cane bagasse are not good materials for biogas production.

Previous studies have shown that cow dung is the best substrate for biogas production (Garba et al, 1998). The poultry droppings have a very offensive odour when formed into slurry. Rice husk has odour on digestion of the slurry but not very offensive. The neem tree leaves and sugar cane bagasse have little or no odour on digestion hence their low yield of biogas. The offensive odour of poultry droppings is due to the nutrient contained in it. Most of its nitrogen is in the form of uric acid which turns in storage, first to urea and then to ammonium carbonate. Under unfavourable storage conditions, the latter soon decomposes into ammonia, carbon (iv) oxide and water which may entail nitrogen losses. Figure 2 shows the correlation of the C/N ratio with biogas yields of different substrates. The results unfold that the yield of biogas depends on C/N ratio of the various feedstocks. The optimum yield of biogas is in the range of C/N ratio of 20 – 30:1 as shown in Table 1. The variation of the C/N values can affect the pH of a slurry. The increase in carbon content will give rise to more carbon dioxide formation and lower pH value, while high value of nitrogen will enhance production of ammonia gas that could increase the pH to the detriment of the micro-organisms.

CONCLUSIONS

Biogas production depends on various parameters that affect the yields of the gas from different substrates. Prominent among the factors are the pH, concentration of slurry, temperature and more importantly, the C/N ratio that controls the pH value of the slurry. The total solids, volatile matter, mineral concentrations are among the factors affecting biogas yields. Production of biogas will enhance clean environment through the killing of the pathogens, during anaerobic digestion and thus producing fertilizer very rich in NPK. Biogas finds application in cooking, lighting, electricity generation amongst other uses.

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