



Kinetics of Anaerobically Co-Digested Crop Residues and Buffalo Dung

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Abstract: The aim of this work was to assess the kinetics of co-digestion of crop residues and buffalo dung, through the modified Gompertz model and cone model. Selected crop residues were analysed for moisture content, total and volatile solids, and pH. Methane production was measured by biochemical methane potential through the test automatic methane potential test system. Discrimination of the models were done by employing the two statistical parameters, i.e. coefficient of multiple determination (R^2), standard deviation of residual (SDR) The assessment of kinetics of the anaerobic co-digestion results that, the cone model better described the experimental data, than that of the modified Gompertz model under mesophilic temperature. Moreover, the results of the present study also reveals that the BMP test is a suitable way to assess the kinetics of crop residues and buffalo dung co-digestion.

Keywords: kinetics, anaerobic co-digestion, crop residue, buffalo dung, modified Gompertz model, cone model.

1. INTRODUCTION

Anaerobic digestion (AD) is a biochemical process that produces energy in the form of biogas (Romano and Zhang, 2008). Biogas comprises of methane (CH_4) and carbon dioxide (CO_2), which is renewable and the replacement of fossil fuels (Chynoweth *et al.*, 2011). Pakistan is an agrarian country and produces a huge amount of crops annually, which generates a large quantity of residues. Most of the crop residues are either wasted or inefficiently used as reported by Sahito *et al.* (2012). Out of the possible solution to utilize the crop residues, one might be the production of biogas through AD.

The study of the kinetic of AD is beneficial in terms of predicting the performance of the process and is a helpful tool in the design of the digesters. There are several models to assess the kinetics of anaerobic digestion of organic waste. The first-order model is the modest, which can compare the performance of AD under practical conditions (Rao and Singh, 2004). On the contrary, Anaerobic Digestion Model No. 1 (ADM1) is the multifaceted model, which represents great complexity and includes an excessive number of parameters (Batstone *et al.*, 2002). Such a complexity increases the precision of the model, but conversely produces practical complications as all the required data is not often collected (Golkowska *et al.*, 2012). The modified Gompertz model is another frequently used model that describes the kinetics of AD (Shin *et al.*, 2008, Borja *et al.*, 1995 and Patil *et al.*, 2012). It is a simple model that not only encounters the lag phase period, but also requires less number of parameters.

AD of crop residues and buffalo dung can be termed as co-digestion. Gelegenis *et al.* (2007) reported that the understanding of anaerobic co-digestion is difficult. Thus further research is needed in order to determine the impact of various combinations of substrates on the stability of the process. The aim of present work was to assess the kinetics of seven crop residues, namely canola straw, bagasse, cotton stalks, banana plant waste, sugarcane trash, rice straw and wheat straw co-digested with buffalo dung. The kinetics was assessed by using two models, i.e. modified Gompertz model and Cone model. Moreover, these models were compared to determine the best model describing the cumulative methane production under mesophilic temperature.

2. MATERIAL AND METHODS

2.1 Substrates and inoculant

The substrates for this study were seven crop residues, collected from the agricultural fields. The samples were dried at room temperature and their size was reduced to ≤ 1.0 mm. Inoculant used was the effluent of mesophilic lab scale anaerobic digester.

2.2 Substrates and inoculant

Moisture content (MC) and total solids (TS) volatile solids (VS) were determined in accordance with APHA, (1998), whereas the pH was determined by the lavibond pH meter.

2.3 Experimental setup

The biochemical methane potential (BMP) is a simple method to quantify renewable methane from biodegradable organic matter. It allows the comparison

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of biogas potentials from different substrates and is useful in assessment of the AD kinetics. The BMP test was performed on AMPTS with reactors of 0.5 liter glass bottles. For statistical significance, the test was performed as triplicate batch experiments at the temperature of 37 ± 0.2 °C. Each bottle was filled with 2 gVS of crop residue and inoculant of 5 gVS. Three bottles were filled as blanks determine the methane production from the inoculant alone.

Nitrogen was flushed through the reactors, before they are incubated. The biogas produced was passed through the 3M NaOH solution to absorb CO₂ (Borja *et al.*, 1995 and Shanmugam and Horan, 2009). The BMP assays were terminated after 30 days. The BMP test setup is shown in the Fig. 1.

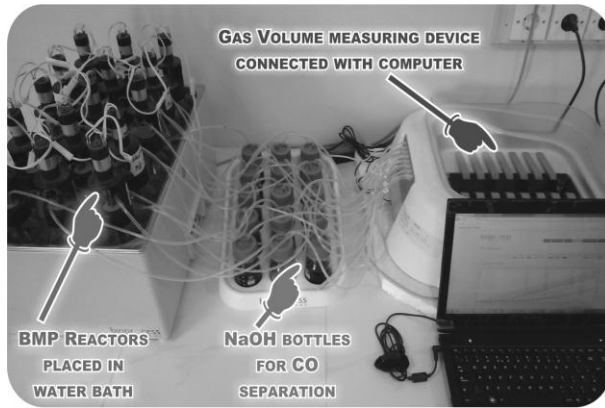


Fig. 1: BMP test setup

2.4 Kinetics of anaerobic co-digestion

First-order kinetic model is the simplest model and works on the assumption that the rate of methane production is directly proportional to the concentration of the reactants and had used by several researchers (Tong *et al.*, 1990, Chen and Hahimoto, 1996 and Mahar *et al.*, 2007). The first order model does not encounters the lag phase period, but only the methane generation rate constant and generally poorly fits to the experimental data (El-Mashad, 2013).

The Gompertz model was modified by Lay *et al.* (1998) to estimate the accumulative CH₄ production from a landfill bioreactor, assuming that methane production is a function of bacterial growth. The modified Gompertz equation is given by Eq. (1).

$$V = V_u \cdot \exp \left[- \exp \left\{ \frac{R_m \cdot e}{V} (\lambda - t) + 1 \right\} \right] \quad (1)$$

Where V was the cumulative methane production (Nml) at the time t (d), V_u was the ultimate methane production (Nml), R_m was methane production rate (Nml/ d), λ was lag-phase time (d), and e was exponential of 1. In present study, the cumulative

methane production was also simulated by using Cone model (Pitt *et al.*, 1999), which is first-order model and is given in Eq. (2).

$$V = \frac{V_u}{1 + (kt)^{-n}} \quad (2)$$

Where V was the cumulative methane production (Nml) at time t (d), V_u was ultimate methane production (Nml), k was first-order methane production rate constant (1/d), and n was a dimensionless shape factor. The parameters V_u , R_m , λ , k and n for both models were estimated by performing non-linear regression using the least square method. These parameters were determined for the best fit and their standard errors were also estimated.

2.5. Discrimination of models

To compare the modified Gompertz and Cone models, two statistical parameters; the coefficient of multiple determination (R^2), standard deviation of residuals (SDR) were estimated as per Eqs. (3-4), where V_{exp} is experimental methane production, V_{mod} is modelled methane production at time i for the m number of days. These parameters are comprehensive to quantify the accuracy of the mathematical models against the experimental data. The model with a higher R^2 value makes a better estimation, while the model with the lowest value of SDR makes a better estimation.

$$R^2 = 1 - \frac{\sum_{i=1}^m (V_{exp_i} - V_{mod_i})^2}{\sum_{i=1}^m (V_{exp_i} - \bar{V}_{mod_i})^2} \quad (3)$$

$$SDR = \sqrt{\frac{\sum_{i=1}^m (V_{exp_i} - V_{mod_i})^2}{m}} \quad (4)$$

3. RESULTS AND DISCUSSION

3.1 Composition and features of substrates

The composition and features (MC, TS, VS and pH) of the substrates used in present study are given in the Table 1. The results show that crop residues have substantial VS contents ranging from 83.4% to 98.3% and buffalo dung has VS content of 71.8%. The nature of the crop residues was acidic, while the buffalo dung was alkaline.

Table 1: Composition and features of substrates

S No	Name of the substrate	MC (%)	TS (%)	VS (% TS)	pH
1	Bagasse	6.1	93.9	98.3	4.6
2	Banana Plant Waste	85.5	14.5	83.0	6.8
3	Buffalo Dung	80.5	19.5	71.8	7.5
4	Canola Straw	6.6	93.4	90.8	5.4
5	Cotton Stalks	6.6	93.4	95.7	5.3
6	Rice Straw	2.1	97.9	83.4	6.0
7	Sugarcane Trash	2.4	97.6	87.0	5.4
8	Wheat Straw	7.1	92.9	86.8	5.5

3.2 Results of BMP test

The cumulative CH₄ production from the co-digestion of crop residues and the inoculant is shown in Fig. 2. The highest methane was obtained from wheat straw, i.e. about 1206 Nml followed by canola straw, rice straw, cotton stalks, banana plant waste, sugarcane trash and bagasse about 1081, 901, 859, 844, 836 and 814 Nml respectively. The contribution of the inoculum in the cumulative CH₄ was only 561 Nml.

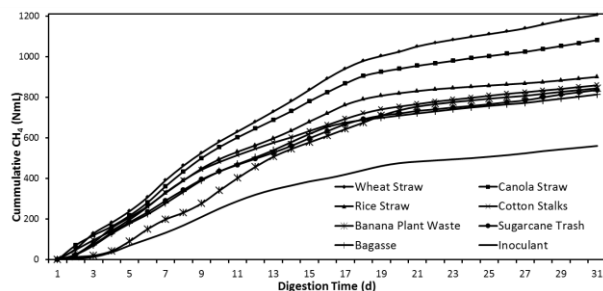


Fig. 2: Cumulative CH₄ production obtained in BMP assays

Figs. 3-10 depicted that the maximum methane flow rate was observed as 83 Nml/d for wheat straw followed by 80, 72, 70, 67, 58 and 57 Nml/d for canola straw, rice straw, cotton stalks, banana plant waste, sugarcane trash and bagasse respectively. Referring to the specific methane potential, it can be stated that higher the methane flow rate, higher the specific methane potential of crop residues.

3.3 Results of the kinetics

Table 2 represents the results of non-linear regression and statistical parameters of BMP test data for the modified Gompertz model. It also contains the values of experimental methane production from BMP test (V_{BMP}), while Figs. 3-10 illustrate the experimental and predicted cumulative methane productions from different crop residues co-digested with buffalo dung and from the inoculant. It can be observed that the experimental cumulative methane productions from all the crop residues are in good agreement with the projected values. The R^2 values also highlights the above statement as they are close to unity and are ranging from 0.996 to 0.999 (Table 2). Moreover, the results of the present study also reveal that the BMP test is a suitable technique to assess the kinetics of crop residues and buffalo dung co-digestion.

The inoculant alone has a lowest estimated methane production rate of 35.85 Nml/d, which increases by the addition of crop residue and became highest up to 66.74 Nml/d for wheat straw. The lowest lag phase period was estimated as only half day for sugarcane trash, while the highest was estimated about 3 days for banana plant waste. The predicted values of methane production were in good correspondence with the experimental values as their standard errors for

cumulative methane production were less than 10 Nml. The SDR was observed in the range of 9.2 Nml and 16.3 Nml for banana plant waste and wheat straw respectively.

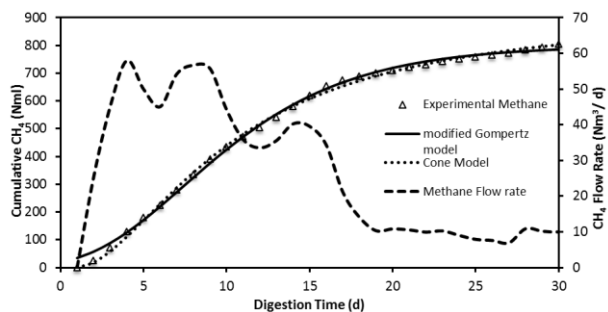


Fig. 3: The cumulative methane production and flow rate for Bagasse

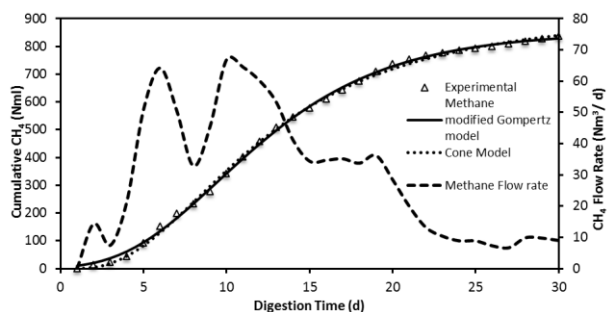


Fig. 4: The cumulative methane production and flow rate for banana plant waste

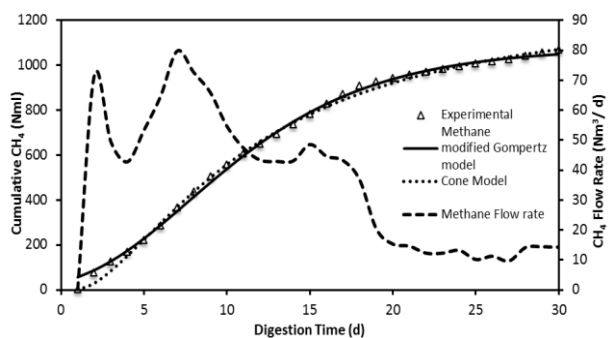


Fig. 5: The cumulative methane production and flow rate for canola straw

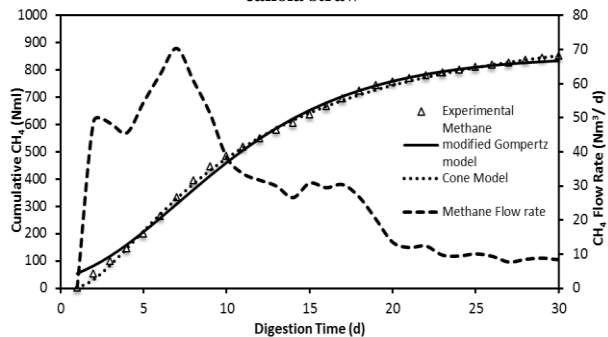


Fig. 6: The cumulative methane production and flow rate for cotton stalks

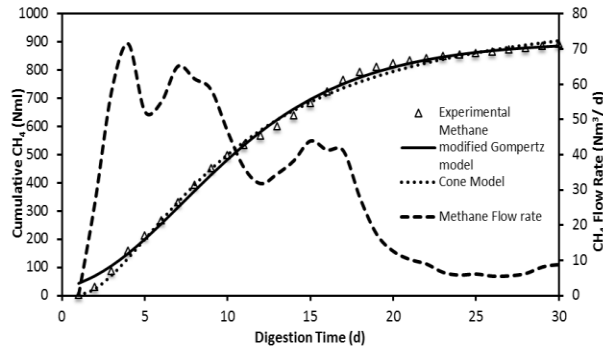


Fig. 7: The cumulative methane production and flow rate for rice straw

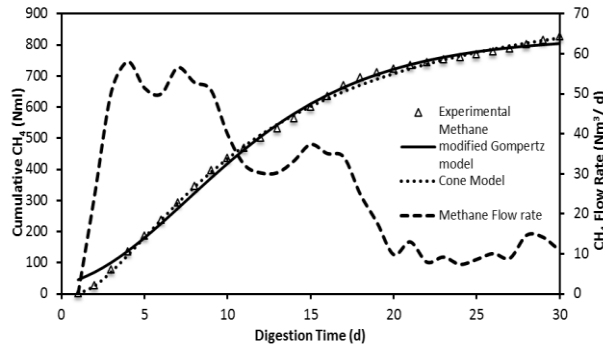


Fig. 8: The cumulative methane production and flow rate for sugarcane trash

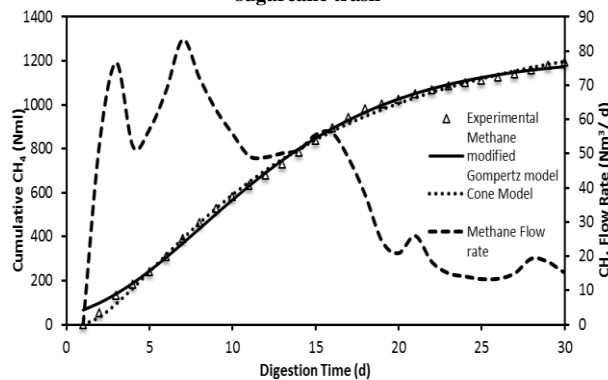


Fig. 9: The cumulative methane production and flow rate for wheat straw

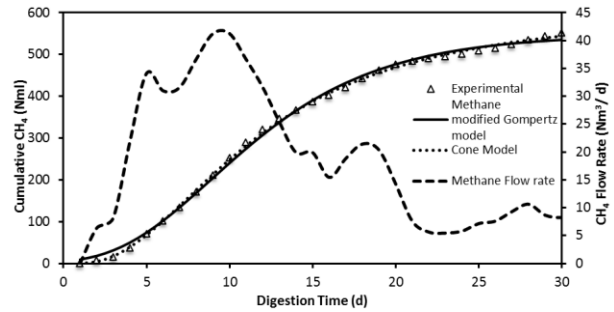


Fig. 10: The cumulative methane production and flow rate for inoculant

Table 2, 3 represents the results of non-linear regression and statistical parameters of BMP test data for the Cone model. It can be observed, that the estimated maximum cumulative methane productions from all the crop residues are higher than that of the experimental values and have higher standard errors, but the values of R^2 were almost same, to the values obtained from the modified Gompertz model, i.e. close to unity and ranging from 0.997 to 0.999 (Table 3).

Meanwhile, the values of *SDR* were lowest for the Cone model with a few exceptions, because the Cone model has the lower residual sum of squares as compared to modified Gompertz model. This fact can also be observed through Figs. 3-10, that the estimated values of cumulative methane production through Cone model are closer to the experimental values than to the values estimated through modified Gompertz model. Based on *SDR*, the Cone model better describes the experimental data, than that of the modified Gompertz model. This observation is also in correspondence to the observation of El-Mashad (2013), that the Cone model best described the experimental data in most of the digesters. The kinetic gas production rate constant varied for different crop residues and was ranging from 0.082 1/d and 0.106 1/d for wheat straw and rice straw respectively.

Table 2: Results of non-linear regression and statistical analysis for the modified Gompertz model

Name of Substrate	V_{BMP} (Nml)	V_u (Nml)	R_m (Nml/d)	λ (d)	R^2	<i>SDR</i> (Nml)
Bagasse	814	800 ± 5.5	52.5 ± 1.12	0.821 ± 0.160	0.998	12.4
Banana Plant Waste	844	851 ± 4.7	55.3 ± 0.81	2.800 ± 0.107	0.999	9.2
Canola Straw	1081	1079 ± 6.7	63.9 ± 1.07	0.513 ± 0.136	0.999	13.1
Cotton Stalks	859	853 ± 7.7	52.3 ± 1.40	0.092 ± 0.213	0.996	16.2
Rice Straw	901	903 ± 7.1	58.5 ± 1.41	0.647 ± 0.183	0.997	15.8
Sugarcane Trash	836	827 ± 8.3	49.1 ± 1.35	0.417 ± 0.223	0.996	16.3
Wheat Straw	1206	1221 ± 9.6	66.7 ± 1.24	0.465 ± 0.159	0.998	16.3
Inoculant	561	548 ± 5.2	35.9 ± 0.94	2.292 ± 0.192	0.997	10.6

Table 3: Results of non-linear regression and statistical analysis for Cone model

Name of Substrate	V_{BMP} (Nml)	V_u (Nml)	k (1/d)	n	R^2	SDR (Nml)
Bagasse	814	920 ± 13.7	0.105 ± 0.002	1.721 ± 0.049	0.998	10.4
Banana Plant Waste	844	938 ± 11.1	0.089 ± 0.001	2.265 ± 0.055	0.999	10.1
Canola Straw	1081	1288 ± 29.7	0.094 ± 0.003	1.592 ± 0.058	0.997	17.1
Cotton Stalks	859	1020 ± 14.2	0.102 ± 0.002	1.506 ± 0.034	0.999	8.4
Rice Straw	901	1043 ± 22.6	0.106 ± 0.004	1.675 ± 0.068	0.997	16.6
Sugarcane Trash	836	999 ± 18.7	0.094 ± 0.003	1.537 ± 0.044	0.998	10.2
Wheat Straw	1206	1525 ± 38.9	0.082 ± 0.003	1.500 ± 0.050	0.998	16.8
Inoculant	561	613 ± 6.8	0.093 ± 0.001	2.099 ± 0.046	0.999	5.8

Furthermore, modified Gompertz and Cone models differ in their zero-time behaviour and the existence of lag. The modified Gompertz model gives a non-zero gas volume at time zero, which is an artefact of the model. In an actual situation initially, not only the cumulative methane production is zero but also the biogas.

Moreover, modified Gompertz model contains time parameter, which is mentioned as “lag-phase”. On the contrary, the Cone model gives a zero gas volume at time zero, but does not contain any lag-phase. Literature reveals that the lag-phase period of the animal dung ranges from 8 to 11 days (Yusuf *et al.*, 2011, Adiga *et al.*, 2012), whereas addition of the inoculant shortens the start-up of the AD process as in case of anaerobic batch digestion of spent wash, i.e. 0.5 to 1.5 days (Budiyono *et al.*, 2013). In present study methane production was started by day one, because of the addition of the inoculant in the batch reactors of the BMP test. Thus, decreases the significance of the lag-phase period in the model.

4. CONCLUSIONS

The present work shows that, the experimental cumulative methane productions from crop residues co-digested with buffalo dung follows both the modified Gompertz and Cone models. Based on SDR , the Cone model better define the experimental data, than that of the modified Gompertz model under mesophilic temperature. This observation also establishes that the BMP test is a suitable way to assess the kinetics of crop residues and buffalo dung co-digestion.

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Nomenclature

λ	Lag-phase time (d)
e	exponential of 1
k	First-order methane production rate

m	constant (1/d)
n	Number of days
R^2	Dimensionless shape factor
Rm	Coefficient of multiple determinations
SDR	Methane production rate (Nml/ d)
t	Standard deviation of residuals (Nml)
V	Time (d)
V_{exp}	Cumulative methane production (Nml)
V_{mod}	Experimental methane production (Nml)
V_u	Modelled methane production (Nml)
	Ultimate methane production (Nml)

Abbreviations

°C	Degree Celsius
ADM1	Anaerobic Digestion Model No. 1
AMPTS	automatic methane potential test system
BMP	Biochemical methane potential
CH ₄	Methane
CO ₂	Carbon dioxide
MC	Moisture content
NaHCO ₃	Sodium hydrogen carbonate
NaOH	Sodium hydroxide
TS	Total solids
VS	Volatile solids

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