Wobbe Index Determination of Cattle Dung Biogas

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Abstract
This paper is aimed at determining the Wobbe Index (W I) of cattle dung biogas which is the amount of energy delivered to a burner through an injector or orifice especially during combustion. The biogas was produced by anaerobic digestion of cattle dung in a batch digester within two weeks. Pressure and temperature of the digester were monitored at 12 noon daily. The analysis of the combustible biogas using thermal conductivity detector (TCD) revealed CH_4 at 0.562, CO_2 0.395, H_2S 0.018, CO 0.019 and 0.005 moles for NH_3 by volume. Its calorific value (C V) using gas calorimeter Junkers was 19.5 MJ/m^3. The cumulative specific volume of the biogas rose from zero through day 1 to 0.622732 m^3/kg on the sixth day before recording daily marginal increments with the rest of the days of incubation. The relative density of the biogas also had a sharp rise on the second day at 5.039208 before dropping to 2.51126 and then gradually decreased daily to the end of digestion. The Wobbe Index equally rose from zero on the first day through to 12.08434 MJ/m^3, 14.07783 MJ/m^3 and 15.87665 MJ/m^3 on days 2, 3, 4 and 5 respectively after which it had logarithmic increments. The volatile solids destroyed also recorded logarithmic rise while the bacterial growth rate followed the zigzag pattern as those of internal energy and enthalpy. It is therefore concluded that parameters like the cumulative specific volume and Wobbe Index increased throughout the incubation period while those that are directly temperature dependent varied with the temperature of the digester.

Keywords: Wobbe Index, calorifc value, cattle dung, biogas, batch digester, specific volume, relative density, internal energy, enthalpy

1.0 Introduction

The energy crises as a result of unacceptable upsurge in the prices of the fossil fuels in the 1970s compelled the developed nations to intensify the research in to alternative energy drives. In addition, the realization in the 1980s that products of combustion of these fuels which is principally carbon dioxide having the highest percentage, being underlying compound responsible for the global warming phenomenon, really increased the research momentum of these countries in to renewable energy sources. Furthermore, the observation that the fossil fuels sources are being depleted without corresponding refurnishing made it absolutely necessary, this time around for both the developed and the developing nations to radially launch researches in to alternative and renewable energy sources. Renewable energy sources are many and include: Hydropower, solar, wind, ocean, geothermal and wastes among others. These renewable energy resources except for the wastes do not degrade in the process of usage but are capital intensive and some like hydropower are affected by seasonal changes and are also location specific. The wastes on the other hand are not capital intensive as such. They can however be either synthetic or biological in nature.

The synthetic wastes once attained this status are not biodegradable and as such require reasonable thermal energy in order to degrade. Examples of these wastes are used tyres, polythenes, plastics, and even charcoal. They now undergo processes like pyrolysis, gasification and so on to release energy in the form of gaseous fuels, liquid fuels and chars. For instance, Fernandez, *et al.*, (2009) carried out pyrolysis of waste granulated tyres and tyre reinforcement fibres in a thermobalance horizontal oven at 550 ^oC and 900 ^oC to obtain 50-57 % by weight on dry basis tar, 25-35 % gases mainly butane and iso-butane while the rest was char. Quek and Balasubramanian (2013) reported that the pyrolysis of a whole tyre could be done at a temperature as high as 950^{o}C at 101325 Pa to produce 24 % oil by weight. The pyrolysis of 300g of shredded tyre scrap on a static batch reactor yielded solid (char), liquid (water and oils) and gas (light hydrocarbons, hydrogen, carbon monoxide and carbon dioxide) at a temperature range between 400 and 700^{o}C (Berrueco, *et al*., 2005).

Biological wastes on the other hand are biodegradable through enzymatic reactions especially in an anaerobic environment. This gives rise to biogas which is a mixture of almost naturally occurring gases. The principal components of biogas are methane (CH_4) at 50-60% and carbon dioxide (CO_2) with 30-40% by volume with traces of hydrogen sulphide (H_2S), hydrogen (H_2), oxygen (O_2), nitrogen (N_2) and water vapour. For example, Ezekoye and Ezekoye (2009) reported that raw biogas contains about 55-65% methane, 30-45% carbon dioxide, traces of hydrogen and fractions of water vapour.

For a combustible biogas, the heating values vary like any other gaseous fuel depending on its source. The heating value determination is done in the form of calorific value and Wobbe index. It is a measure of energy delivered through an injector to a burner. It shows the compatibility between the natural gas supplied and the burner (GQHWG, 2004). A lot of work has been reported on the calorific value of biogas but little was done on Wobbe index for biogas. For instance, Raja, *et al.,* (2012) conducted a variable calorific value tests on biogas and they showed that biogas with 56% methane had calorific value of 20 MJ/m^3, 62% with 22.1 MJ/m^3 and 70% methane had 25 MJ/m^3. Beddoes, *et al.,* (2007) reported that the heating value of biogas is 212 MJ/m^3. Adegun and Yaru (2013) generated biogas from cattle dung and its analysis using thermal conductivity detector showed CH_4 with 56.20%, CO_2 with 39.50%, H_2S, 1.08%, CO 1.90% and ammonia (NH_3) 0.50%. They also reported that the calorific value of the biogas was 19.50 MJ/m^3. Wobbe Index of biogas with 60% CH_4, 38% CO_2 and 2% others had 19.5 MJ/m^3 and that of natural gas to be 39.9 MJ/m^3 (DTI, 2012).

The objective of this paper therefore is to determine the Wobbes index of the biogas generated from cattle dung only.

2.0 Theory of biogas production

Biogas is a product of metabolism of methane-bacteria and is created when bacterial decompose a mass of organic material anaerobically. The energy needed for the activities of bacterial involves reduction and oxidation process (electron donor and acceptor). This may be endogenous (from within the cell) or exogenous (from outside the cell). The use of internal electron is known as fermentative metabolism (Tchobanoglous, *et al.,* 2003).The bacteria can only work and produce the biogas if the substrate is sufficiently bloated with water at least 50% (Vindin, *et al.*, 2008). It is produced from a three-phase process; namely hydrolysis (which converts polymer to monomer) by hydrolytic bacterial (Iyagba, *et al*, 2009), acid-forming (acidogenesis) and methane-forming (methanogenesis). In the hydrolysis phase extra cellular enzymes secreted breakdown the complex organic substances into simple soluble molecules. The acidogenesis stage involves the breakdown of the simple molecules to volatile fatty acids (VFAs) such as propionic and butyric acids, carbon dioxide, ammonia and hydrogen while the methanogenesis phase converts the VFAs to methane, carbon dioxide, nitrogen, and hydrogen sulphide. Fusarium fungai and staphylococcus bacteria are involved in the anaerobic digestion process (Itodo, 2007).

Enzymatic activities of micro-organisms responsible for the bioconversion of substrates to biogas are affected by temperature in ranges. Psychrophilic temperature range being below 20°C, mesophillic temperature range, 20-40°C and the thermophilic temperature range is 40-65°C. Thermophilic temperature range allows for shorter retention time and because of the high temperature of this phase there is little or no room for pathogens to thrive. The mesophilic range is the most common especially in the tropics where ambient temperature of 40°C is naturally attainable.

3.0 Generation of biogas

Cattle dung was collected from a local cattle ranch in Ilorin, Nigeria. This was crushed by beating it to pulp in synthetic fibres sacks. 8 kg of the cattle dung was mixed with equal volume of water charged to a digester up to 75% of its volume. The digester was made of 2 mm thick mild steel. The mixture was stirred thoroughly to make uniform slurry before being closed tightly and subjected to anaerobic incubation in the laboratory at the Kwara State Polytechnic, Ilorin, Nigeria. The gas was daily tested for combustion and it burnt with a blue flame on the 13th day of incubation. The raw biogas was collected in a cylinder and was analyzed using thermal conductivity detector.

4.0 Calculations for biogas parameters

The following assumptions were made in the course of the design calculations for the determination of the biogas parameters: the calorific value of the biogas is constant throughout the incubation period; the density of air is constant at all temperatures referred to herein; the temperature of the biogas in the digester is the same as that of substrate during the incubation period; equations (13) and (14) of plug flow digesters reported by Gebremedhin and Inglis (2007) were adaptable to batch digesters.

The additional equations employed in the determination of the biogas parameters were obtained from Rajput, (2011), Rajput, (2003), Rogers and Mayhew (1988), www.hobre.com

$$n = \frac{m}{M} \tag{1}$$

The mass fraction, m_a is as given in equation (2)

$$m_a = \frac{m_i}{m} \tag{2}$$

The specific biogas constant (R) was estimated as given in equation (3)

$$R = \sum_{i=1}^{n} R_i = \frac{R_o}{m}\sum_{i=1}^{n}\frac{m_i}{M_i} \qquad (3)$$

Specific heats at constant pressure, c_p, and at constant volume, c_v of the biogas are given in equations (4) and (5) respectively.

$$c_p = \sum_{i=1}^{n}\frac{m_i}{m}(c_p)_i \qquad (4)$$

$$c_v = \sum_{i=1}^{n}\frac{m_i}{m}(c_v)_i \qquad (5)$$

For diatomic gases

$$(c_v)_i = \frac{5}{2}R_i \qquad (6)$$

and

$$(c_p)_i = \frac{7}{2}R_i \qquad (7)$$

For poly atomic gases

$$(c_v)_i = 3R_i \qquad (8)$$

and

$$(c_p)_i = 4R_i \qquad (9)$$

Determination of specific volume and relative density of the biogas was done using equations (10) and (11)

$$\upsilon = \frac{R_T T}{P_e} \qquad (10)$$

$$RD_{biogas} = \frac{\rho_{biogas}}{(\rho_{air})^{0.5}} \qquad (11)$$

$$WI = \frac{H}{(RD_{biogas})^{0.5}} = H\upsilon^{0.5}(\rho_{air})^{0.25} \qquad (12)$$

$$\mu_m = 0.013T - 0.129 \qquad (13)$$

$$V_d = 13.7\log_e(SRT_{dest}) + 18.9 \qquad (14)$$

The specific internal energy and specific enthalpy of the biogas were done using equations (15) and (16)

$$u = c_v T \qquad (15)$$

$$h = c_p T \qquad (16)$$

Where:

R_o is the Universal gas constant (kJ/kgK);

R_i is the specific gas constant of a component gas in the biogas mixture (kJ/kgK); m_i is the mass of a component gas in the mixture (kg); $(c_v)_i$ and $(c_p)_i$ are respectively the specific heat at constant volume and at constant pressure for component gas of the biogas mixture (kJ/kgK); u and h are specific internal energy and specific enthalpy of the biogas (kJ/kgK); T is the inside absolute temperature of the digester; ρ_{biogas} and ρ_{air} are densities of biogas and air (kg/m^3) respectively; RD_{biogas} is the relative density of the biogas; μ_m is bacterial growth rate per day; V_d is volatile solids destroyed; H is the calorific value of biogas; and v is specific volume of biogas; and SRT_{dest} is the solids retention time which is also the days of incubation.

5.0 Gas Chromatography (GC)

The chromatography system is composed of the chromatograph and a recorder for plotting chromatographs. The experiment was conducted using thermal conductivity detector (TCD) at Multi- Environmental Management Consultants Ltd, Igbe, Ikorodu, Lagos, Nigeria.

6.0 Gas Calorific value determination

Combustion of a gas in an open flame calorimetric method with open flame for the determination of the calorific values of gaseous samples was employed using gas calorimeter Junkers. The basic principle was based on the specific amount of gas that was metered and completely burnt. By a heat exchanger, the heat of combustion released by the burner was transferred to a metered heat absorbing air. As a result, the temperature of the fluid increased. The temperature increase was a measure of the calorific value. The calibration of the equipment was carried out by using gases of known calorific value.

7.0 Results and Discussions

The results obtained by using equations (1) to (9) are as shown in Table 1

Table 1: Constituents of the cattle dung biogas and their thermo-physical properties

Constituent	Mole (n_i)	Molar mass (kg)	Mass in the mixture (kg) ($m_i= n_iM_i$)	Mass fraction (m_i/m)	Specific gas constant (R_i) (kJ/kgK)	Constant volume specific heat $(c_v)_i$ (kJ/kgK)	Constant pressure specific heat $(c_p)_i$ (kJ/kgK)
CH_4	0.562	16	8.992	0.3257853	.1692862	.5078585	.6771447
CO_2	0.395	44	17.38	0.6296873	.1189823	.3569469	.4759292
H_2S	0.018	34	.612	2.2173E-02	5.421977E-03	1.626593E-02	2.168791E-02
CO	0.019	28	.532	1.9275E-02	5.723198E-03	.014308	.0200312
NH_3	0.005	17	.085	3.0796E-03	1.506105E-03	4.518315E-03	6.02442E-03
Total			27.601		0.3009197	0.8998976	1.200817

The thermo-physical properties of the biogas are as shown in Table 1. The biogas constituents are in column 1, the moles of the constituents in 2nd column and their respective molar masses are in column 3. The mass of every constituent in the mixture is located in column 4, mass fraction and the specific gas constant in columns 5 and 6 respectively. The specific heats at constant volume and pressure of the component gases are in columns 7 and 8.

The six rows in Table 1 show gas constituents with CH_4, being first, CO_2 is second, H_2S being third, CO fourth and NH_3 fifth. The values of the parameters except for the ratios of the specific heats are added as shown in row 6. Each constituent gas in the biogas mixture had total mole with CH_4 as 0.562, CO_2 0.395, H_2S 0.018, CO 0.019 and 0.005 for NH_3 thus bringing the total mole of the biogas to 0.999 in column 2. The molar masses of the constituent gases are in the order of 16 kg, 44 kg, 34 kg, 28 kg and 17 kg. The sum of the respective properties of constituents in each column is shown in the 6th row for columns 2, 4, 6, 7 and 8. Constituents' total mass in the biogas mixture was 27.601kg, biogas constant R was 0.3009197 kJ/kgK, specific heat at constant volume (C_v) was 0.8998976 kJ/kgK and specific heat at constant pressure (C_p) was 1.200817 kJ/kgK. The calorific value of the biogas was 19.50 MJ/m^3.

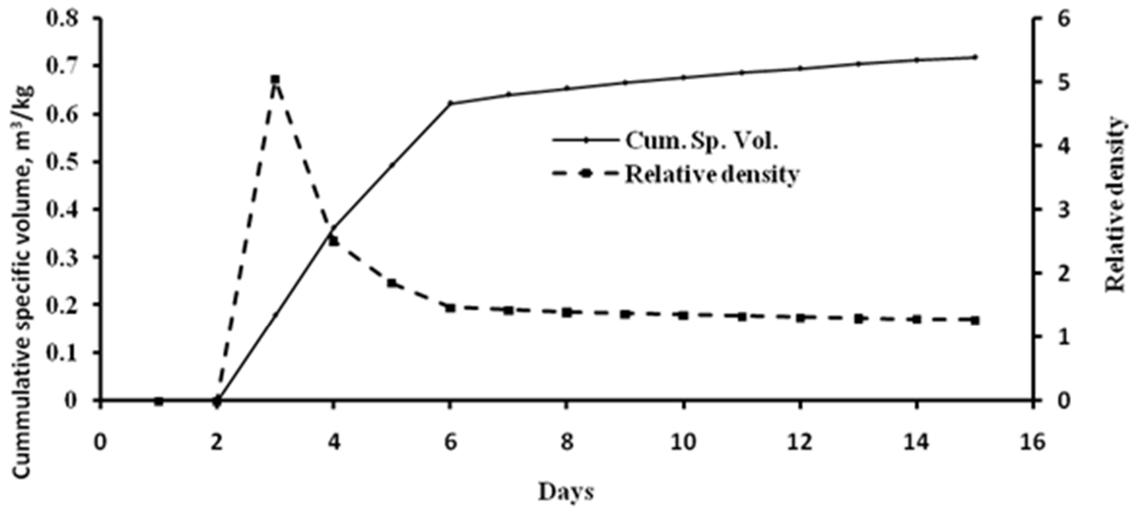

Figure 1: Relative density and cummulative specific volume of cattle dung biogas against time

Figure 1 shows the variation of relative density and the cummulative specific volume of the cattle dung biogas with timefor the two weeks of the incubation period. The relative density of the biogas rose sharply on the second day of incubation to 5.039208 before dropping sharply to 2.511261 on the third day. Thereafter it assumed a relatively slower fall or gentle downward turn through 1.850403 and 1.465913 till day 6 with 1.424475. It marginally decreased till the end of incubation with a value of 1.270801. The sharp rise of the relative density in the second day was as a result of air eclosed in the digester during charging which reacted with the substrate. This gave rise to production of carbon dioxide. As the carbon dioxide was used up as anaerobic digestion progressed there was slower production of the other components like methane of the biogas.

The cummulative specific volume of the biogas also rose steadily on day 2 from zero to 0.622732m^3/kg on fifth day of incubation. After this period there was marginal increament of its specific volume, hence the graph assumed logarithmic behaviour to the end of incubation with 0.718343 m^3/kg occuring on the last day.

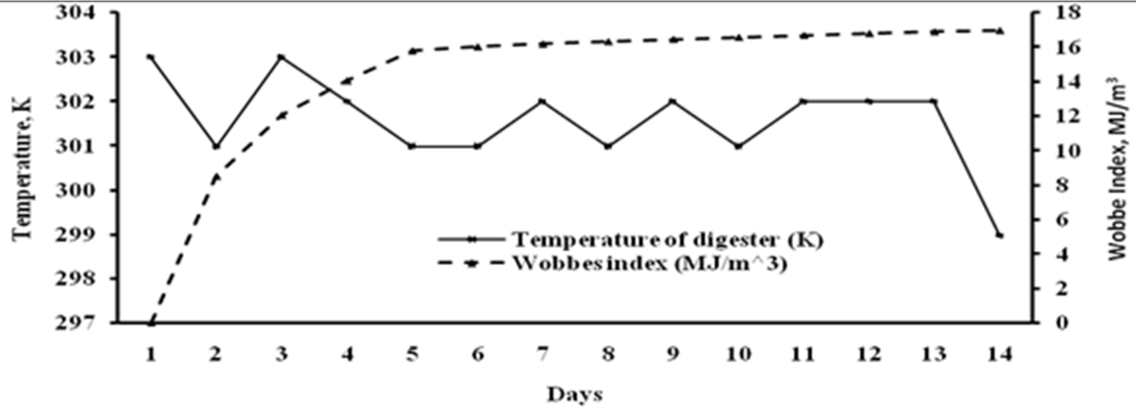

Figure 2: Variation of temperature and Wobbes index of raw cattle dung biogas with days of incubation

In Figure 2, the temperature plot had a zigzag behaviour because the digester was placed in an uncontrolled environment and therefore the temperature varied with the environmental conditions, hence its hapzard nature. On the other hand the Wobbe Index had a sharp rise from day 1 at zero to day 2 with 8.530758 MJ/m^3 thus indicating a high value, this is due to the reaction between the substrate and the air in the digester. The plot assumed a logarithmic shape from day 2 with 12.08434 MJ/m^3 through today 5 with a value of 15.81665 MJ/m^3 and thereafter Wobbe Index recorded marginal increament as the anaerobic digestion progressed with 16.98752 MJ/m^3 on the last day.

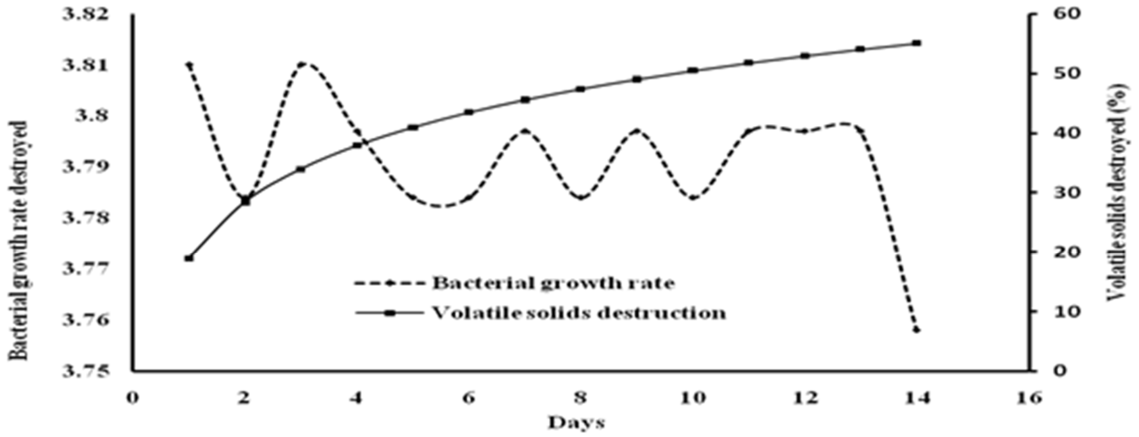

Figure 3: Variation of bacterial growth rate per day and volatile solids destroyed with days of incubation of cattle dung biogas

Figure 3 shows the plots of bacterial growth rate and voaltile solids destroyed against the the days of incubation. The daily bacterial growth rate had a zigzag behaviour because it was temperature dependent and so it varied with temperature of the digester. This was about 3.81 on the first day but dropped to almost 3.78 on the second to rsie again on the third day. The whole process went on that way till the last day when the growth rate was about 3.76.

The volatile solids destroyed increased from almost 18.9 % on the second day, assumed a logarithmic shape to 40.9493% on the fifth day and after then marginally increased throughout the rest incubation period thus indicating that the process of destruction of the volatile solids to produce biogas was slow but sure especially at the prevailing temperature at which the incubation took place.

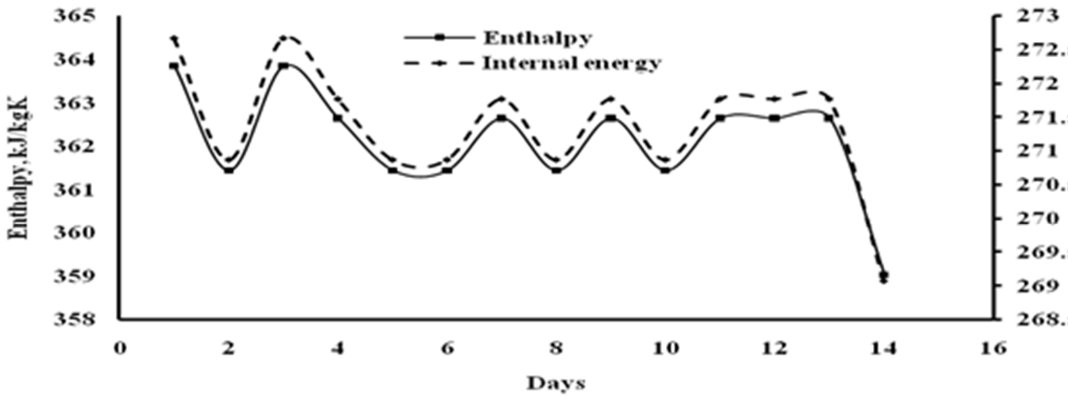

Figure 4: Internal energyand enthalpy of cattle dung biogas versus days of incubation

In Figure 4, the the plots of enthalpy and internal energy also recorded zigzag behaviours because they were dependent on the digester temperature which invarably interacted with the ambient temperature. As the ambient temperature rose, the digester temperature, the enthapy and the internal energy rose and they dropped with the fall in the ambient temperature. The enthalpy plots however had higher values with the highest being almost 364 kJ/kgK and the lowest 359 kJ/kgK than that of the internal energy of the biogas as it had the highest value of about 273 kJ/kgK and the lowest 269 kJ/kgK. This is reasonable as the internal energy is a component part of enthalpy of the biogas.

7.0 Conclusion

The analysis of biogas generated from the anaerobic digestion of cattle dung using the GC/TCD showed its constituents as CH_4, CO_2, H_2S, CO and NH_3 with the respective moles as 0.562, 0.395, 0.018, 0.019 and 0.005. The total mass in the biogas mixture was 27.601kg, biogas constant R was 0.3009197 kJ/kgK, specific heat at constant volume (C_v) was 0.8998976 kJ/kgK and specific heat at constant pressure (C_p) was 1.200817 kJ/kgK. The relative density of the biogas rose sharply to about 4.28 before dropping to 2.14 to assume a slower and marginal downward turn. The cummulative specific volume of the biogas also rose steadily from zero to about 0.64 m^3/kg before its logarithmic marginal increament to the end of incubation. The Wobbes index and volatile solids destroyed increased from 8.530758 MJ/m^3 and 20% respectively and assumed logarithmic shapes followed with marginal increment till the day of incubation. The bacterial growth rate per day, the enthalpy and the internal energy of the varied with the digeter temperatures.

References

Adegun, I. K. and Yaru, S. S (2013), Cattle Dung Biogas as a Renewable Energy Source for Rural Laboratories, Journal of Sustainable Technology, Vol. 4, No 1, pp 1-8

Beddoes, J. C., Bracmort, K. S., Burns, R. T. and Lazarus, W. F (2007), An Analysis of Energy
Production Costs from Anaerobic Digestion Systems on U. S. Livestock Production Facilities, National Resources Conservation Service, United States Department of Agriculture, Technical Note, No. 1

Berrueco, C., Esperanza, E., Mastral, F. J., Ceamanos, J. and Garcia – Bacaica (2005), Pyrolysis of Waste Tyres in an Atmospheric Statuc-bed Batch Reactor: Analysis of the Gases Obtained, Journal of Analytical and Applied Pyrolysis, Science Direct, Vol. 74, pp 245-253. Available online from www.sciencedirect.com

DTI (2012), Danish Technological Institute Report on Biogas and bio-syngas upgrading, Laura Dailon Allegue and Jorgen Hinge Kongsvang Alle 29, DK-800, Aarhus C

Ezekoye, V. A. and Ezekoye B. A. (2009), Characterization and Storage of Biogas Produced Anaerobic Digestion of Cow Dung Spent Grains/Cow Dung and Cassava Peels/Rice Husk, The Pacific Journal of Science and Technology, Vol.10, No. 2, pp 898-904. Available online from http://www.akamaiuniversity.us/JPST.htm

Fernandez, M. A., Diez, A., Alvarez, R. and Barrocanal, C. (2009), Pyrolysis of Tyre Wastes , 1st Spanish National Conference on Advances in Material Recycling and Eco-Energy, Madrid, SO 1-2

GQHWG (2004), Gas Quality Harmonization Working Group, Energy Charter Secretariat, Occasional Paper (2), LNG and Natural Gas Quality Standard, Boulevard de la Woluwe, 56, B-1200, Brussels. Available from: www.encharter.org

Gebremedhin and Inglis (2007), Validation of a Biogas Production Model and Determination of Thermal Energy from Plug- Flow Anaerobic Digesters, Transactions of the American Society of Agricultural and Biological Engineers, Vol. 5, No. 3, pp 975-979

Hobre Instrument, General Information, Wobbe Index and Calorimeters, Available from www.hobre.com

Iyagba, E. T., Mangibo, I. A. and Mohammad, Y. S. (2009), The Study of Cow Dung as Co-substrate with Rice Husk in Biogas Production, Scientific Research and Essay, Vol. 4, No. 9, pp 861-866

Itodo, I.N. (2007), Agricultural Energy Technology, Aboki Publishers, Makurdi.

Quek , A. and Balasubramanian, R. (2013), Liquefaction of Waste Tyres by Pyrolysis for Oil and Chemicals – A review, Journal of Analytical and Applied Pyrolysis, Vol. 101, pp 1-16

Rajput, R. K. (2011), A Textbook of Engineering Thermodynamics, 4th Edition, Laxmi Publishers Ltd, New Delhi

Rajput, R. K. (2003), Thermal Engineering, Laxmi Publications Ltd, New Delhi.

Raja, A. S. and Lee, R. L. C. (2012), Biomethanation of Water Hyacinth Using Additives under Forced Mixing in a Bioreactor, Int., J. Chem. Res., 2012vi02i4 (15-24).

Roger, G. F. C. and Mayhew, Y. R. (1988), Engineering Thermodynamics, ELBS/Longman, Hong Kong

Tchobanoglous, G., Burton, F. L. and Stensel, H. D. (2003), Waste Water Engineering (Treatment snd Resource), Metcalf and Eddy, Tata Mcgraw-Hill publishers, New Delhi.

Vindin, P., Mursec, B., Rozmac, C., Janzekovic, M. and Cus, F. (2008), Biogas Production with the use of Mini Digester, Journal of Achievements in Materials and Manufacturing Engineering, Vol. 28, No. 1, pp. 99-102.