

# Modelling the kinetics of biogas degradability rate: The effect of algae in co-digestion with cow dung and POME

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## Abstract

The effect of algae on the fraction of readily available degradable substrate in co-digestion with cow dung and POME was examined at an ambient temperature range of 28°C-32°C for a 40-day period. The experimental set-up comprised samples of POME, cow dung and algae with percentage composition of 100% POME and 100% cow dung designated as S1 and S2 respectively; 50% POME and 50% cow dung as S3; 40% POME, 40% cow dung and 20% algae as S4. The modified Gompertz model was used to validate the experimental biogas production potential of all four samples and the kinetic model generated from the first order decay equation was used to develop a mathematical model that can be used to estimate the fraction of readily available degradable volatile solid of the substrates at minimum retention time. The results from the cumulative biogas production from the experimental study showed that S4 performed better with a yield of 172L followed by S1, S3 and S2 with corresponding values 133L, 128L and 94L respectively. The linear regression analysis plot from the MS-Excel solver for the four samples generated a k-value of -0.094, -0.1159, -0.0845 and -0.0968 for S1, S2, S3 and S4 with corresponding STABI values 0.121, 0.3509, 0.2146 and 0.4402 respectively. S2 which comprised 100% POME had the highest negative K-value hence, the degradability rate was fast and production end-time began with it. The STABI value for S4 was higher than that of the other samples therefore, it can be predicted to have the largest fraction of readily available degradable volatile solid in the substrate at a short hydraulic retention time (HRT) resulting in a high biogas production yield which indicates that, algae has the tendency to improve the STABI value when used as a blend with cow dung and POME.

Keywords: Biomass, Biogas, Algae, Anaerobic digestion, Methane.

## 1.Introduction

The demand for energy is rapidly increasing over the years with increase in the global world's population leading to intensive research on ways of improving the available energy sources. These sources are categorized into two major groups on the basis of their replenishing ability as renewable and non-renewable energy forms. The non-renewable energy sources (e.g. fossil fuel, natural gas, coal etc.) have limited reserves and the present utility make them unsustainable in a long term resulting in price instability. More also, the green-house gas emission generated from the production of fossil fuel resulting in ozone layer depletion has been a major environmental concern globally leading to the search for alternative clean and sustainable energy sources like solar energy, wind, hydro energy and energy generated from biodegradation of biomass. Biomass is any organic matter that can be used to generate energy in different forms like combustion (the burning of flammable material in the presence of oxygen to release gas),

gasification (the conversion of biomass into a combustible gas mixture), Pyrolysis (thermal decomposition in the absence of oxygen, and anaerobic digestion (AD) which involves the fermentation of carbon compounds to yield gaseous mixture of methane( $\text{CH}_4$ ), carbon dioxide ( $\text{CO}_2$ ) and other trace gases[1] with percentage composition of approximately 60-70% and 30-40% respectively termed biogas [1]-[5].

AD of biomass is a technology that promotes waste management practices and also, the end product of the biodegradation is a strong organic matter that is rich in nutrient and humus commonly known as compost [20]. Compost is an organic fertilizer that improves the soil nutrient and water holding capacity when applied to the soil. Hence, AD process in addition to gas production helps in the conversion of farm waste to useful farm resources [21]. The biomass for AD application comprises plant and animal materials including their waste but recent concerns has been on the negative effect it has on food production when the edible plant substances are utilized for gas production; Hence, emphasis has been on the utilization of the waste materials instead of their edible forms. Therefore, this study focuses on the waste materials from plant and animal as substrates for the biogas production.

The biogas yield generated from the AD process is greatly influenced by the substrate type used among other factors (e.g. environmental and physiochemical properties of the substrate) and as such, several studies have been on ways of improving the biogas yield by using co- digestion and also regulating the major parameters that influences the yield (e.g. Temperature, Pressure solid to liquid ratio etc.)[2-10] without giving much consideration to the effect of degradability rate on the yield. Hence, this study is on using the modified Gompertz model alongside modified kinetic model of the first order decay mass balance equation to evaluate the effect of algae on the biodegradability of substrate in AD co-digestion process with cow dung and POME.

## **2 Materials and Methods**

### **2.1 Substrate Collection and Preparation:**

The substrate used in this experimental study are POME, cow dung and algae. The POME was collected from the oil palm mill located at Omuhuewhan community, Aluu in Ikwerrri Local Government Area of Rivers State; the cow dung was obtained from the farm of the Agricultural department located in the University park of University of Port Harcourt, Choba, Rivers State while the algae were collected from a site in Rumualogu community, Obio-Akpor Local government area of Rivers state. The samples were first analyzed to determine the carbon to nitrogen ratio by method of complete combustion before preparation for feeding into the reactor. The algae were sun dried for about three days in line with [7] to weaken the ligno-cellular cell wall so that biodegradation process would be enhanced before were grinding into smaller particles to speed up the degradation rate while the cow dung was neatly matched to obtain a homogenous mixture so that the tendency of clogging the inlet and outlet pipe of the digester during feeding and discharge of slurry would be prevented.

### **2.2 Experimental design**

The samples used for the experimental study were denoted as S1, S2, S3 and S4. S1 and S2 comprised 100% cow dung and POME respectively; S3 comprised 50% cow dung and 50% POME while S4 comprised 40% cow dung, 40% POME and 20% algae. The cow dung was mixed with water to obtain a slurry before percentage fraction of the mixture was obtained but since the POME was in liquid state no water addition was required. The material composition of the substrates is shown in table 1.

Table 1: Material composition of substrate.

Sample	Mass of Cow dung (kg)	Mass of POME (kg)	Mass of Algae (kg)	Volume of Water (L)	Amount of Slurry (kg)
S1	12	0	0	12	24
S2	0	24	0	0	24
S3	8	12	0	4	24
S4	6	8	4	6	24

### 3 Results and Discussion

#### 3.1 Experimental Results

The daily biogas production yield for a period of 40 days was examined for the four samples S1, S2, S3 and S4 at an ambient temperature range of 28°C-32°C. Biogas production was observed to kick off with S2 which comprised 100% cow dung. There was an observed time lag of about 2, 4 and 6 days before production commencement for S3, S4 and S1 respectively. The observed early biogas production of S2 can be attributed to the already existing microbial activities in the substrate because the sample collection point was a closed container thereby promoting the activities microorganisms responsible for degradation and also, the processing it underwent subjected it to intense heat resulting in cellulose walls break-down enhancing biodegradation. Maximum production was obtained on day 17, 8, 14 and 15 for S1, S2, S3 and S4 respectively with production terminating on day 32, 17, 23 and 34 for samples S1, S2, S3 and S4 respectively. The early production termination and low yield of S2 is as a result of the high C:N ratio which made methanogens consumed the available nitrogen at a fast rate without reacting with the left-over carbon present in the substrate [8]. This problem was reduced by the addition of cow dung to S3 and further improved by the addition of algae to S4 resulting in better production yield although there was an observed delay in the production start-up time for S3 and S4 compared to S2 due to the cellulose cell wall of the materials of the cow dung making it recalcitrant to biodegradation. In terms of cumulative production has shown in Fig 1, S4 had the highest yield of 172L followed by S1, S3 and S2 with corresponding values 133L, 128L, 94L respectively.

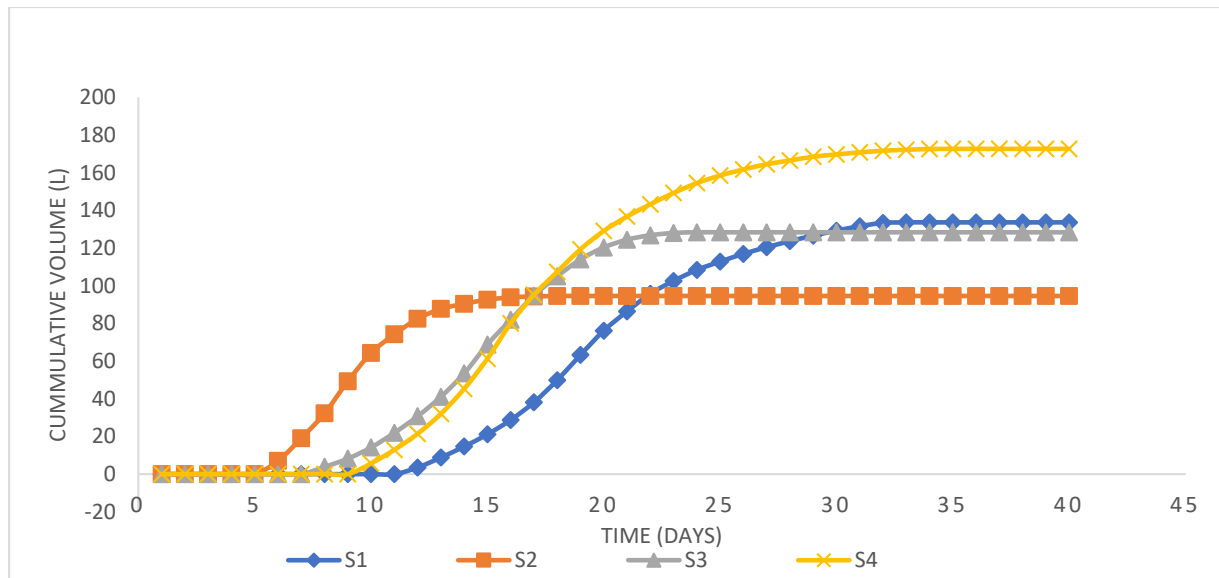


Fig. 1: Comparison of experimental Cumulative biogas production for S1, S2, S3 and S4

### 3.2 Mode development and Application

The modified Gompertz model which has been employed by several researchers in computing the cumulative biogas yield over a given time period was used to validate the cumulative experimental yield in this research similar to [5]. The model is expressed as:

$$Y(t) = y_m \exp \left[ -\exp \left[ \frac{k_m \times e}{y_m} (\lambda - t) + 1 \right] \right] \quad (1)$$

Where,

$Y(t)$  is the cumulative biogas yield at any given time

$y_m$  is the maximum production yield or biogas production potential

$k_m$  is the maximum rate of production

$\lambda$  is the production lag time

$t$  is the required time

But the maximum production potential can be computed from the mass balance equation along with the correlation between biogas production and fraction of volatile solid degradation expressed in the work of [5]. The biogas produced at any given time can be expressed as:

$$y_t = y_m [1 - e^{-Kt}] \quad (2)$$

The biogas production yield at any given time from the model was computed with the aid of MS- excel solver and presented in Fig 3. Interest might also be on knowing the relationship between the biodegradability rate and the fraction of readily and moderately degradable fraction of the substrate with respect to time, this can be computed from Eq (2)

by taking the derivative with respect to time and the natural logarithm of both sides in line with [5]. Taking the derivative of Eq (2) gives:

$$\frac{dy_t}{dt} = y_m K e^{-Kt} \quad (3)$$

Taking the natural logarithm of both sides one obtains:

$$\ln \frac{dy_t}{dt} = (\ln y_m + \ln K) - Kt \quad (4)$$

A comparison of Eq (4) with the general equation of a straight-line expressed as  $y = mx + c$  with  $x$  as the slope and  $c$  the intercept on the  $y$  axis results in a slope of  $-K$  and intercept  $(\ln y_m + \ln K)$  when  $\ln \frac{dy_t}{dt}$  is plotted against  $t$ . The first part of the equation is a measure of the availability of readily and moderately degradable fraction of the substrate. Author [22] reported in his work that, because of the limited time range available for most experimental study, only the readily and moderately degradable fractions are consumed while the poorly and recalcitrant fraction are unaffected. This factor which is termed as the short-term anaerobic biodegradability index (STABI) can be used for selecting substrate with high production yield under minimum retention time [5]. A comparison of the cumulative production yield of the four samples as depicted by Fig 2 shows that S4 has the highest production yield followed by S2, S3 then S1 which corresponds to the experimental findings with alternation of S1 and S2.

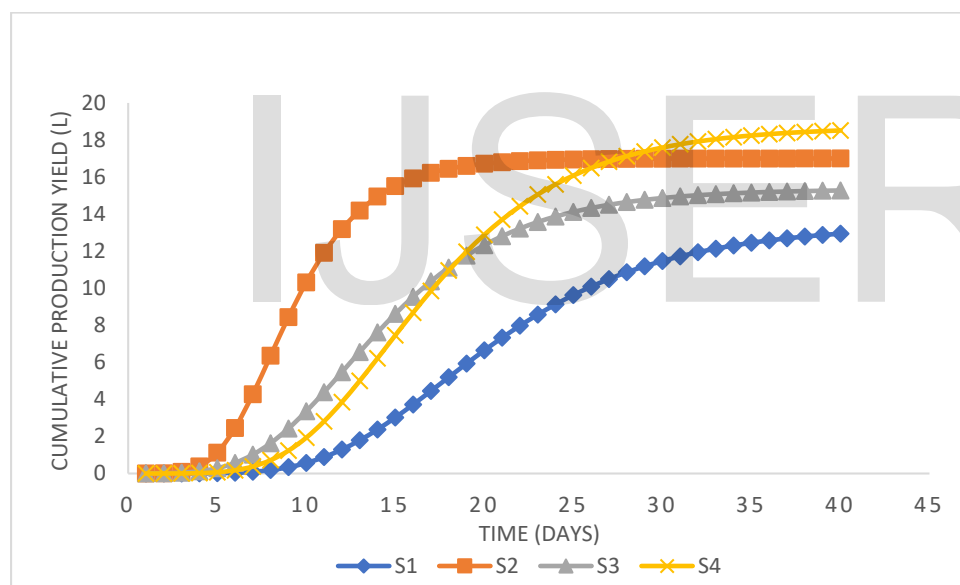


Fig. 2: Comparison of model Cumulative biogas production for S1, S2, S3 and S4

The plot of  $\ln dy/dt$  against  $t$  as computed by the MS-excel linear regression analysis tool gave an exponential decay curve with goodness of fit ( $R^2$ ) of 0.80 for S1 and corresponding equation  $y=0.0942x-0.121$  which indicates a degradability constant of  $-0.094$  and a STABI value of  $0.121$ . S2 resulted in a  $R^2$  value of  $0.78$  with a linear equation,  $y=0.1159x-0.3509$  indicating a  $K$  value of  $-0.1159$  and STABI of  $0.3509$  while S3 and S4 had a  $R^2$  value of  $0.888$  and  $0.841$  with corresponding equations;  $y=0.0845x-0.2146$  and  $y=0.0968x-0.4402$  resulting in a  $K$  value of  $-0.0845$  and  $-0.0968$  and STABI of  $0.2146$  and  $0.4402$  respectively. A comparison of the  $K$  value for the four samples shows that S2 with a  $k$  value of  $-0.1159$  has a fast rate of biodegradable fraction removal at a low retention time followed by S4, S1 and S2 which can be attributed to the fact that the more negative the  $K$  value the faster the rate of biodegradable substrate fraction removal and more positive values of  $K$  indicates a slow removal rate. The fast substrate degradation

of S2 that comprised 100% POME compared to other substrates composition can be attributed to the cellulose cell wall that has been broken down by the heat application during the processing operation of the substrate

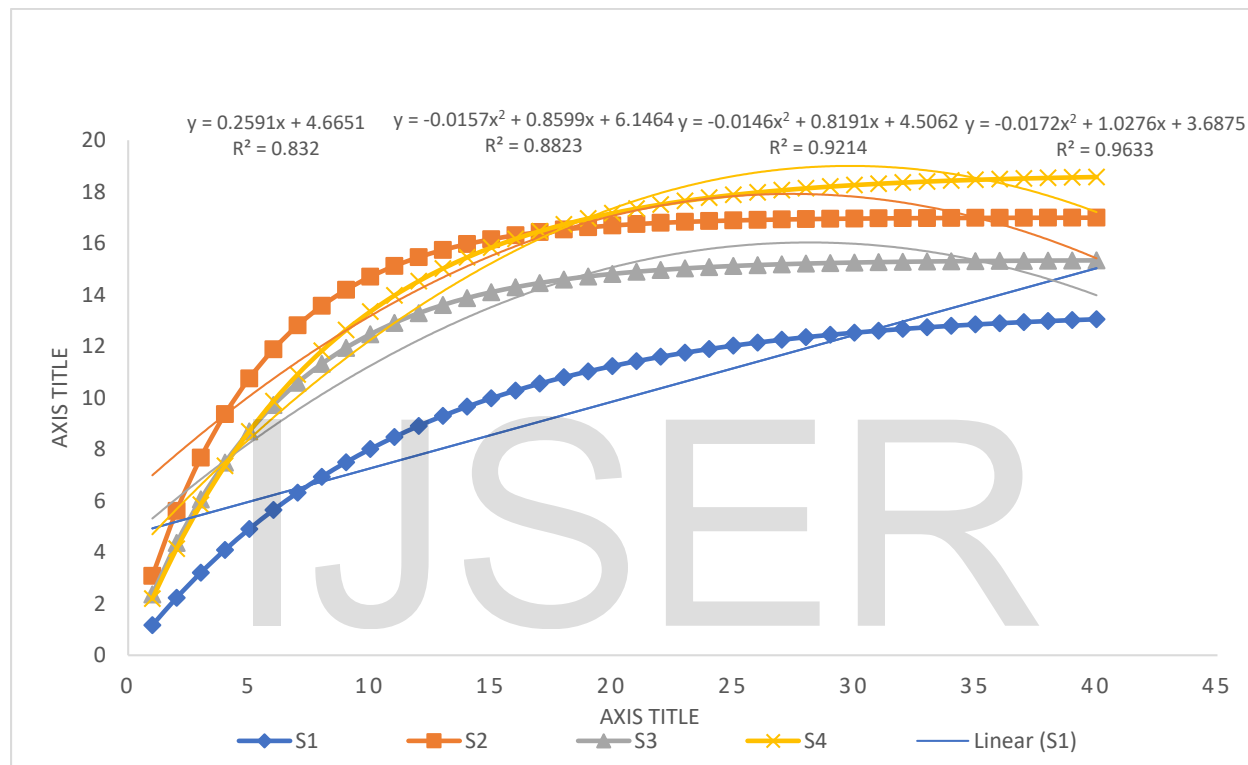


Fig. 3: Comparison of model production yield for S1, S2, S3 and S4

In terms of the STABI value, S4 had the highest value of 0.4402 followed by S2, S3 and S1 which indicates that, at limited hydraulic retention time S4 which comprised a blend of POME, cow dung and algae in a ratio of 2:2:1 would have a more degradable substrate fraction which shows that the presence of algae and cow dung improved the fraction of degradable substrate compared to when POME and Cow dung were used independently as a substrate.

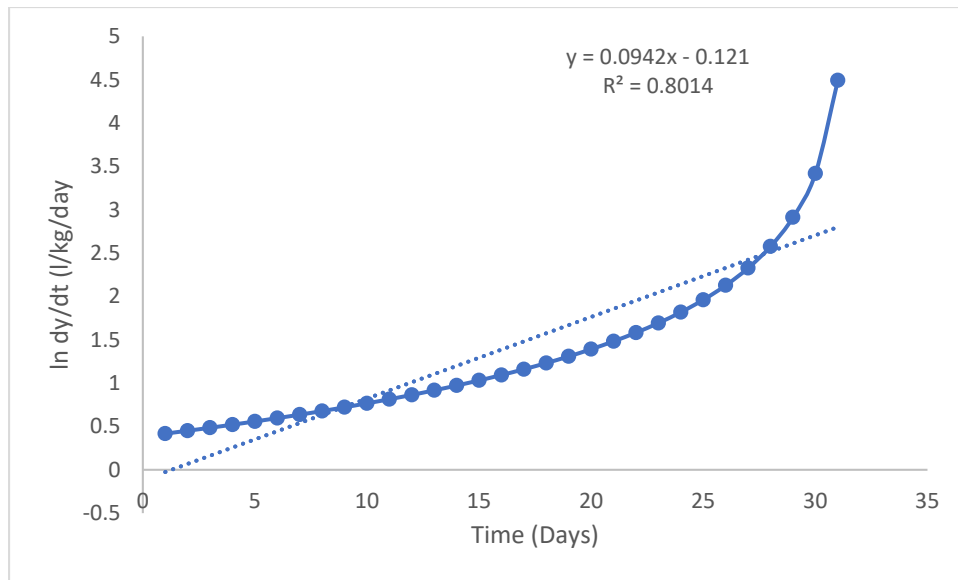


Fig. 4: A plot of  $\ln dy/dt$  against  $t$  for S1

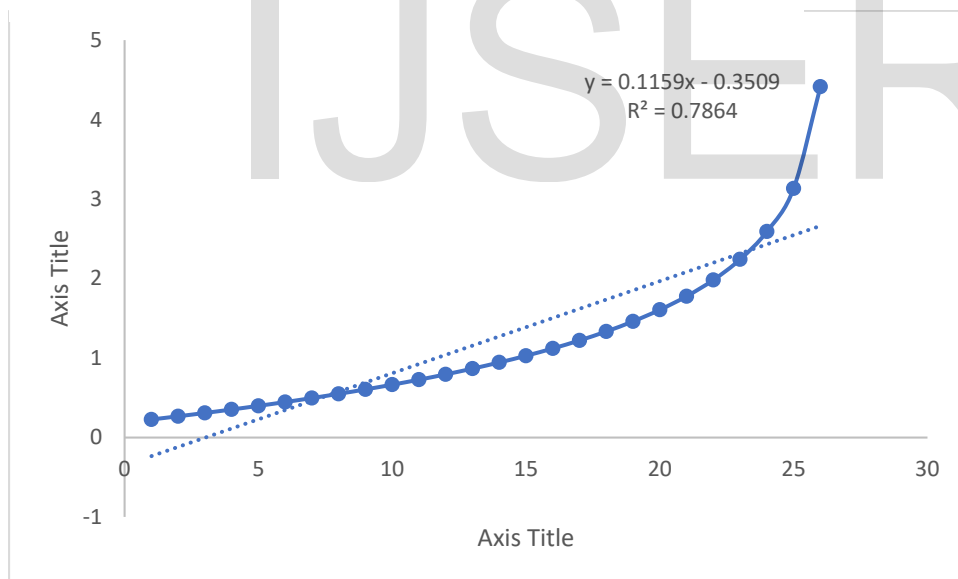


Fig.5: A plot of  $\ln dy/dt$  against  $t$  for S2

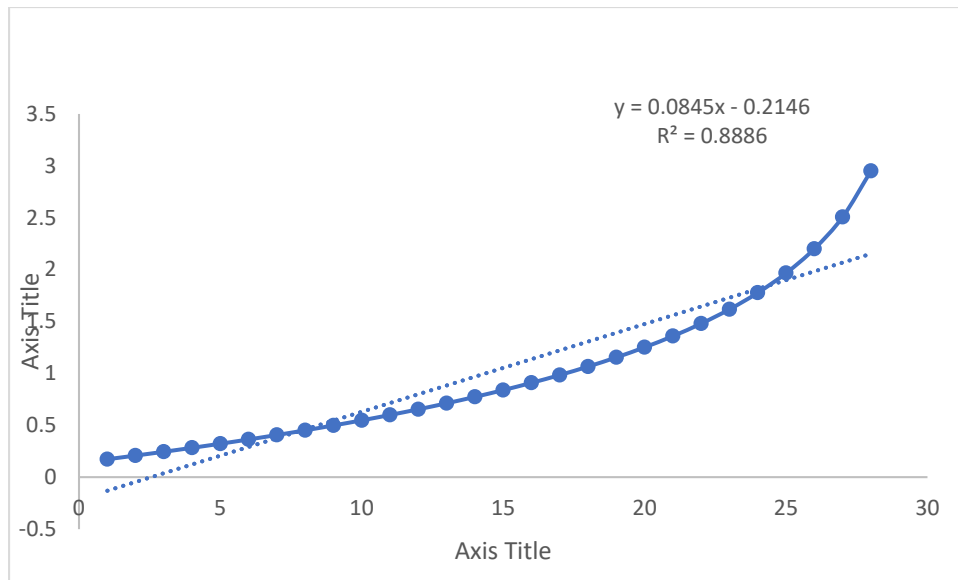


Fig. 6: A plot of  $\ln dy/dt$  against  $t$  for S3

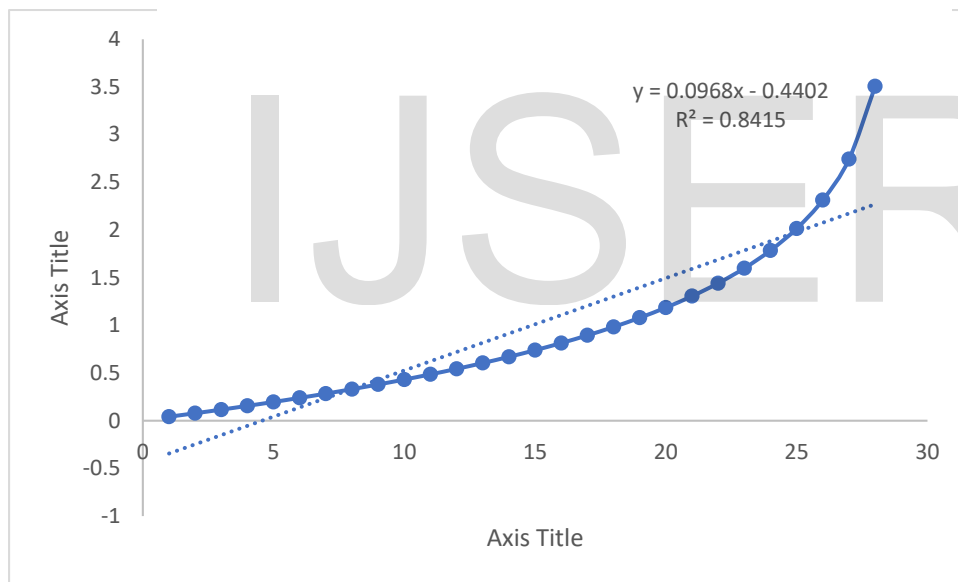


Fig. 7: A plot of  $\ln dy/dt$  against  $t$  for S3

## 2.5 Conclusion

Anaerobic digestion of algae in co-digestion with cow dung and POME can be used to improve the biogas production yield compared to when POME and cow dung biomass are used independently and as co-digestate. More also, the fraction of readily available degradable solid in the substrate could be improved by this application. The model developed from the first order kinetic decay equation used to estimate the fraction of readily available degradable solid in the substrate with respect to time in this study would be useful to researchers in understudying and selecting



suitable substrate blend since most research works are carried out at short HRT. Furthermore, the result of this study showed that S1 had the highest production yield followed by S1, S3 and S2 which indicates the study of algae in co-digestion with cow dung and POME is feasible.

Table 2: Physiochemical properties of the samples

Samples	Moisture content	C:N	K(day <sup>-1</sup> )	Volatile solid (%)	Y <sub>m</sub> (L)	R <sup>2</sup>
S1	48.9	19.9:1	0.091	27.2	13.4	0.82
S2	75.9	36.7:1	0.2	18.9	17.0	0.88
S3	59.6	22.3:1	0.167	25.7	15.35	0.92
S4	55.4	25.4:1	0.125	29.3	18.7	0.96

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