Ambient temperature kinetic assessment of biogas production from co-digestion of horse and cow dung

M.O.L. Yusuf[1], A. Debora[1], D.E. Ogheneruona[2]

[1]*Department of Civil and Environmental Engineering, University of Port Harcourt, Port Harcourt, Rivers State, Nigeria*
[2]*Department of Mechanical Engineering, University of Port Harcourt, Port Harcourt, Rivers State, Nigeria*

Abstract

Yusuf M.O.L., Debora A., Ogheneruona D.E., 2011. **Ambient temperature kinetic assessment of biogas production from co-digestion of horse and cow dung**. Res. Agr. Eng., *57*: 97–104.

Biogas production from 5 batch digesters containing varying ratio of mix of horse and cow dung was studied for a period of 30 days at ambient temperature. It was observed that biogas production was optimized when horse and cow dung were mixed in a ratio of 3:1. The modified Gompertz equation was used to adequately describe the cumulative biogas production from these digesters. In addition, a modified first order model was developed to assess the kinetics of the biodegradation process. It was observed that the rates of substrate biodegradability and of removal of the biodegradable fractions of the substrate could be obtained by plotting $1/t$ ($\ln(dyt/dt)$) against the inverse of time of digestion. This modified first order model also showed that the digester containing horse dung and cow dung in the ratio of 3:1 had the highest short term anaerobic biodegradability index (STABI) of 3.96 at room temperature.

Keywords: cow dung; horse dung; anaerobic; modified Gomperzt; biodegradability; kinetics

The need for alternative sources of energy for both decentralized and centralized power generation has led to the proliferation of research into alternative energy sources. Anaerobic digestion (AD) received considerable interest as one of such means of meeting both decentralized and centralized power sources in recent years (Sixt, Sahm 1987). The process of anaerobic digestion has the potential of converting biodegradable organics into biogas which comprises methane (55–75%) and carbon dioxide (25–45%) (Steffens et al. 2000) with calorific value of 20 MJ/m^3 (Myles 1985). Biogas can therefore be a source of decentralized energy source for developing countries especially in this era of insecurity and unpredictability in fossil fuel supply.

The study of biogas production from biodegradable substrates is essential for an efficient selection of suitable substrate in anaerobic digestion. The presence of recalcitrant fractions in substrate utilized in biogas production in the form of cellulose and lignin may make most of these biodegradable volatile matter not to become available for biodegradation especially, when anaerobic digestion is carried out at suboptimum conditions (such as room temperature conditions). Numerous sources of biodegradable organic waste exist in nature and any technology that utilizes organic waste of high nuisance value, such as animal wastes from cattle, horses, pigs, poultry etc., in anaerobic digestion, may just provide suitable means of not only managing these wastes but also protecting water quality and aesthetic beauty. Vaa (1993) viewed any technology that tries to harness optimum use of available resource in a given environment while minimizing the negative environmental consequence as appropriate technology.

In many instances, the generation rate of animal waste types varies significantly in nature and in situation of relative abundance of a particular animal waste, the need for combining animal waste from different sources may become imperative in biogas generation. Hence, the implications of combining or co-digesting animal wastes for biogas production need to be properly assessed for successful implementation of such anaerobic process. Co-digestion was used by researchers such as (Callaghan et al. 1999; Gelegenis et al. 2007; Chellapandi et al. 2008) to improve biogas yield by controlling the carbon to nitrogen ratio.

The source of animal waste used in anaerobic digestion is important in ensuring a successful operation of the process because of the lignin components of animal manure. Monogastric animals are known to produce wastes that contain more nutrients than ruminants. Ruminants are known to excrete more lignocelluloses material due to extensive enzymic exposure in their four chamber stomach (Warner et al. 1989; Wilkie 2005). The high presence of lignin in animal waste can resist anaerobic degradation even after long retention time (Van Soest 1994) or may prevent the anaerobic process from commencing (Haug 1993). Thus, a high volatile solid contents of substrates may not necessary translate to high biogas yield due to the presence of non-available volatile solids in form of lignin. It is important to note that the volatile matter content of any substrate accounts for the proportion of solids that is transformed into biogas (Wilkie 2005). Other important criteria that were shown to affect biodegradability of substrates include the carbon to nitrogen ratio (Kayhanian, Tchobanoglous 1992) or the presence of specific substances like proteins, carbohydrate lipids etc. (Jung et al. 1997). Thus, the chemical composition of organic substrate can be said to contribute to the pattern of degradation of such substrate and attempts to quantify this biodegradable substrate fractions were carried out by authors such as Chandler et al. (1980) and Haug (1993).

Hence, for a successful biodegradation to take place, the process of co-digestion of animal waste must provide a balance between the lignin content and the carbon to nitrogen ratio. In this research the utilization of a more abundant substrate in the form of cow dung was co-digested with less abundant form of substrate in the form of horse dung in order to select an appropriate mix ratio for optimum biogas production rate kinetics at room temperature.

MATERIAL AND METHODS

Substrate collection

Substrates that were utilized in this research work were cow dung and horse dung which were obtained from slaughter house and polo club respectively, situated in the city of Port Harcourt, Rivers State, Nigeria. These substrates were sun dried prior to being used for biogas production.

Chemical analyses of these substrates were carried out to determine their volatile matter and carbon to nitrogen ratio. The volatile matter was determined in accordance with procedure outlined in standard methods (Clescerl 1985) that is, a portion of these samples was dried and ashed in a muffle furnace at 550°C. Also, the carbon to nitrogen ratio was determined by the method outlined at Standard methods (Clescerl 1985).

Experimental design

The experimental design for the anaerobic digestion of cow dung and horse dung was carried out at ambient temperature that ranged between 28°C to 33°C in five batch digesters labeled A–E. The total solid content of the five digesters was set at 8% (w/w) as recommended by Tchobanoglous et al. (1993) for low solid loading as follows:

Digester A: comprised 100% horse dung in 250 ml of water (i.e. 21.74 g of horse dung),

Digester B: comprised 75% horse dung and 25% cow dung in 250 ml of water (i.e. 16.31 g of horse dung and 5.44 g of cow dung),

Digester C: comprised 50% horse dung and 50% cow dung in 250 ml of water (i.e. 10.87 g of horse dung and 10.87 g of cow dung,

Digester D: comprised 25% horse dung and 75% cow dung in 250 ml of water (i.e. 5.44 g of horse dung and 16.31 g of cow dung),

Digester E: comprised 100% of cow dung in 250 ml of water (i.e. 21.74 g of cow dung).

The digesters were set up as described by Itodo et al. (1992), Chellapandi (2004), Momoh and

Nwaogazie (2008) and biogas measurement was carried out by using the water displacement method in which the amount of saline water (20% NaCl (w/v), pH 4) displaced was proportional to the volume of biogas produced. Ambient temperature measurement was determined with a mercury bulb thermometer.

The scope of this research was restricted to the studying of the cumulative biogas generation using the modified Gompertz equation in studying the kinetics of biogas production Eq. (1) and also a modified first order equation as equation developed here (9)

$$(Bt) = B \exp\left[-\exp\left[\frac{Rb \times e}{B}(\lambda - t) + 1\right]\right] \quad (1)$$

where:

Bt – cumulative of biogas produced (ml) at any time (t)
B – biogas production potential (ml)
Rb – maximum biogas production rate (ml/day)
λ – lag phase (days), which is the min time taken to produce biogas or time taken for bacteria to acclimatize to the environment in days

The constants B, Rb and λ were determined using the non-linear regression approach with the aid of the solver function of the MS Excel ToolPak.

This equation was utilized by researchers to study the cumulative methane production in biogas production. Zwietering et al. (1990) and Lay et al. (1996) applied this equation to study bacteria growth. Recently, Budiyono et al. (2010) utilized this modified equation to describe biogas yield from cattle manure.

RESULTS AND DISCUSSIONS

In this study, animal wastes are evaluated for suitability for biogas production at sub-optimum condition (such as room temperature with no form of physical treatment). Cattle manure was established to have lower available volatile solids because ruminants extract much of the nutrients from the fodder and the leftover is rich in lignin complexes which were extensively exposed to enzyme action of the four chamber stomach of ruminants (Werner et al. 1989; Wilkie 2005). The volatile solids content for cow dung and horse dung used in this research were determined to be 58.7% and 87.5% respectively while the ambient room temperature ranged between 27–32°C.

The study of biogas production from cow dung and horse dung and their mixtures was conducted in digesters labeled A–E as shown in Table 1. Biogas production was monitored and measured until biogas production reduced significantly. The modified Gomperzt equation was then used to fit the cumulative daily biogas production which was observed to adequately describe the biogas production from these substrates. The estimated kinetic constants using non-linear regression and other characteristics of the digesters A–E are shown in Table 1.

At the end of 30-day period, it was observed that digester B produced the highest biogas production potential (B) of 360 ml at a maximum biogas production rate (Rb) of 36.99 ml/day with a lag phase (λ) of 8.07 days. Digester A had biogas production potential estimated to be 254.5 ml at a maximum biogas production rate of 37.87 ml/day with a lag phase of 9.03 days. Yet, in digester C, which comprised equal amount of horse dung and cow dung, the biogas production potential was 167.85 ml at a maximum biogas production rate of 18.95 ml/day with a lag phase of 8.71 days. The modified Gompertz equation was observed to adequately describe biogas production with a goodness of fit (R^2) of 0.996, 0.998 and 0.997 for digesters A, B and C, respectively (Fig. 1).

Digester D and E failed to produce any significant amount of biogas and this could be attributed to

Table 1. Composition of digesters and their corresponding kinetic parameter

Digester	Weight of cow dung (g)	Weight of horse dung (g)	C/N	Volatile solid (g)	Biogas produced (ml)	B (ml)	R_m (ml/day)	λ (day)	R^2
A	0	21.74	30.2:1	18.48	257.2	254.5	37.87	9.03	0.996
B	5.44	16.31	23.78:1	17.05	353	360	36.99	8.07	0.998
C	10.87	10.87	17.65:1	15.62	165.5	167.85	18.95	8.71	0.997
D	16.31	5.44	11.38:1	14.19	–		–	–	–
E	21.74	0	5.1:1	12.76	–	–	–	–	–

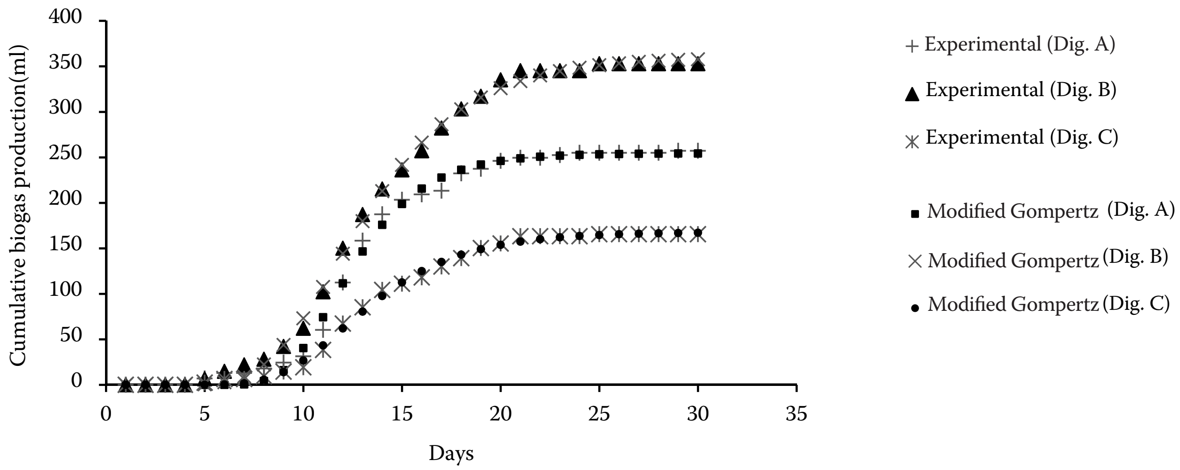

Fig. 1. Comparison of experimental data and modified Gompertz model for biogas production

the sub-optimum carbon to nitrogen ratio present and/or the increase in the lignin content of this mixture as percentage of cow dung increased. It is worthy to note that the volatile matter content of the cow dung used in this study was 58.7%, which is indicative of a low carbon source. Thus, if the biodegradability of the cattle cow dung is assumed to be 41.6% (Chen, Hashimoto 1980) or 36% (Hill 1983), then the level of lignin in the digesters D and E would be significantly high to prevent degradation of these substrates in these digesters (Haug 1993). This is also coupled with the low carbon to nitrogen ration of these digesters, hence, subsequent discussions would be limited to digesters A–C.

Digester B provided an adequate balance between the carbon to nitrogen ratio, which lies between the optimum of 20:1–30:1 (Marchaim 1992) and the lignin content. Also, the time taken for the bacteria to acclimatize was the fastest in the digester B, which may be attributed again to the optimum level of carbon to nitrogen ratio of substrate in this digester and possible presence of sufficient bacteria population in the cow manure used as the co-substrate.

In order of performance, digester B could be rated as the most efficient, which was immediately followed by digester A and lastly by digester C. The digesters D and E could be classified as failed digesters for their inability to produce significant amount of biogas.

Substrate biodegradability was assessed in this study by developing a mathematical model that was based on the first order kinetics. According to Linke (2006), the transformation of biodegradable solids into biogas can be correlated as shown in Fig. 2, which can further be described by Eqs (2–6) for a batch reactor system.

$$\frac{ym}{ym - yt} = \frac{Co}{Ct} \qquad (2)$$

This relationship was linked to the first order rate degradation of the volatile solids in which Co is the initial volatile solids while Ct is the volatile solids concentration at time (t) given by,

$$\ln\left(\frac{Ct}{Co}\right) = -kt \text{ or } \ln\left(\frac{Co}{Ct}\right) = kt \qquad (3)$$

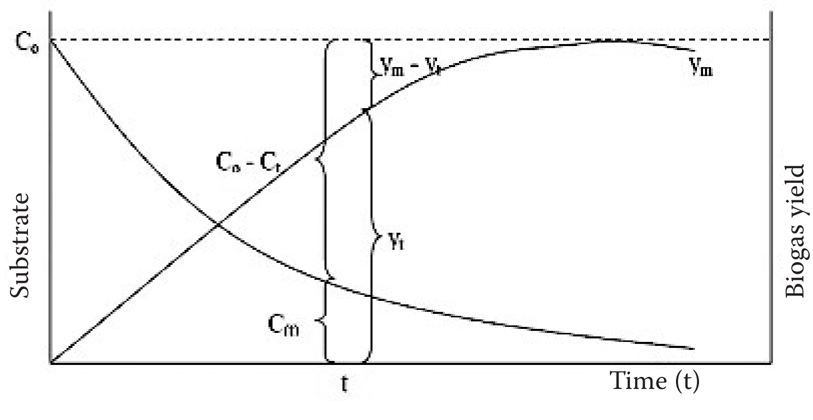

Fig. 2. Pattern of transformation of volatile solids into biogas

Replacing $\frac{Co}{Ct}$ in Eq. (3) with $\frac{ym}{ym - yt}$ (4)

$$\left(\frac{ym - yt}{ym}\right) = \exp(-(kt)) \quad (5)$$

$$\therefore ym(1 - \exp(-(kt))) = yt \quad (6)$$

where:

yt – volume of biogas produced per unit mass of volatile solids fed at any time (t)

ym – volume of biogas per unit of mass of volatile solids converted at maximum time

The rate constant associated with the degradation of the biodegradable fractions is represented by k (1/days), while the period of digestion is represented by t (in days).

The application of Eq. (6) in assessing substrate biodegradability and the rate constant was accomplished by attempting to linearize Eq. (6) as shown below. By differentiating Eq. (6), we obtain,

$$\frac{dyt}{dt} = ym\,k\exp(-(kt)) \quad (7)$$

Taking natural logarithm on both sides of the equation we obtain

$$\ln\left(\frac{dyt}{dt}\right) = (\ln ym + \ln k) - kt \quad (8)$$

This equation can be reduced to the form

$$\frac{1}{t}\ln\left(\frac{dyt}{dt}\right) = \frac{1}{t}(\ln ym + \ln k) - k \quad (9)$$

Eq. (9) is analogous to the straight line equation $y = mx + c$, in which ($\ln ym + \ln k$) represents the slope while, ($-k$) represents the intercept of

$$\frac{1}{t}\ln\left(\frac{dyt(ml/kgVS)}{dt(day)}\right)$$

the plot of against the inverse of the retention time. The term ($\ln ym + \ln k$) is a measure of the availability of readily and moderately degradable fractions of the substrate. Godley et al. (2003) reported that, because of the limited time range of most biodegradability test, only the readily and moderately degradable fractions are consumed while the poorly or recalcitrant fractions are hardly affected. Thus, the term can be used to select substrate with the potential for high biogas production from a given substrate volatile solid under short retention time and was referred to as the short term anaerobic biodegradability index (STABI). Higher values of this term depict substrate with the potential to produce high quantity of biogas under short retention periods while lower values are indicative of substrate with the potential to produce low quantity of biogas under short retention periods from a given substrate volatile solids.

The term ($-k$) is a measure of the rate of removal of the biodegradable fractions as the biogas yield increases with time. This rate constant is an aspect of the first order rate constant. The first order kinetic constant was described by Eastman and Ferguson (1981) as purely an empirical function that reflects the cumulative effects of many processes such as pH, temperature, quantity and quality of substrate, rate of removal of the biodegradable fractions, rate of inhibition by other components of the substrate such as lignin or by- product of the reaction process such as fatty acids etc.

The more negative the value of (k), the faster the rates of removal of the biodegradable fractions while

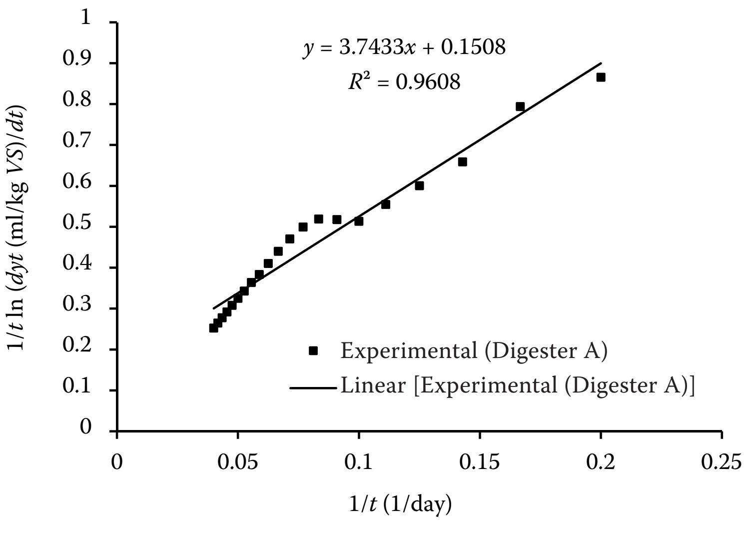

Fig. 3. Plot of $1/t$ (ln(dyt (ml/kg VS)/dt against $1/t$ for digester A

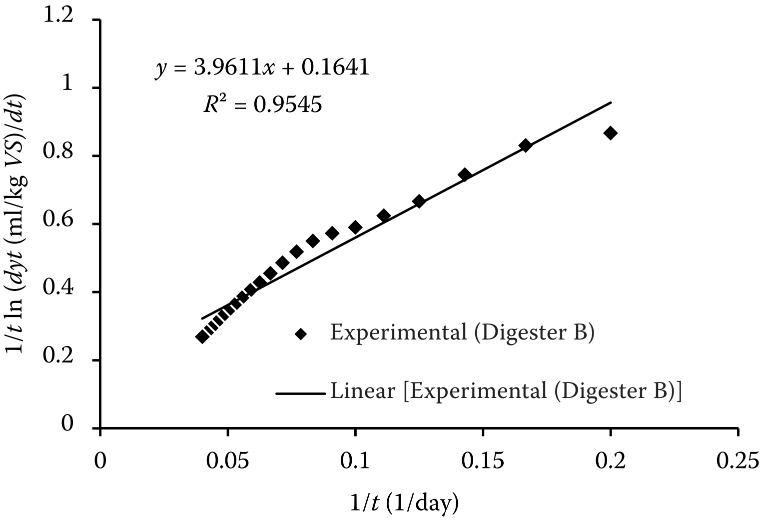

Fig. 4. Plot of $1/t$ (ln(dyt (ml/kg VS)/dt against $1/t$ for digester B

the more positive the value of (k), the slower the rate of removal of the biodegradable fractions. Thus, Eq. (9) can be used to measure the room temperature short term biodegradability and also identify anaerobic processes that are progressive or stressed.

The application of this modified first order model equation in assessing the room temperature short term biodegradability and removal rate of the biodegradable fractions was carried out for the substrates in digesters A–C. A plot of

$$\frac{1}{t}\ln\left(\frac{dyt(ml/kgVS)}{dt(day)}\right)$$

versus

$$\frac{1}{t} \qquad (1/\text{day})$$

revealed that the modeled equation could suitably assess the room temperature short term biodegradability and removal rates of biodegradable fractions of substrates used in anaerobic digestion as shown in Figs 3–5.

From Fig. 3, the room temperature short term biodegradability of the substrate in digester A for the period under study was observed to be 3.7433 while the intercept, depicting the removal rate of biodegradable fractions was estimated to be –0.1508. The model was able to fit the data set with a goodness of fit (R^2) of 0.9608. Similarly, digester B and C had room temperature short term biodegradability of 3.9611 and 2.9196 with a removal rate constant of –0.1641 and –0.1818 and a goodness of fit of 0.9545 and 0.913 as shown in Figs 4 and 5, respectively.

In essence, substrate in digester B, with a room temperature short term biodegradability of 3.9611, had the highest potential to produce more quantity of biogas for a given substrate volatile solid, followed by substrate in digester A and lastly by substrate in digester C. This may be attributed to the adequate

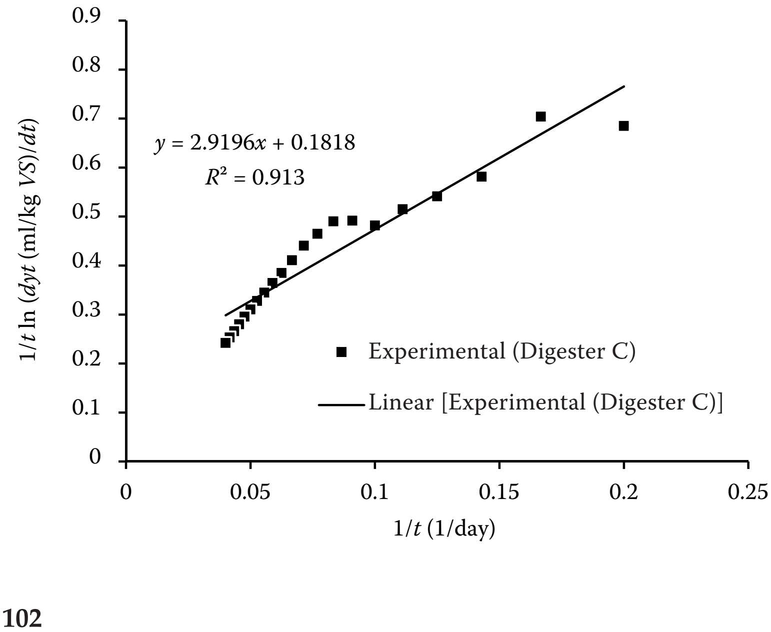

Fig. 5. Plot of $1/t$ (ln(dyt (ml/kg VS)/dt against $1/t$ for digester C

carbon to nitrogen ratio of substrate in digester B. Carbon to nitrogen ratio of 25:1 were described as optimum for biogas production (Marchaim 1992). This finding is corroborated by estimates provided by the modified Gompertz equation for the biogas production potential (*B*) of digester B, observed to be the highest (about 360 ml), which was followed by substrate in digester A (254.5 ml) and lastly by substrate in digester C (167.85 ml).

Similarly, the modified first order model revealed that substrate in digester A with a rate constant of –0.1508 had the highest removal rate of biodegradable fractions (i.e. highest rate of biogas production), followed by substrate in digester B (–0.1641) and lastly by substrate in digester C (–0.1818). This finding is again corroborated by estimates determined using the modified Gompertz equation. Substrate in digester A was observed to have the maximum biogas production rate of 37.87 ml/day, which was closely followed by substrate in digester B (36.99 ml/day) and lastly by substrate in digester C (18.95 ml/day).

CONCLUSIONS

Biogas production from cow dung and horse dung was established here to be feasible at room temperature. Application of the modified Gomperzt equation in studying the biogas production was able to predict the pattern of biogas production with time. It was observed that the maximum biogas production could be obtained from substrate in digester B (25% cow dung and 75% horse dung) which was closely followed by substrate mixture containing (100% horse dung) and lastly by substrate mixture comprising (50% cow dung and 50% horse dung). Digesters D and E were classified as failed digesters because of their inability to produce any measurable amount of biogas at the end of the digestion period.

Furthermore, these observations were corroborated using a modified first-order equation. This model was able to establish that substrate in digester B have the highest room temperature short term biodegradability. This was followed by substrate in digester A and lastly by substrate in digester C. Also, the observed *k* values for the digesters A–C indicated that the reaction could have progressed efficiently. In essence, the short term room temperature kinetic of biogas production from cow dung and horse dung can be effectively studied using the modified Gompertz model and also a modified first-order equation as developed here.

References

Budiyono, Widiasa I.N., Johari S., Sunarso, 2010. The kinetics of biogas production rate from cattle manure in batch mode. International Journal of Chemical and Biomolecular Engineering, *3*: 39–44.

Callaghan F.J., Wase D.A.J., Thayanithy K., Forste C.F., 1999. Co-digestion of waste organic solids: batch studies. Bioresource Technology, *67*: 117–122.

Chandler J.A., Jewell W.J., Gossett J.M., Van Soest P.J., Robertson J.B., 1980. Predicting methane fermentation biodegradability. Biotechnology and Bioengineering Symposium, *10*: 93–97.

Chellapandi P., 2004. Enzymes and microbiological pretreatments of oil industry wastes for biogas production in batch digesters. In: Pathade G.R., Goel P.K. (eds), Biotechnology and Environmental Management. Jaipur, ABD Publishers.

Chellapandi P., Prabaharan D., Uma L., 2008. A preliminary study on co-digestion of ossein industry waste for methane production. EurAsian Journal of BioSciences, *2*: 110–114.

Chen V.R., Hashimoto A.G., 1980. Substrate utilization kinetic model for biological treatment processes. Biotechnology and Bioengineering, *22*: 2081–2085.

Clescerl L.S., Greenberg A.E., Eaton A.D., 1985. Standard Method for the Examination of Water and Wastewater. 16th Ed. Washington D.C., APHA.

Eastman J.A., Ferguson J.F., 1981. Solubilization of particulate organics carbon during the acid phase of anaerobic digestion. Journal Water Pollution Control Federation, *53*: 352.

Gelegenis J., Georgakakis D., Angelidak I., Marris V., 2007. Optimization of biogas production by co-digesting whey with diluted poultry manure. Renewable Energy, *32*: 2147–2160.

Godley A., Lewin K., Graham A., 2003. Estimating biodegradable municipal solid waste diversion from landfill. Available at: www.ecn.nl (accessed September 16, 2011)

Haug R.T., 1993. The Practical Handbook of Compost Engineering. Baco Raton, FL, CRC Press LLC.

Hill D.T., 1983. Simplified monod kinetics of methane fermentation of animal wastes. Agricultural Waste, *5*: 1–5.

Itodo I.N., Lucas E.B., Kucha E.I., 1992. The effect of media material and its quality on biogas yield. Nigeria Journal of Renewable Energy, *3*: 45–49.

Jung H.G., Mertens D.R., Payne A.J., 1997. Correlation of acid detergent lignin and klason lignin with digestibility of forage dry matter and neutral detergents fibre. Journal Diary Science, *80*: 1622–1628.

Kayhanian M., Tchobanoglous G., 1992. Computation of C/N ratio for various organic fractions. BioCycle, *33*: 58–60.

Lay J.J., Li Y.Y., Noike T., 1996. Effect of moisture content and chemical nature on methane fermentation characteristics of municipal solid wastes. Journal of Environmental Systmem and Engineering JSCE, 552/VII-1: 101–108.

Linke B., 2006. Kinetic study of thermophilic anaerobic digestion of solid wastes from potato processing. Biomass and Bioenergy, *30*: 892–896.

Marchaim U., 1992. Biogas processes for sustainable development. Rome, FAO.

Momoh O.L.Y., Nwaogazie I.L., 2008. Effect of waste paper on biogas production from co-digestion of cow dung and water hyacinth in batch reactors. Journal Applied Science and Environmental Management, *124*: 95–98.

Myles R.M., 1985. Practical Guide to Janata Biogas Plant Technology. New Delhi, India, AFPRO Action Food Production.

Sixt H., Sahm H., 1987. Biomethanation. In: Sidwich J.M., Holdom R. (eds) Biotechnology of Water Treatment and Exploitation. Chichester UK, Ellis Horwood.

Steffen R., Szolar O., Braun R., 2000. Feed stock for anaerobic digestion. Making energy and solving modern waste problem. Available at: www.adnett.org (accessed 16 September, 2011)

Tchobanoglous G., Theisen H., Vigil S., 1993. Integrated Solid Waste Management Engineering: Principle and Management Issues. Singapore, McGraw-Hill U.S.

Vaa M., 1993. Towards more appropriate technologies? Experience from the Water and Sanitation Sector, Research Report 93 Nordiska Afrikain-Stitutet Uppsala. Available at: http//nai.diva-portal.org (accessed 16 September, 2011)

Van Soest P.J., 1994. The Nutritional Ecology of the Ruminant. 2nd Ed. Ithaca, Cornell University Press.

Werner W., Stohr U., Hees N., 1989. Biogas Plant in Animal Husbandary. Available at: http://www.cedecap.org.pe/uploads/biblioteca/9bib_arch.pdf.

Wilkie A.C., 2005. Anaerobic digestion of diary manure, design and process consideration. National Resource, Agricultural and Engineering Service, *176*: 301–312.

Zwietering M.H., Jongenburger I., Rombouts F.M., Van't Riet K., 1990. Modeling of the bacterial growth curve. Applied and Environmental Microbiology, *56*: 1875–1881.

Received for publication June 2, 2010
Accepted after corrections May 5, 2011

Corresponding author:

Dr. M.O.L. Yusuf, University of Port Harcourt, Department of Civil and Environmental Engineering,
Choba PMB 5323, Port Harcourt, Rivers State, Nigeria
phone: + 234 803 538 6779, e-mail: yusuf_mom@yahoo.com