IOSR Journal of Applied Chemistry (IOSR-JAC)
e-ISSN: 2278-5736.Volume 8, Issue 7 Ver. I (July. 2015), PP 01-05
www.iosrjournals.org

Activation Energy Determination of A Batch Process Biogas Generation From Organic Wastes

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Abstract: *Energy requirement is increasing around the world due to changes in life styles, population increase as well as industrialization efforts.The standard of living of a given country can be directly related to the per capital energy consumption. Kinetics of anaerobic digestion and gas generation from organic sources has posed several new challenges because of the variety in the feedstock as well as the different processes for gas generation. Bio-wastes were used for this study and gas production rate was developed from the solution of mass balance equation with equal flow of input and output. Anaerobic digestion reaction followed a first order kinetics. The trend of Ea (Cow dung > Poultry > Domestic > Combined) shows that the system with the lowest Ea gives the highest yield. Delay in commencement of gas production is explained by their higher value of activation energy. Different feed stocks have different rates of gas production as well as varied retention time.*
Keywords: *Activation energy, biogas, reaction rate, organic waste.*

I. Introduction

Energy generation and utilization has in contemporary times been of global concern owing to the fact that all activities involving both plants and animals are the expression of flow of energy in one of its forms. Energy requirement is increasing around the world due to changes in life styles, population increase as well as industrialization efforts. It is the primary and most universal measure of all kinds of work by human beings and nature. Energy can exist in various forms such as mechanical energy, electrical energy, solar energy, bio-energy etc. Major energy sources can be categorized as conventional energy sources and non – conventional energy or alternative energy sources.

Conventional energy mainly from fossil fuel produced by dead plants and animals takes millions of years to be formed and replaced, thus reserves are being depleted much faster than new ones are formed that for practical purposes, they are considered as non-renewable and non-sustainable. The production and use of conventional energy raise environmental concerns that its supplies cause regional global conflicts as stated by Anthony, (1988) [1]. They range from very volatile materials with low carbon:hydrogen (C/H) ratios e.g. methane to liquid petroleum like gasoline and to non-volatile materials with high percentage of carbon like coal.

According to the US department of energy on greenhouse gases [2], the combustion of fossil fuels accounts for about 6.3% of the total emission of carbon dioxide (a green house gas), but it is estimated that natural processes can only absorb about half of that amount so that there is an increase of atmospheric carbon dioxide yearly. Combustion of fossil fuels additionally generates sulphuric acid, carbonic acid as well as natural and man-made structures [3]. Monuments and sculptures made from marbles and limestone are particularly vulnerable as the acid dissolves calcium carbonate. Transportation of fossil fuel again requires the further combustion of additional fossil fuels that increases their combustion problems.

Alternative energy classified as energy that is not derived from conventional sources like, hydro-sources,biomass, solar, etc are often regarded as renewable energy. Unlike fossil fuel that takes millions of years to form, biomass is considered renewable since plant and animal life renew and add to themselves every year. Biogas a derivative of biomass is mainly produced by the anaerobic digestion of the organic materials. The biogas produced is very rich in methane which is a combustible gas.

. Biomass was the dominant source of energy throughout the world until the advent of fossil fuel [4]. It remains a major source in the developing countries especially in rural settings where it is closely linked with agricultural and forestry production and processing. Thus, it continues to play a crucial role in energy supply despite the use of other energy sources.Research in the field of bio-energy production reveals that organic waste generated from farms as well as municipal/domestic waste can be used as good sources of biogas. The biogas produced is very rich in methane which is a combustible gas (5) Management of domestic and municipal waste has been of significant concern to the government of many nations across the globe in recent times [6]. In the world of energy technology, energy is seen as a commodity to be bought and sold in the market place, a commodity which provides the basis of life and wealth on our planet. It is an important input in all sectors of any country's economy. The standard of living of a given country can be directly related to the per capita energy consumption [7].

Statement of problem

In today's energy demanding lifestyle, it is clear that there is a gap both now and in the future between energy needs for economic development and the ability of both the traditional and the conventional modern energy sectors to meet up with this need [8].In Nigeria for instance, poor energy supply has greatly after the nation's economy. There has been a lot of documentation on the wealth of Nigeria's natural resources [9], however, the benefits of the contribution of renewable energy are very negligible and worst still a greater percentage of the Nigerian populace are ignorant of the benefits. Many developed and developing countries are focusing on new technologies for sourcing fuel from sustainable means especially from the agricultural sector and municipal waste to help mitigate the growing dependence on imported oil and gas. In Nigeria [10] as well, efforts are now made to initiate the development of renewable energy technology such as will focus on biogas generation and utilization. Though the technology of bio-energy production is understudied, it has the potential to deliver a number of benefits including the reduction of greenhouse gas emissions, improved air quality and increased energy security.While several outstanding works have been done to ascertain the viability of sourcing biogas from biodegradable wastes in various parts of the world, the kinetics of anaerobic digestion and gas generation has posed several new challenges because of the variety in the feedstock as well as the different processes for gas generation.

Aim of the Study

This study therefore sets out to determine the activation energy and order of the rate of the biogas generation in, hydraulic retention time as it affectsgas production per g of raw material will be studied. Each waste material was anaerobically digested and observations made under experimental conditions to determine order of rate of gas production.

II. Materials And Methods

The biomaterials that were used as samples for this study include, (i) Cow dung, (ii) Poultry droppings, (iii) Domestic waste (iv) Combination of (i), (ii) and (iii). All were sourced from Owerri Municipal Council of Imo State, Nigeria. 50g each of the prepared samples were mixed with 150cm^3 and then fed into the anaerobic digester in a batch process whereby the feedstock was ingested into the digester (reactor) at the beginning of the digestion as well as gas production period and sealed for the complete retention time, after which it was opened and the effluent discharged before another batch was fed into the digester. The co-digestate for the combined waste is in the ratio of ½:½:1 for cow dung, poultry dropping and domestic waste respectively.

Gas production rate was developed from the solution of mass balance equation with equal flow of input and output.

$$V_r = \frac{S_{\max} Y}{M} - Z \quad (1)$$

where; Vr = biogas production rate, Smax = maximum substrate utilization rate, Y = mass of effluent, M = mass of substrate input, Z = microorganism decay rate.

By the first-order kinetics model in 2;

$$-\frac{dM}{dt} = \frac{Y(1 + Z\phi)}{S_{\max}\phi} \quad (2)$$

the biogas production rate was related with the hydraulic retention time since this study was undertaken through a batch process [11]. Beyond the tendency to attribute the rate of gas production on hydraulic retention time, other factors play significant role in anaerobic microbial conversion process.

III. Results

From the volume of gas produced after every 24h, it was observed that the anaerobic digestion reaction followed a first order kinetics as closely related values were obtained for the rate constants, k, using the first order integrated rate equation;

$$k_1 = \frac{2.303}{t} \log \frac{a}{a - x} \quad (3)$$

where t = time (days), a = vol. of gas produced from the first day of gas production and $a - x$ = vol. of gas produced at any other stated time.

Using the data obtained for cow dung at 40°C at the pH range of 6.5-7.2 (fig 1); the obtained rate constants, k, were; - 0.121, -0.125, -0.127 and-0.136 for 5, 10, 15 and 20 days respectively (Fig. 2). The rate constants for the combined waste system were -0.105, -0.087, -0.068 and -0.054 for 5, 10, 15, and 20 days respectively (Fig. 3).It is also assumed that poultry droppings and domestic waste followed first order rate kinetics.

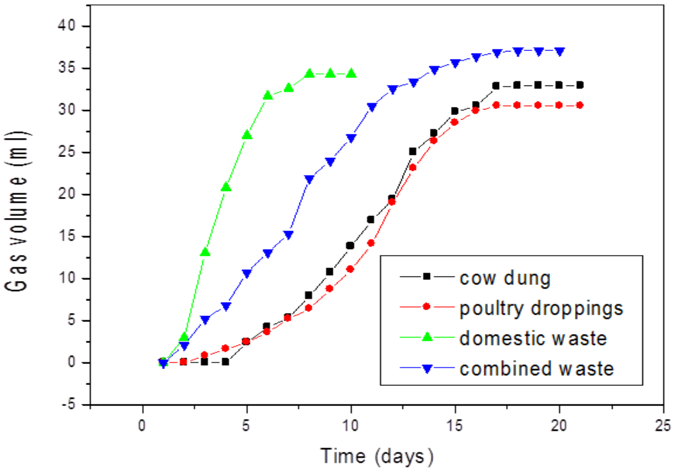


FIG 1 Daily gas yield of the various wastes at 40°C

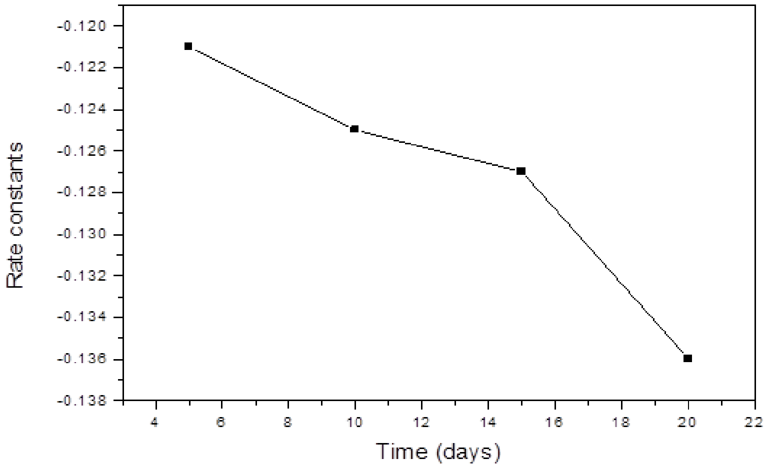


Fig 2: Rate constants for cow dung at 40°C

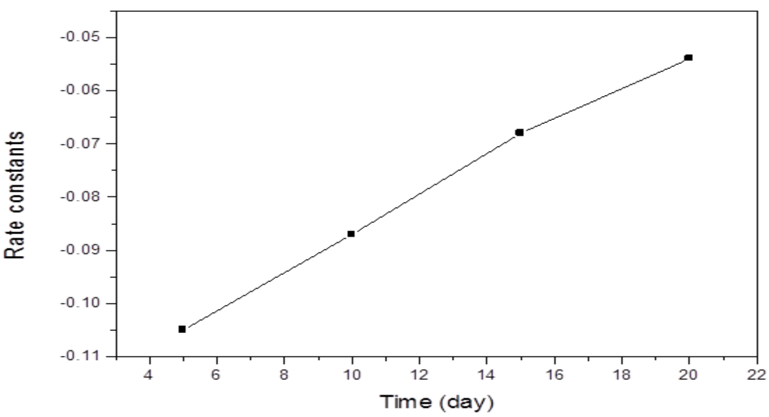


Fig 3: Rate constants for combined waste at 40°C

The activation energy for gas generation from each was evaluated using the Arrhenius equation [4];

$$\ln k = -\frac{E_a}{RT} + \ln A \quad (4)$$

The calculated values of the activation energies obtained from the lnk vs. 1/T plots

Table 1: Activation energies for the various wastes.

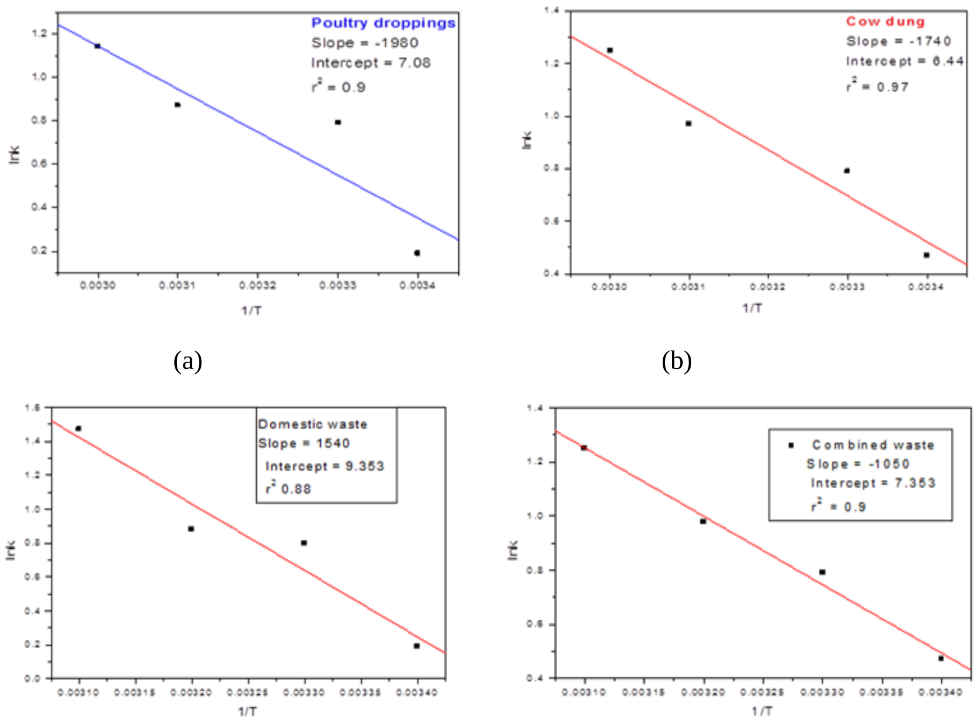
Waste materials	Activation energies (Ea) kJmol-1
Cow dung	37.82
Poultry droppings	37.23
Domestic waste	30.08
Combined waste	26.60

The trend of Ea (Cow dung > Poultry > Domestic > Combined) corroborates our earlier findings with respect to gas yield from the different waste materials. The system with the lowest Ea gives the highest yield. The delay in commencement of gas production as observed in poultry droppings and cow dung is explained by their higher value of activation energy which must be attained to cause biogas production.
Using the calculated activation energies obtained the enthalpy of activation, (ΔH*) and entropy of activation (ΔS*) were calculated using the relation;

$$\ln \frac{k}{T} = -\left(\frac{\Delta H^*}{RT}\right) + \ln\left(\frac{R}{N_A h}\right) + \left(\frac{\Delta S^*}{R}\right) \quad (5)$$

where k = rate of gas production, N_A = Avogadro's number, h = Planck's constant, R = gas constant and T = temperature (K).

From the plots of ln k/T vs 1/T, lines with slope and intercepts as $\frac{\Delta H^*}{R}$ and $\ln\left(\frac{R}{N_A h}\right) + \left(\frac{\Delta S^*}{R}\right)$ respectively were obtained.



(a) (b)

(c) (d)

Fig 4: Arrhenius plots for (a) poultry droppings (b) cow dung (c) domestic waste and (d) combined waste
From the slope and intercept, ΔH* and ΔS* were calculated for the various wastes and given in the table below.

Table 2: Calculated values of enthalpy of activation ΔH* and entropy of activation ΔS*

Wastes	ΔH*	ΔS*
Cow dung	21.12	-1.33 x 10-30
Poultry	19.46	-1.01 x 10-30
domestic	14.47	-9.17 x 10-31
Combined	8.73	-6.23 x 10-31

The activation enthalpies vary in the same manner as activation energies; the enthalpies of activation are higher in cow dung and poultry droppings. This explains the higher incubation period for both wastes as higher internal energy is required for the degradation of the organic material. Negative values of entropies imply that there is a decrease in entropy. This is why the reaction does not proceed spontaneously but goes through a period of incubation.

IV. Conclusion

A critical look at the results of this study and the literature gives an assurance that if the technology of anaerobic digestion is applied in sourcing for biogas, the uncertainty of sustenance surrounding fossil fuel could be arrested.The different feedstocks have different rates of gas production and their retention time for maximum gas production also varies. This implies that each feedstock should be left for the appropriate retention time that will give maximum yield.

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