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Spent maize grains wastes produced more qualitative and quantitative biogas than pp-wastes in the leakage and corrosion free biodigester. This is due to wider pH-value range indicating energization of micro-organisms resulting to more stability of micro organisms in SMG-wastes in the initial stage and other environmental factors such as moderately low. $^C/_N$ ration. Other reasons for low production of biogas from pp-wastes include the presence of cellulose and indigestible like materials.

This study recommends SMG as a better raw materials for biogas productions for domestic and small / medium scale industries in the developing countries of the world.

Keywords : Biogas-volume, pH, digestion, regression-approximations.

I. Introduction

Many of the world's present problems are closed related to those of energy production, supply, distributions and utilizations. This is due to upholding to one major source – conventional source of energy . This source especially fossil source is unreplenishable and the energy produced is hazardous to life as it pollutes the environment.

The need to diversify the dependence on conventional energy sources such as oil and other non – renewable sources of energy especially in developing countries can not be overemphasized. The sun is an already made source of energy if carefully harnessed and handled. Solar energy is free, natural and non – polluting energy that man can harness for many useful applications according to Nnabuchi, 2004. In some countries of the world for example, the United State of American, until the late 19th century, depended on renewable sources of energy in its many forms as their sole energy resources (Paul, 2007).

Solar energy includes not only direct sunlight but also several indirect forms such as photosynthetic fuels, energy from water power and winds. They are regarded as solar energy because their energies are derived from the sun: the energy of wood and other plant materials is solar energy fixed by the process of photosynthesis (Chang, 2003). Biomass materials are also examples of indirect sources of energy from the sun. The lack of utilizations of this source of energy is much observed in the developing countries like Nigeria. World over, the use of the common types such as cow dung, poultry droppings, peels of cassava, rice husks etc for biogas productions provided clean energy, organic fertilizers, reduction of wastes and pathogens. In Nigeria such biomass include wood, forage grasses and shrubs, other animal wastes and wastes arising from forestry, agricultural, municipal and industrial activities as well as aquatic materials and some of them have been tried (ECN, 1997) .But, over decades, some wastes have not been tried for energy supply - biogas yields though they have the same nutrients especially, carbon, nitrogen and phosphorus which maintained the growth and catabolism of microbes that help in biogas production just like the above mentioned wastes (Dioha ,et. al. 2006) and the energy produced can be used in small and medium scale business enterprises. Examples of such wastes are pineapple peels (PP) and spent maize grains (SMG).

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The chemistry of the biogas production from biomass including the above is as given in the three stage process below: This perspective is divided into two sections. They are the biogas formations and yields which exist in the three stages and the pH-parameter involvements.

The three stage process can be chemically described as the first consisting of micro organisms attacking the organic materials, that is, complex organic compounds such as cellulose, soluble organic compounds such as glucose and fructose. Polymers are transformed into soluble monomers through enzymatic hydrolysis (http:// www.cropgen.soton.Ac. UK., 2007)

ie

$$n\,(C_6H_{10}O_5) + n\,H_2O \xrightarrow{\text{Hydrolysis}} n\,(C_6H_2O_6) \quad (1.0)$$

The monomers become the substrate for the micro organisms in the second stage where soluble organic compounds are converted into organic acids by a group of bacteria collectively called 'acid formers'.

$$n\,(C_6H_{12}O_6) \xrightarrow{\text{acid forming bacteria}} 3n\,(H_3\ COOH) \quad (2.0)$$

The soluble organic acids consisting primarily of acetic acid, form the substrate for the third stage (http:// www.Biotank10.UK, 2007)

$$\text{ie } 3n\,CH_3\ COOH \xrightarrow{\text{methane forming bacteria}} CH_4 + CO_2 \quad (3.0)$$

In this very last stage, methanogenic bacteria generate methane by two distinct routes. One is by fermenting acetic acid to methane and carbon dioxide, the other consisting of reducing carbon dioxide gas generated by other species;

$$CO_2 + 4H_2 \xrightarrow{\text{Reduction}} CH_4 + 2H_2O \quad (4.0)$$

carbondioxide hydrolysed to carbonic acid;

$$CO_2 + H_2O \xrightarrow{\text{Hydrolysis}} H_2CO_3 \quad (5.0)$$

Then the carbonic acid generated is reduced to methane and water by hydrogen as follows

$$H_2CO_3 + 4H_2 \xrightarrow{\text{Reduction}} CH4 + 3H2O \quad (6.0)$$

The organic matter used in the methane fermentation generally contains volatile solids and ashes. And the remaining non-digestible materials along with dead bacteria (digestate) are used as fertilizer as mention in section 1.0.

Therefore the generic chemical equation for the formations and yields of biogas as depicted in four key biological and chemical stage of anaerobic digestion; hydrolysis, acidogenesis, acetogenesis and methano - genesis above is given by

$$C_6H_{12}O_6 + 4H_2 \longrightarrow 3\,CH_4 + 3CO_2 \quad (7.0)$$

The medium environmental factors such as temperature and pH affect the production of the biogas. Maishanu and Seekimpi, (1988) and Anonymous, (1992) observed that micro organisms never require a too acidic or too alkaline environment but a neutral or mild alkaline condition for optimal biogas productions. This is a measure of the pH of the system. The organic matters contain volatile solids which are made up of carbohydrates, proteins, fats and tannins. Also ashes are components of the organic materials. The proteins, lipids etc are responsible for variations in pH - values affecting methanogenesis and possibly improve biogas generations (Meybell, 1981). For optimal biogas production in slurries http://www.green-trust.org/methane.htm, (2008), Buren (1983), Maishamu and Seekimpi, (1988), Dioha et al. (2003), Anonymous (1992) and Blandchard and Gill, (1964) maintained 6.2 – 7.8, 70 - 8.5, 6.6 – 7.5, 6.6 – 7.6, 6.0 – 8.0 and 5.5 – 8.0 for wastes respectively.

For these two wastes the researchers wanted to investigate the generations of biogas of the wastes in terms of the PH – values of their slurries. This is hoped to determine whether the PH- parameter of these wastes aid their biogas production and to aligned developing countries like Nigeria of the usage of these common and available wastes in addressing our domestic/ rural energy problems. It is also hoped to help improve our small and medium scale energy needs. The use of their constructed galvanized iron fixed - dome biodigester was made. This is an improved version of the Chines fixed – dome biogas plant developed from the State – planning institute Lukenows first concrete fixed – dome biodigester in 1978. The construction cost is Low. The digester has very low corrosion effects and more life span and has simple technologies as against the old version and other classes of digesters. The biodigester slurries absorbed solar energy radiations including heat through the surface of the digester. The slurries comprising of carbohydrates, proteins, fats and water are worked upon by the consortium of bacteria to produced biogas.

II. Materials and Methods

The 0.459 m^3 galvanized iron fixed-dome biodigester was constructed with the help of technicians of engineering workshop of National Centre for Energy, Research and Development, NCERD, University of Nigeria, Nsukka.

The fresh bio-wastes were collected from Abakaliki meat market. Also the pineapple peels and spent maize grains were prepared, after sorting, in the mixing ratios of 1:2.5 ((ie 77: 193 of wastes (kg): water (kg)), and 1:2 ((ie 90: 180 of wastes (kg): water (kg)) respectively and each introduced in batch mode operations into the biodigester. Each engagement lasted for about 100 days. Five goat model Z 051299 weighing balance graduated in kilogrammes (kg) was used in the weight measurements.

After introducing the slurry, all openings were closed tightly. The setup was monitored and the readings and measurements of the biogas volumes in litres and pH-values were carried out each day at 9.30 am, 12.00 noon and 2.30 pm with occasional stirring to break the sum formed on the surface of the slurry and redistribute the even temperature within the content. The pH-values were measured with pH-meter and the volumes of the biogas produced were measured by subsequent downward displacements of water in the 25 litres calibrated jerry can. The volume measurements were carried out successively until the biogas produced was exhausted in the constructed digester below. The flammability tests were carried out each day using a burning burnsen burner.

Fig 1.0 : The Picture of the constructed Biodigester

III. Results and Discussions

The results of this study were displayed in figure 2.0 – 7.0 using Mathcad 7 professional package. Figures 2.0 and 3.0 below showed the novel 5th and 6th order regression approximations of biogas volumes (litres) at stp with retention time (days) of pineapple peels and spent maize grains wastes.

The regression approximated curves

$$y_{pp} = -0.18 + 0.0161\,x - 2.478 \times 10^{-3}\,x^{2} + 4.069\,10^{-5}\,x^{3} - 3.091 \times 10^{-7}\,x^{4} + 9.046 \times 10 - 10 \times 5 \text{ of } R - \text{squared } 0.562$$

and

$$y_{smg} = 0.382 + 0.144\,x - 0.017\,x^{2} + 7.140 \times 10^{-4}\,x^{3} - 1.409 \times 10^{-5}\,x^{4} + 1.304 \times 10^{-7}\,x^{5} - 4.589 \times 10^{-10}\,x^{6} \text{ of } R - \text{squared}$$

0.437, have peak values of 0.33 7 litres at stp on 22nd day and 0.7814 litres at stp on 7th day respectively.

Also the minimum volumes (litres) obtained from the curves are 0.0017 litres at stp on 89th day and 0.090 litres at stp on 73rd day respectively.

The cumulative flammable biogas volumes (litres) at stp shown in figures 4.0 and 5.0 which indicated 11.848 litres and 23.140 litres showed production rates of 0.1518 litres per day and 0.2822 litres per day for pp and SMG wastes respectively (see table 1.0). The flammable biogas productions with the two wastes commenced on 12th day for pp and 8th day for SMG.

Also presented are the 6th order and cubic order regressive approximated curves indicating the variations of the pH-values of pp and SMG-wastes with retention time in figures 6.0 and 7.0. These are represented by approximated curve equations:

$$y_{pp} = 5.568 - 0.084\,x + 0.018x^{2} - 9.16 \times 10^{-4}\,x^{3} + 2.006 \times 10^{-5}\,x^{4} - 1.984 \times 10^{-7}\,x^{5} + 7.285 \times 10^{-10}\,x^{6} \text{ of } R - \text{squared } 0.436$$

and

$$y_{smg} = 6.381 + 6.678 \times 10^{-3}\,x - 1.303 \times 10^{-3}\,x^{2} + 1.17 \times 10^{-5}\,x^{3} \text{ of } R - \text{squared } 0.725$$

From the two curves pH peak values of 6.558 on 68th day and 6.3395 on 1st day existed for PP and SMG wastes. Also minimum values of 5.568 on the 3rd day and 4.475 on the 22nd days existed respectively.

From figure 2.0 and 3.0, 4.0 and 5.0, and table 1.0 above, SMG-wastes produced more flammable biogas faster and with higher production rate per day although the pp - wastes lasted longer. Though the micro-organisms in SMG medium seemed to be much viable, the gas production reached maximum within few days than in pp-medium. Cumulatively biogas production is higher in SMG-slurry than in pp-slurry although we have few cases of fluctuations in the volumes of biogas production in SMG-wastes.

From figures 6.0 and 7.0 of pH -value ranges, 5.56 – 6.54 and 4.47 – 6.39 pH-value for pp and SMG – wastes existed respectively. The R-squared in pH-plot of SMG is higher showing that the graph better represents the relationship. The maximum value was obtained at the initial stage showing that the organisms were almost stable and active. Within the first 20 days the SMG organisms were stabilized than the pp organisms. It takes more time for the organisms in pp-slurry to reach stability. Hence they were not stabilized until very late and after few weeks from this point, the nutrients got exhausted. Also here more acids were obtained at the initial stage in order to break down the wastes and this reduced the gas production. The wide pH-value range with more biogas productions of SMG-slurry was due to non availability of the cellulose and wax-like materials as in the pp-slurry. This wideness in pH-value range quite conformed with those values obtained by Buren (1983), Maishanu and Seekimpi, (1988), Dioha et. al., (2003), Anonymous (1992), and http://www.green-- htm, (2008), although the alkalinity level was lower than that of PP – waste.

Hence this wide pH-value range indicated that the micro-organisms in SMG-slurry have been energized more by other environmental factors such as optimal temperature and moderate $^{C}/_{N}$ - ratio than in pp-slurry which contains more cellulose and some indigestible wax -like materials. The moderate / optimal ambient and slurry temperatures in the medium are very important indications that the bacteria are stable and lead to optimal biogas production. Also low C/N – ratio value which corresponds to moderate and relative proportions of carbon and nitrogen aid the stability of the micro organisms in the charged digester.

IV. Conclusions

Spent maize grains wastes produced more quantitative and qualitative biogas than pineapple wastes. This is due to more stability of micro organisms in the SMG-slurry especially at the initial stage than in pp-slurry. Also this is as a result of the wide PH value range due to the energization from other factors such as moderate $^{C}/_{N}$ - ratio, since the initial stage value is within the more expected range for more stability and higher production of biogas indicated by other researchers. Also the pp-slurry contains more cellulose and undigested wax-like materials which aided lower production rate than in SMG-slurry.

Therefore, the researchers recommended the use of spent maize wastes as better wastes for biogas production than pineapple peels wastes. The SMG-wastes are more readily available than pp-wastes as raw materials for biogas production in linkage and corrosion free biodigester in Nigeria. Also material resources such as steel, polyethylene or rubber are available as potential materials and in large quantity too, for the construction and sustainable usage of galvanized iron fixed dome – biodigester. Hence uncentralized power units can be established and operations of small and medium scale industries which is a sine qua non for the achievement of poverty alleviation as described by the united Nation MDG_S of which Nigeria is a part too, is possible.

V. Acknowledgement

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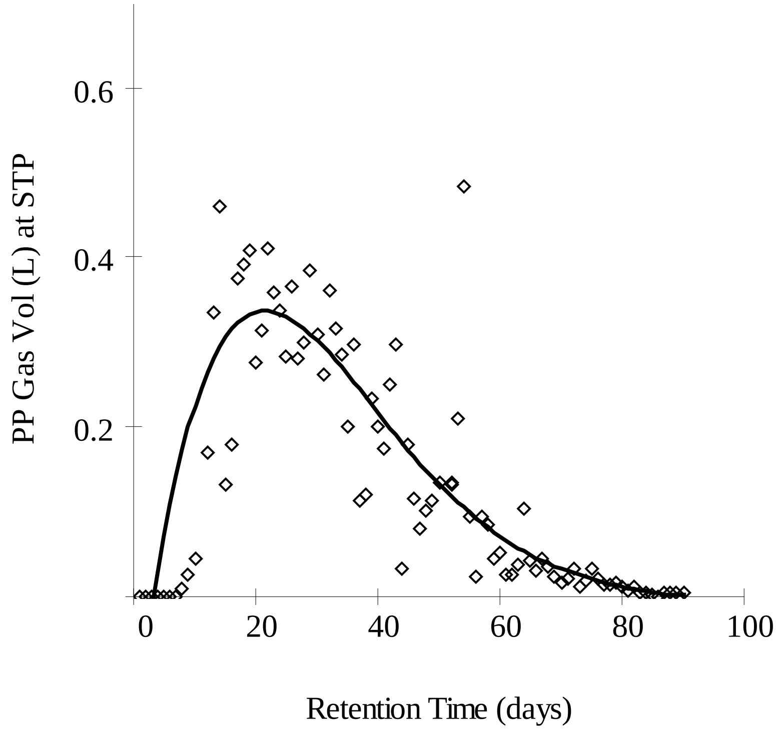
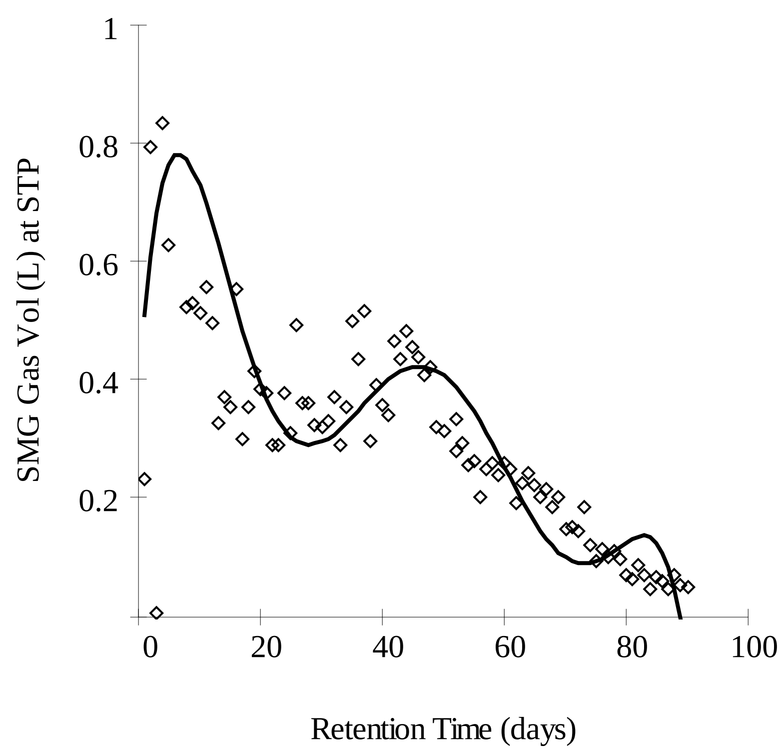
Appendix (1.0) : Figures and Tables



Max value = 0.33782 at RT = 22 Min value = 0.001753 at RT = 89, $R^2 = 0.562$

$$y = -0.18 + 0.061x - 2.478\times10^{-3}x^{2} + 4.069\times10^{-5}x^{3} - 3.091\times10^{-7}x^{4} + 9.046\times10^{-1}x^{05}.$$

Fig. 2.0 : Graph of PP Biogas Volume (L) at stp And Retention time (days)



Max value = 0.78147 at RT = 7 Min value = 0.090136 at RT = 73, $R^2 = 0.432$

$$y = 0.383 + 0.144x - 0.017x^{2} + 7.14\times10^{-4}x^{3} - 1.409\times10^{-5}x^{4} + 1.304\times10^{-7}x^{5} - 4.589\times10^{-1}x^{06}.$$

Fig. 3.0 : Graph of SMG Biogas Volume (L) at stp And Retention time (days)

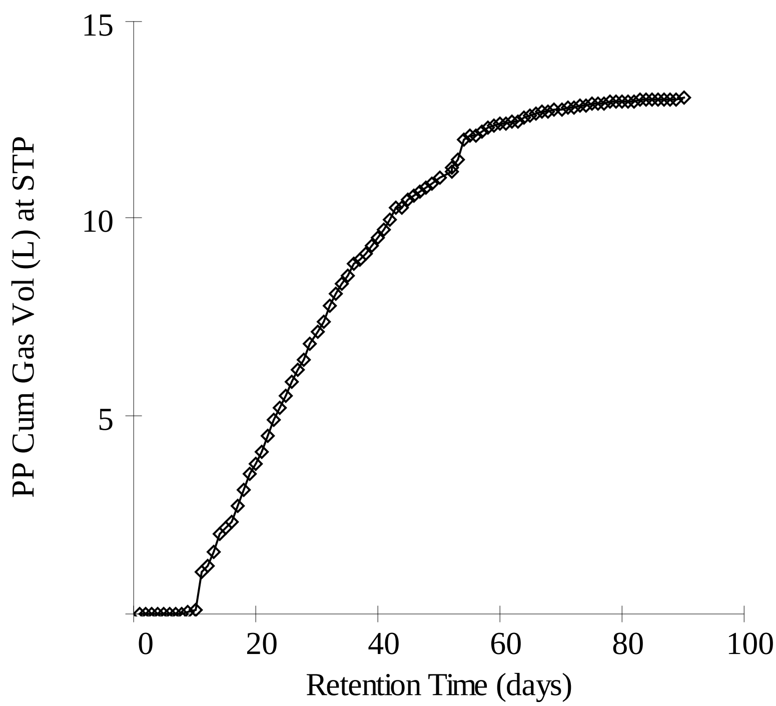


Fig. 4.0 : Graph of PP Cumulative Gas Volume (L) at stp Against Retention Time (days)

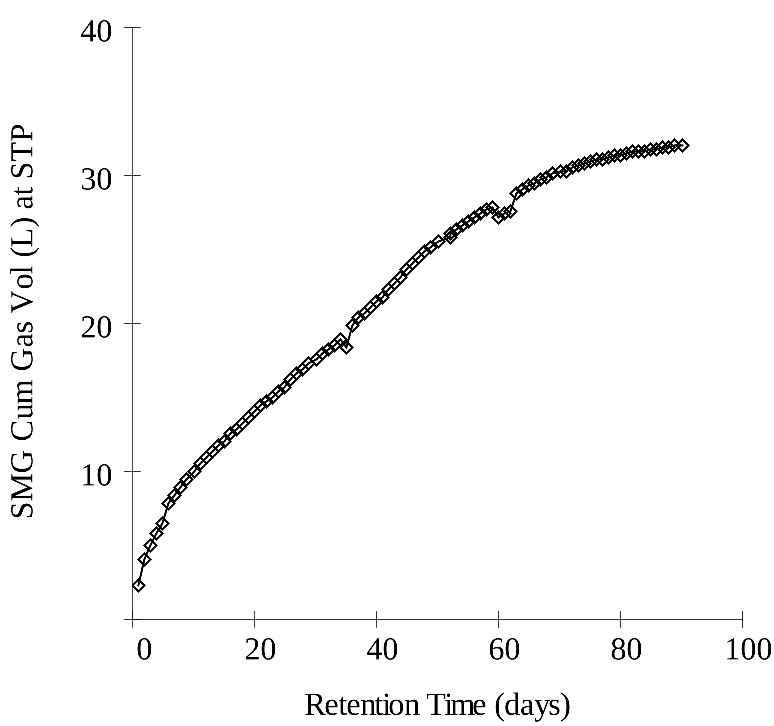
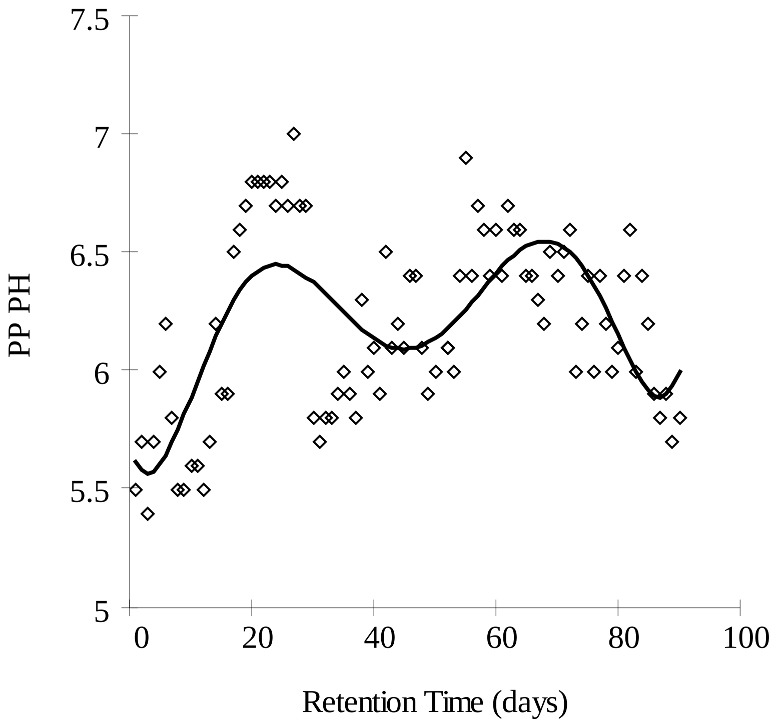


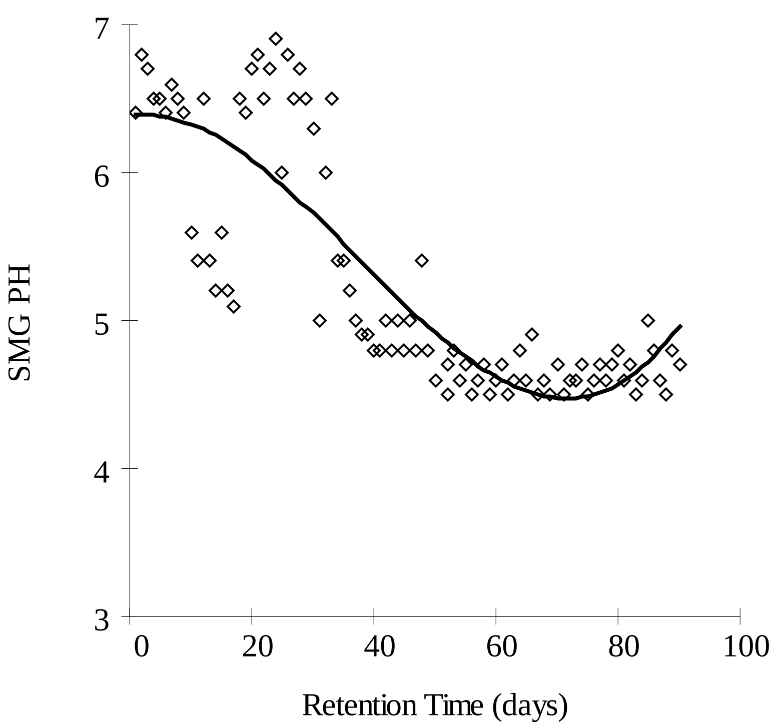
Fig. 5.0 : Graph of SMG Cumulative Gas Volume (L) at stp Versus Retention Time (days)



Max value = 6.5482 at RT = 68   Min value = 5.5682 at RT = 3, R2 = 0.436

$$y = 5.568 - 0.084x + 0.018x^2 - 9.16\times10^{-4}x^3 + 2.006\times10^{-5}x^4 - 1.984\times10^{-7}x^5 + 7.285\times10^{-\ 1}x^{06}$$

Fig. 6.0 : Plot of PP pH Against Retention Time (days)



Max value = 6.3959 at RT = 1   Min value = 4.475 at RT =72, R^2 = 0.725

$$y = 6.381 + 6.678\times10^{-3}x - 1.303\times10^{-3}x^2 + 1.17\times10^{-5}x^3$$

Fig. 7.0 : Plot of SMG pH Versus Retention time (days)

S/N	Name of Wastes	Commencement of Gas Production (Days)	Commencement of Gas Flammability (Days)	Volume of Inflammable Gas at stp (L)	Volume of Flammable Gas at stp(L)	Flammable Gas Production Rates (L/day)
1	PP	8th	12th	1.2334	11.8480	0.1518
2	SMG	1st	8th	8.8953	23.1407	0.2822

Table 1.0 : Data on Gas Flammability and Flammable Volumes (L) at stp for the Wastes