PRODUCTION OF BIOGAS USING PETROLEUM SLUDGE

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ABSTRACT

Biogas, a source of sustainable energy useful for electrical power generation and heating is a better substitute for natural gas in that it contains less carbon and hence produces less pollutant emissions. Moreover, being produced from a natural source it is renewable. Petroleum industries generate large quantities of sludge. This constitutes health hazard to personnel on exposure and environmental hazard on disposal if not properly treated before disposal. Anaerobic digestion of sludge in bioreactors yields biogas and biosolids. Anaerobic digestion of 200 grams of sludge in an anaerobic jar for a solids retention time of 16days gave 10,5000m^3 per day biogas meaning 1 gramm of sludge could yield 840m^3 biogas for a solids retention time of 16days. This show that substantial amount of biogas could be produced from Anaerobic digestion of petroleum sludge. Nigerian industries are therefore encouraged to stop incineration of petroleum sludge as anaerobic digestion of the sludge could produce substantial amount of biogas. This could enhance the realization of the Nigerian vision of zero gas flaring by the year 2020. Moreover, Biogas could replace natural gas as domestic fuel source while natural gas could be used solely for exports. This of course could increase the Nigerian foreign exchange earnings and gross domestic product hence advancing the Nigerian economy.

Keywords: *Biogas; Petroleum Sludge; Anaerobic Digestion; Zero gas flaring; Biological Carbonaceous Oxygen Demand; Volatile Suspended Solids.*

1.0. INTRODUCTION

Petroleum industries generate large quantities of sludge which is a major source of environmental pollution (Islam, 2015). Sludges are hazardous waste according to environmental protection act and hazardous waste handling rules. In Nigerian Petroleum industries sludges are heaped with the hope of incinerating them in a burn pit. This is evidenced by the authors numerous visits to various Nigerian Petroleum industries. Sludges have to be treated and made harmless before disposal. The treatment of sludge in bioreactors will eliminate the odour, health and environmental hazard associated with disposal of untreated sludge. Moreover, biogas a substitute for natural gas will be produced. This will enhance the realization of the Nigerian quest for self sufficiency in renewable energy (Emberga *eta*l., 2014; Osai, 2012; Fasina & Simonyan, 2013; Temilade, 2008). For Nigeria to realize her vision of zero gas flaring by the year 2020, incineration of Sludge in Nigerian industries must be stopped with the adoption of anaerobic digestion technology. Zero gas flaring is important as flared gases deplete the ozone layer hence increasing green house effect.

1.1. Steps to Sludge Biodegradatiion.

Green & Perry (1997) state that the sludge is first hydrolysed to become water soluble and then degraded to produce volatile organic acids primarily acetic acid and hydrogen. *Methanogenic* bacteria then split the acetic acid to methane and carbondioxide (biogas).

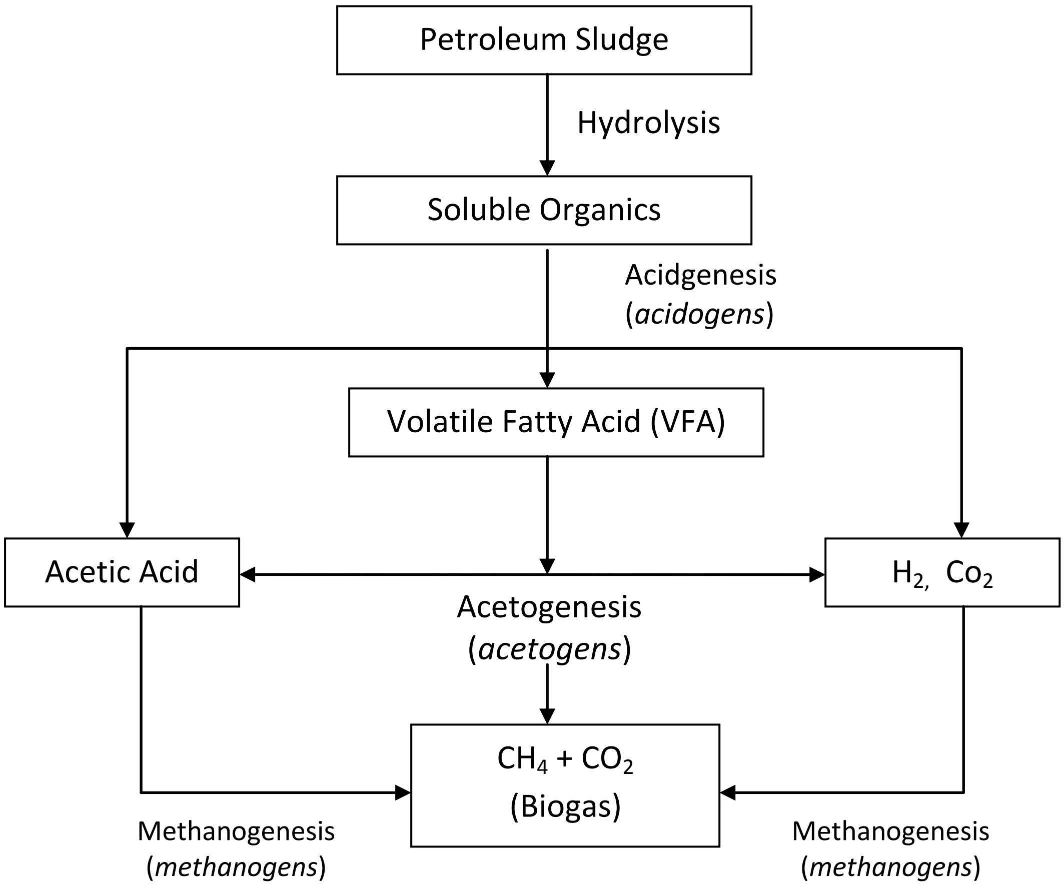

Fig.1 : Steps in Anaerobic Digestion of Petroleum sludge
Source: Appels *etal*. (2008)

Impurities in the biogas are removed by pressure swing adsorption (PSA) on activated carbon. Since adsorption takes place at high temperature and pressure, desorption is achieved by depressurizing. Moisture is removed from the biogas by drying. The active site of the adsorbent retains water vapour and other pollutants thus decreasing adsorbent life hence desorption is frequently carried out by depressurizing. Moreover, siloxanes are difficult to desorb from the adsorbent beds, so the adsorbent beds should be replaced regularly e.g. weekly. The biogas is dried, compressed and sent to storage.

Technical & Regulatory Guideline (2006) state that *methanogenic* bacteria prefer a relatively neutral pH of 6.6 to 7.4 and not acidic conditions. If acid formation is excessive the activity of the *Methanogenic* bacteria can be inhibited.

It is good practice to destroy the volatile acids as quickly as they are produced otherwise the volatile acids build up and depresses the pH and eventually inhibits the *methanogenic* bacteria. To prevent this occurrence feed to the digester should be as uniform as possible and at short intervals as possible.

Appels *et al.* (2008) give the steps to sludge biodegradability as follows: Hydrolysis, Acidogenesis, Acetogenesis and Methanogenesis; among these, Hydrolysis is the rate limiting step. This rate limiting hydrolysis is enhanced by biological, chemical and mechanical interventions to the sludge. These interventions result in lysis or disintegration of sludge cells hence transforming the sludge into a biodegradable material. Hence, a test for the rate of biodegradability of sludge species, results in experimental data which fit into equations developed from kinetic models.

Anaerobic digestion results in the conversion of the biodegradable sludge to methane, carbon dioxide and microbial cells. Volatile suspended solids (VSS) produced are quite low. Biological carbonaceous oxygen demand (BCOD) is destroyed. Biogas produced range from 50 to 80 percent methane and 20 to 50 percent carbon (iv) oxide (CO_2) depending on the chemical characteristics of the sludge digested. The biogas produced is important for heat and power generation.

The pH should be maintained at 6.5 - 7.5 with the help of hydrochloric acid to avoid free ammonia toxicity. The use of nitric or sulphuric acid could result in significant operational problems.

2.0. MATERIALS AND METHODS

2.1. Materials used for the research.

The following materials were used for the research;
Ashles filter paper, oven, desiccators, chemical balance, filter paper, Muffle furnace LMF4, porcelain evaporating dish, beaker, mineral water, reagent dissolved oxygen bottle, winkler A&B reagent, concentrated sulphulric acid, sodium thiosulphate, starch, gallenkamp incubator, labtech anaerobic jar, Bunsen burner, petroleum sludge collected from a typical petroleum industry in Port Harcourt, Rivers State, Nigeria. *Methanog*enic bacteria (*Methano*brevibacter) isolated from the intestine of a cow with the help of Olympus microscope and a spalula and stored in glycerine. Oxide Anaero Gen TM AN 0035A gas park was used in Labtech anaerobic jar to create anaerobic condition.

2.2. Microbial Digestion of Petroleum Sludge

200 grams of the sludge was measured using a chemical balance and put into a beaker. 2 grams of methanogenic methanobrevibacter bacteria was pippeted and put into the sludge in a beaker after which the beaker was put into labtech anaerobic jar with improvise for gas collection point. Anaerobic condition was maintained with the help of oxiod anaerobic Gen TM AN 0035A gas park and Catalyst. The anaerobic jar was corked airtight and kept in a GallenKamp incubator maintained at $37^{o}C$ (Mesophilic) for a solids retention time of Sixteen days.

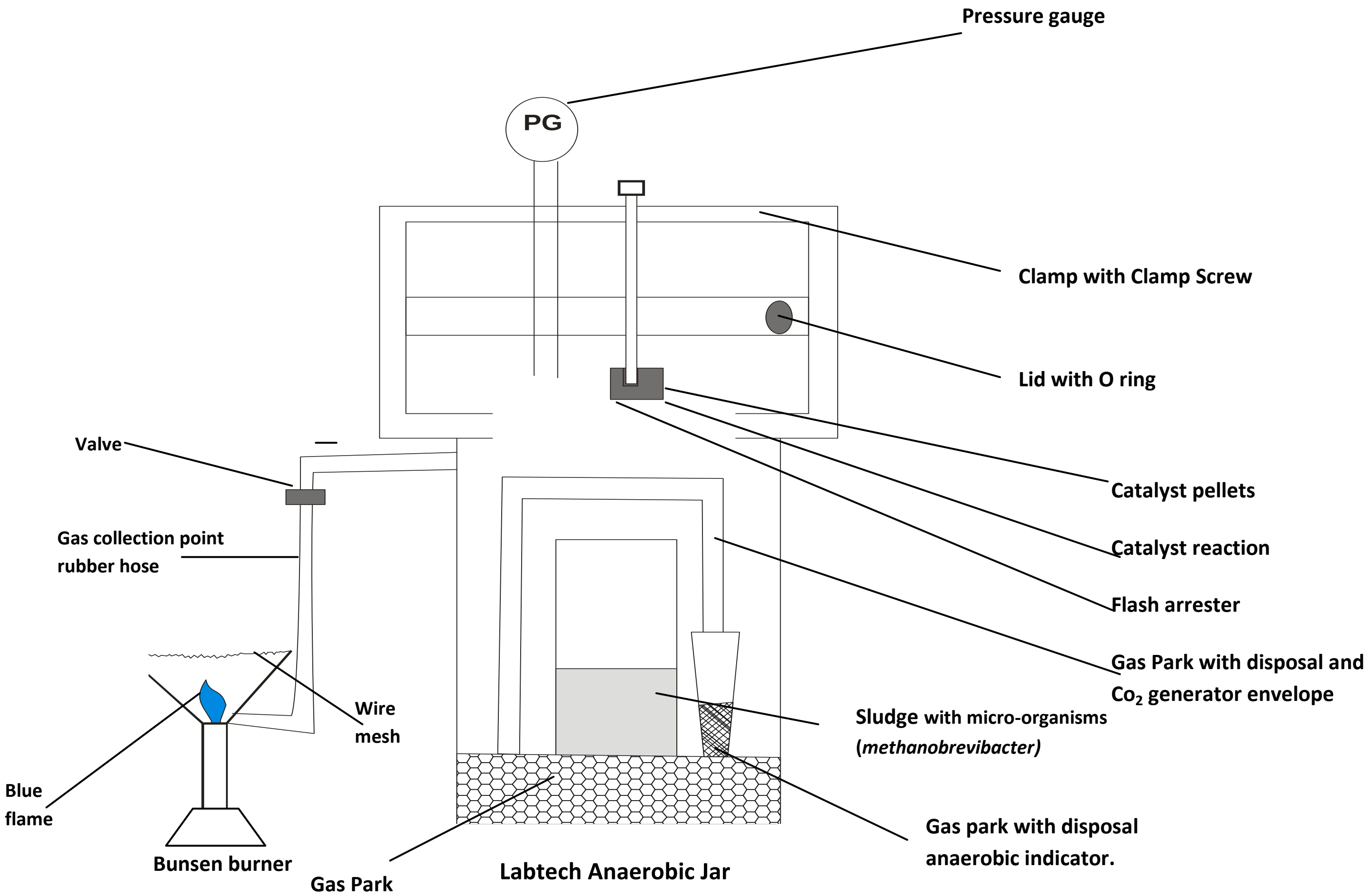

Fig.2: Experiment Set-up for Microbial Digestion of Petroleum Sludge

2.3. Biogas Test

After collecting some of the biogas in a balloon, the gas evolved from the anaerobic jar was made to pass through a 5 mm rubber hose connected to a Bunsen burner. Methane gas was confirmed by the blue colour of the flame. The flow gauge at the gas collection point read 0.122 m^3s^{-1}found to be equivalent to 10,500 m^3 per day.

2.4. Measurement of Percent Volatile Suspended Solids (VSS)

An ashless filter paper was dried in an oven at 105 ^{0}C and cooled in the desiccator and weighed. The weight was recorded. The sample was filtered through the filter paper, dried in the oven and re-weighed.

The residue was burned in the Muffle furnace in the porcelain evaporating dish which was previously weighed. The remnant of the weighed residue was cooled to room temperature and weighed and % VSS calculated using equation (1)

$$\% \, Volatile\ Suspended\ solids = \frac{Weight.\,of\ Volatile\,residue}{Weight\ of residue} \times \frac{100}{1} \quad (1)$$

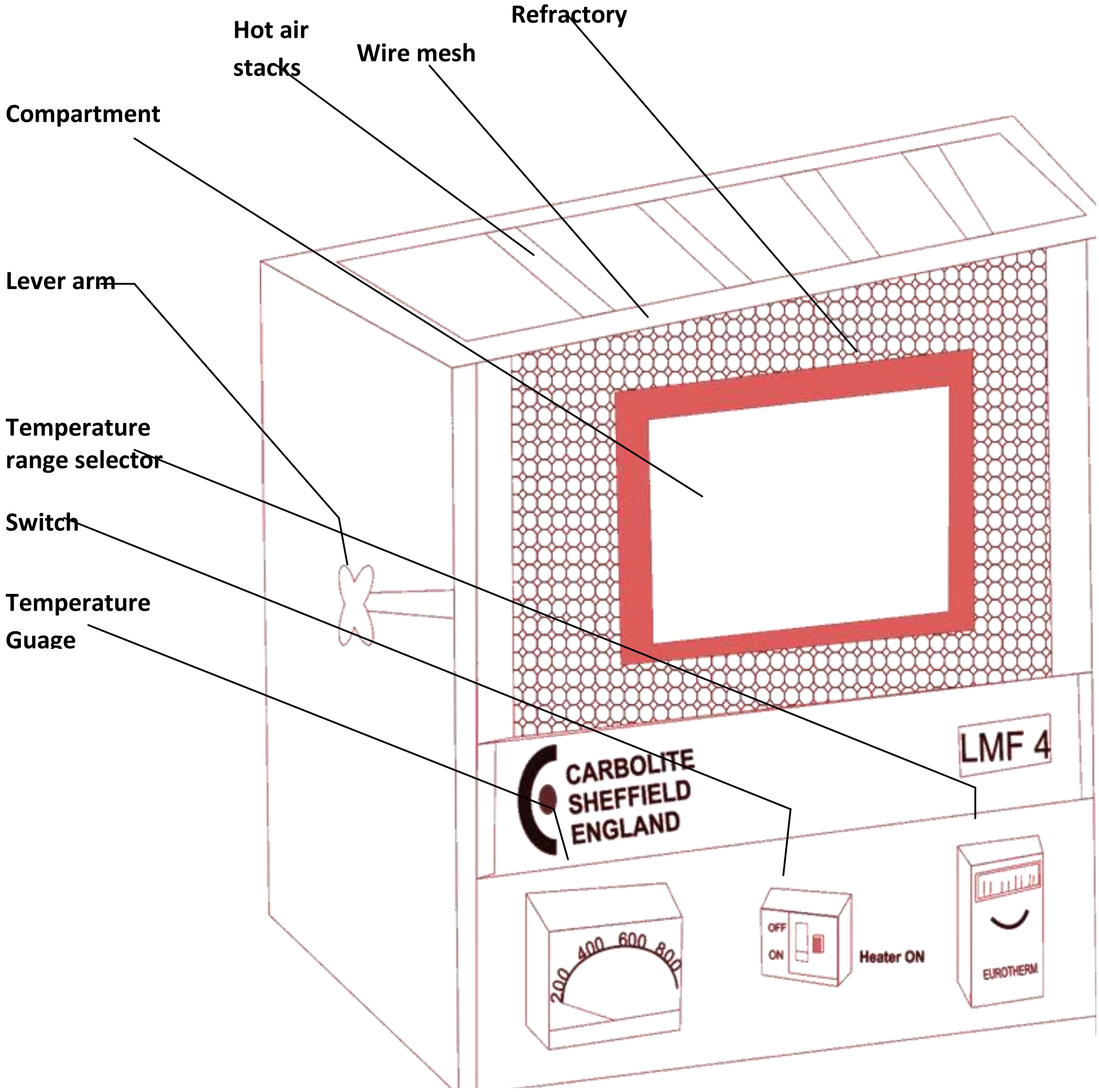

Fig.3: Muffle Furnace LMF4

2.5. Measurement of Biochemical Carbonaceous Oxygen Demand (BCOD)

0.1g sludge was weighed into a clean beaker and 200 *ml* of mineral water from the reagent dissolved oxygen bottle introduced into the sludge. This was stirred to disperse the sludge and obtain a homogenous mixture. The mixture was re-introduced into two dissolved oxygen reagent bottles filled to the brim which had previously been used to measure out the mineral water. The bottles were capped tightly with appropriate cork and the cork was removed and 0.5 ml Winkler A & B reagent pipetted into the reagent dissolved oxygen bottle respectively. The reagent bottle was re-corked and inverted gently for about three times and allowed to stand to sediment the precipitated components.

The reagent dissolved oxygen bottle was carefully opened and about 2 mls concentrated sulphuric acid was added, recapped and inverted gently and carefully thrice for the Precipitate to dissolve completely. 25 ml of this solution was titrated with 0.025 N Sodium thiosulphate using starch as indicator near the end point. The volume of the Sodium thiosulphate that was utilized to obtain colour change was recorded as the titre value.

The other reagent bottle containing the second batch of sludge and mineral salt water solution was placed in an incubator for 5 days and at the end dissolved oxygen analysis was carried out. The titre value of this batch was recorded and the titre at the fifth day. The BCOD value was calculated using equation (2)

$$BCOD_5 = \frac{DO_{initial} - DO_{Final}}{DilutionFactor} \qquad (2)$$

2.6. Equations for Biogas Production

Econotres (2014) give equation for yield coefficient

$$\text{Yield Coefficient (Y)} = \frac{mg\, V_{ss}}{mg\ B_{COD}} \qquad (3)$$

Appels *etal*.(2008) give equation *for* Net mass of cell tissue produced per day

$$P_x = \frac{\text{YES}_0}{1+k_d\theta_c} \qquad (4)$$

The volume of Biogas can be calculated using a relationship from Tchobanoglous *et al.* (2004)

$$V_{CH4} = (0.35)\left[(s_o - s)(Q)\left(\frac{10^3 g}{kg}\right)^{-1} - 1.42P_x\right] \qquad (5)$$

Where s_o is the biochemical carbonaceous Oxygen demand of the influent sludge
S, the Biochemical Carbonaceous Oxygen demand in the effluent biosolids.
Q, the volume of Sludge (m^3/d). 0.35 is the theoretical convwersion factor for amount of methane produced in m^3 from conversion of 1kg BCOD. At 35^{o}C, the conversion factor is 0.40 and 1.42 is the conversion factor for cellular material into the BCOD.

3.0. RESULTS AND DISCUSSION

3.1. Percent Volatile Suspended Solids

Weight of porcelain dish and Residue

$= 125.336\ g$

Weight of porcelain = 123.156 g

Weight of Residue = 125.336 – 123.156

= 2.170 g

Weight of Porcelain dish and ashed residue = 123.165 g

Volatile residue = Weight of residue

=Weight of ashed residue

= (125.336 – 123.156) – (123.165 – 123.156)

= (2.170 – 0.009 g)

% Volatile Suspended Solids

$$= \frac{Weight\ of\ Volatile\ \ Residue}{Weight\ of\ Residue} \times \frac{100}{1}$$

$$= \frac{2.170 - 0.09}{2.170} \times \frac{100}{1}$$

$$= \frac{2.161}{2.170} \times \frac{100}{1}$$

$$= 0.996\ \times\ 100 = 99.6\ \%$$

The high percentage of volatile suspended solids show that anaerobic digestion of petroleum sludge has high potential for the production of biogas.

3.2. Biochemical Carbonaceous Oxygen Demand (BCOD)

$$BCOD_5 = \frac{DO_{initial} - DO_{final}}{DilutionFactor}$$

DO the dissolved oxygen was obtained from:

$$\frac{Titre\ value \times Total\ Volume\ of DObottle}{Volume\ Titrated}$$

$$Dilutionfactor = \frac{0.1\ ml}{100\ ml}$$

$$= 0.001\ ml$$

Volume Titrated = $25\ ml$

Where total volume of DO bottle is regarded as $200\ ml$

$$DO_{initial} = \frac{1.0 \times 200}{25} = 8.00$$

$$DO_{final} = \frac{0.24 \times 200}{25} = 1.92$$

$$BCOD_5 = \frac{8.00 - 1.92}{0.001}$$

$BCOD_5 = 6{,}080\ mg/l$ **in day 1**

Day 4

$$BCOD_5 = \frac{3.12 - 1.92}{0.001}$$

$$= \frac{1.2}{0.001} = 1{,}200\ mg/l$$

Day 16

$$BCOD_5 = \frac{1.9404 - 1.92}{0.001}$$

$$= \frac{0.0204}{0.001} = 20.40\ mg/l$$

Table 1: Biochemical carbonaceous oxygen demand

DAYS	1	4	16
$BCOD/(mg/l)$	6080	1200	20.40

The potential of anaerobic digestion for the treatment of sludge is proved by the decrease in BCOD.

3.3. Yield Coefficient

$$Y = \frac{mg\ (VSS)}{mg\ (BCOD)}$$
$$= \frac{99.6}{6080} = 0.016$$

3.4. Net mass of cell tissue produced per day.

$$P_x = \frac{YES_o}{1 + k_d\theta_c}$$

$$P_x = \frac{0.016 \times 0.9 \times 6080}{1 + 0.025 \times 16} = \frac{87.552}{1.40} = 62.54\ kg/d$$

3.5. Volume of Biogas produced.

$$V_{CH_4} = (0.35)(So - S)(Q)(10^3 g/kg)^{-1} - 1.42P_X$$

$$(0.35)(6080 - 20.4)\ 5000\ \times \frac{1}{1000} - 1.42\ (62.54)$$

$$= 0.35\ (6,059.6)(5) -\ 88.8068$$

$$= 10{,}603.25 - 88.8068$$

$$= 10{,}514.4432\ m^3/d$$

$= 10{,}500\ m^3/d$ of biogas for 16 days

Table 2: Volume of Biogas Produced

Influence BCOD (mg/l)	Effluent BCOD (mg/l)	Flow rate of Biogas (m^3/d)	Net mass of cell Tissue Produced Per day (kg/d)	Volume of Biogas m^3/d	Volume of Biogas from one gram of sludge (m^3)
6080	20.4	5000	62.54	10,500	840

A reasonable volume of biogas can be produced in substantial amount from anaerobic digestion of the sludge as shown in analysis of equation (5). 200 g sludge yielded 10,500 m^3/d biogas for 16 days.1g sludge would yield 10,500/200=52.5 m^3/d biogas for 16 days.52.5×16 = 840 m^3 biogas from 1g of sludge.

4.0. CONCLUSION

It is concluded that the treatment of 5000m^3 per day of sludge could yield 10,500m^3 per day biogas. Hence 1 gram of sludge could yield 840m^3 biogas for a solids retention time of sixteen days. Biogas being a renewable energy source and a better substitute for natural gas, anaerobic digestion of petroleum sludge could enhance the realization of the Nigerian quest for self sufficiency in sustainable energy.

5.0. RECOMMENDATIONS

With the present amendment of the Nigerian petroleum Industry law at the Nigerian National assembly it is recommended that:

i. Sludge incineration in Nigerian Industries be stopped with the adoption of the anaerobic digestion process technology. This will enhance the Nigerian Vision 2020 of zero gas flaring.
ii. Biogas produced from anaerobic digestion should be upgraded and its production maximized so that with rising natural gas exports, biogas could substitute natural gas as a domestic fuel source, being environmentally friendly and a renewable energy source. With this, natural gas should be set aside exclusively for exports.

This could increase the Nigerian Gross Domestic Product and the Nigerian Gross National Income hence advancing the Nigerian economy.

6.0. NOMENCLATURE

Symbol	Definition	Unit
K_d	Endogenous respiration maintenance rate.	(d^{-1})
P_x	Net mass of cell tissue produced per day	kg/d
Q	Volume of Sludge	m^3/d
S	Biochemical Carbonaceous Oxygen Demand (BCOD) in The efluent biosolids.	mg/L
S_O	Biochemical Carbonaceous Oxygen Demand (BCOD) in the influent Sludge	mg/L
V_{CH4}	Volume of Biogas Produced	m^3/d
θ_c	Mean cell residence time	days
E	Efficiency of energy Utilization	%

ABBREVIATIONS

BCOD	Biological Carbonaceous Oxygen Demand
GDP	Gross Domestic Product
SRT	Solids Retention Time
VSS	Volatile Suspended Solids
PSA	Pressure Swing Adsorption
Y	Yield Coefficient

7.0. REFERENCES

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