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Kinetic study of anaerobic co-digestion, analysis and modelling

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Abstract

Anaerobic digestion in insular context can be a good way to treat organic wastes and to dispose of a clean and constant renewable energy. However, insular context implies that waste volumes can be not important enough to provide efficient stocks, so treating mixed wastes is important. In another hand, french regulations obliges big producers of biowaste (kitchen, supermarkets ...) to find a way to recycle the biowaste and can in certain cases prohibit the mixes of waste. This study presents the modelling of household waste biomethane potential measurements, as a mix of pure waste, and the modelling of the different phases of anaerobic digestion via first order and Gompertz models. Results are analyzed. The disintegration coefficients are then used in various model of anaerobic digestion for mixed wastes.

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1. Introduction

Anaerobic process is assumed by anaerobic microorganisms, under controlled atmosphere (temperature and without oxygen). Anaerobic digestion (AD) processes represent a source of renewable energy, allowing to lower pollutions of wastes. AD can with some dispositions produce also good solutions for soils amendments.

Different waste streams can be implied in the process, depending on the partners of the project, and its size. For agricultural installations, expected power ranges around 200 MW, and for wastewaters plants, or collective plants, power production can reach 500 MW [1].

The kinetics of the anaerobic digestion of liquid effluents like vinasse, fruit juice effluents, (generally dry matter less than 15% is considered) can be represented by multiple models like first order. Borja [2] showed that first order model could be used for diluted vinasse, with substrate concentration lower than 6.55 g COD/l.

However, the choice of different aspects like reaction kinetics model can be more difficult for solid wastes [3] like the Organic Fraction of Municipal Solid Waste (OFMSW) using the dry anaerobic digestion process. A number of models can be found in literature like Gompertz, logistic or Richards models including three to four parameters to be determined. However, relations between these parameters, and process or biological parameters are sometimes difficult to highlight.

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This paper proposes to evaluate the biomass methane potential (BMP) of the OFMSW, and green wastes in Reunion Island. The methane production was modelled using modified Gompertz equation. We studied co-digestion performed under mesophilic condition (35°–37°C) in order to observe synergistic or antagonistic responses in methane production by mixing five different solid organic waste (paper, cardboard, fine element, fermentable waste, green waste). Results show a synergistic effect in the mixture with paper, cardboard or green waste, with an increase in the methane production. We will describe the use of BMP curves to describe degradation kinetics prediction for single substrate, and mixtures.

Nomenclature

R_m	methane production rate ($\text{NmL.gVS}^{-1}.\text{days}^{-1}$),
P	ultimate methane production ($\text{NmL}_{\text{CH}_4}.\text{kgvs}^{-1}$)
λ	further nomenclature continues down the page inside the text box
k_{h1}	hydrolysis rate constant of the readily organic matter (days^{-1})
k_{h2}	hydrolysis rate constant of the solid organic matter (days^{-1})
Y_{\max}	maximum methane potential (NmL.gVS^{-1})
$M(t)$	cumulative methane production ($\text{NmL}_{\text{CH}_4}.\text{kgvs}^{-1}$) at a digestion time t
t	time (days)

2. Materials and Methods

2.1. Waste characterisation

Several methods for the characterisation of household wastes exists [4]. For this survey, the French MODECOM method was chosen [5]. This method allowed us to establish a comparison with a previous study conducted in 2006 all over the territory using the same method in order to update the PDEDMA (waste management plan). This method allows us to distinguish 13 main kinds of household wastes, including four types of organic wastes: paper, cardboard, fermentable wastes and fine elements (diameter < 20 mm). OFMSW substrate samples were collected at a transit platform belonging to the CINOR. In order to ensure the bias of the process, the substrates were collected by a backhoe loader who randomly picks about 100 kg of wet household wastes from waste transporting trucks when they arrived at the site. Then the wastes were transported in four plastic bins to CYCLEA, a sorting centre. There the wastes were weighing up and sorted out using the MODECOM method's. Therewith, 2 * 2 kg of each household wastes were placed in 20 L plastic bags, bring back to our laboratory and stored at -20°C. The green waste samples were collected by the society RCE who ensures the collection and the grinding stage of green waste on the CINOR territory. Samples were brought back to our laboratory in a 100L plastic bag. Bio-wastes from a grill restaurant containing food waste and food-soiled paper products were also used as substrates. Wastes collected during the characterisation were used as a substrate for our BMP tests.

2.2. Inoculum for BMP assay

An active inoculum was collected from the mesophilic biogas plant of the sugar-cane distillery Rivière du Mât, Saint-Benoit, Reunion Island. A 900-1000 μm sieve was used to remove the remaining large solid particles from the inoculum. The results for total solids (TS), volatile solids (VS) were 3.25% and 64.22%. Substrate samples were characterised in terms of Dry Solid (DS), Volatile Solid (VS), Chemical Oxygen Demand (COD), Volatile Fatty Acids (VFA), Carbone Organic Total (COT), Nitrogen (Nt) and reported for 1g of raw material (table 1). The dry matter content was measured by drying of 2 kg of the sample at 105°C until weight stabilisation. The volatile matter was measured by burning the dry samples at 550°C for 4.5 hours. The wastes were grinded by Retsch Grindomix GM 200 at 6000 RMP for 3 minutes for homogenization. Then, 5 g. of grinded wastes were mixed with 50 mL distilled water for 5 minutes by Ultra-turrax IKA T25 digital. Chemical tests were run on the wastes and distilled water mix solution supernatant using Hach lange cuvette test system LCK 914, LCK 365, LCK 387 and LCK 338 and Hach lange dry thermostat LT200. Measures were performed using a Hach Lange DR5000 Spectrophotometer.

Table 1 :Biochemical Methane Potential (BMP): Experimental set-up and procedures

Wastes categories	DS (%)	VS (%)	COD (gO_2/L)	Nt (mg/L)	COT (mg/L)	VFA (mg/L)
Fermentable wastes	28.44	81.44	0.11	3.57	76.60	12.92
Fine elements	50.4	71.87	0.67	1.79	162.33	22.60
Cardboard	70.92	80.57	0.53	2.59	158.14	4.42
Paper	56.69	89.33	0.52	0.76	74.13	10.44
Green waste	48.77	86.96	0.26	24.31	54.53	0.73
Bio-waste	16.63	95.99	176.63	5.3	43.48	0.72

2.3. Bio-Methane Potential: Experimental Set-up and Procedures

BMP tests refer to a method used to measure the maximum methane production of organic substrates performed under optimal conditions [6]. In addition, it can be used to estimate the best co-digestion configuration [7]. BMP assays were achieved using Automatic Methane Potential Test System II (AMPTS II - Bioprocess Control) with alkaline solution (NaOH, 3N) for CO₂ trapping. Two systems allow us to carry out 30 analyses at once and monitoring the methane production in real time. Bottles of glasses of 500 ml were used as reactors with a working volume of 250 ml. The reactors were sealed by a septum in order to ensure anaerobic condition. Besides each reactor were connected to a stirring system in order to avoid fatty acids aggregation and ensure a good mass transfer. A total of approximately 7g.VS of feedstocks were added to each reactor with 250 ml inoculum and placed in a thermostatic bath at 35°C, mesophilic conditions until no more significant methane production was observed. No pH adjustments were performed. Then the bio-methane produced was measured by a flow meter and results are given to standard temperature and pressure (0 °C and 1 bar). All experiments were run in duplicates. In addition, blank tests, consisting of bottles of inoculum without the substrate, were performed in order to estimate the endogenous CH₄ production of the inoculum.

Table 2: Experimental design

Mix	Cardboard	Paper	Fine element	Fermentable waste	Green waste
M-1	1	0	0	0	0
M-2	0	1	0	0	0
M-3	0	0	1	0	0
M-4	0	0	0	1	0
M-5	0	0	0	0	1
M-6	0	0	0.5	0.5	0
M-7	0.5	0	0.5	0	0
M-8	0	0.5	0.5	0	0
M-9	0	0	0.5	0	0.5
M-10	0.5	0	0	0.5	0
M-11	0.5	0.5	0	0	0
M-12	0	0	0	0.5	0.5

Table 2 describes a part of the experimental design (simplex centroid mixture design) used in this experimentation to define the proportions of different wastes in each tested mix [8]. In this study, the modified Gompertz equation Eq.(1) [9] was used to predict the maximum biomethane production.

$$M(t) = P * \exp \left\{ - \exp \left[R_m * \frac{\exp(1)}{P} * (\lambda - t) + 1 \right] \right\} \quad (1)$$

The hydrolysis constant of AD process k_h was determined by using the first-order model Eq.(2) [10], by plotting $\ln \left(\frac{P - Y_{max}}{P} \right)$ versus time.

$$M(t) = P * (1 - \exp(-k_h * t)) \quad (2)$$

However, for complex substrates, considering of the easily and the poorly biodegradable organics parts we propose a superimposed first order model [11] with the following form:

$$M(t) = Y_{max} * [(x * \exp(-k_{1h} * t)) + (1 - x) * (1 - \exp(-k_{2h} * (t)^n))] \quad (3)$$

The efficiency of the model was indicated by the R² coefficients. The Root Mean Square Error (RMSE) Eq.(4) was used as statistical criteria to evaluate the deviation between measured cumulative methane production $M_{m,i}$ and calculated cumulative methane production $M_{c,i}$ over the experimental period.

$$RMSE = \sqrt{\left(\frac{1}{n} * \sum_{i=1}^n (M_{m,i} - M_{c,i})^2 \right)} \quad (4)$$

Where, n represents the number of measurements over the experimental period.

2.4. Synergistic effects of co-digestion

Synergistic effects result from inner reactions produced by the co-digestion of the different components [12]. To estimate a possible synergistic effect, we used Eq. (5):

$$\alpha = \frac{\text{Experimental production}}{\text{Theoretical production}} \quad (5)$$

3. Results and Discussion

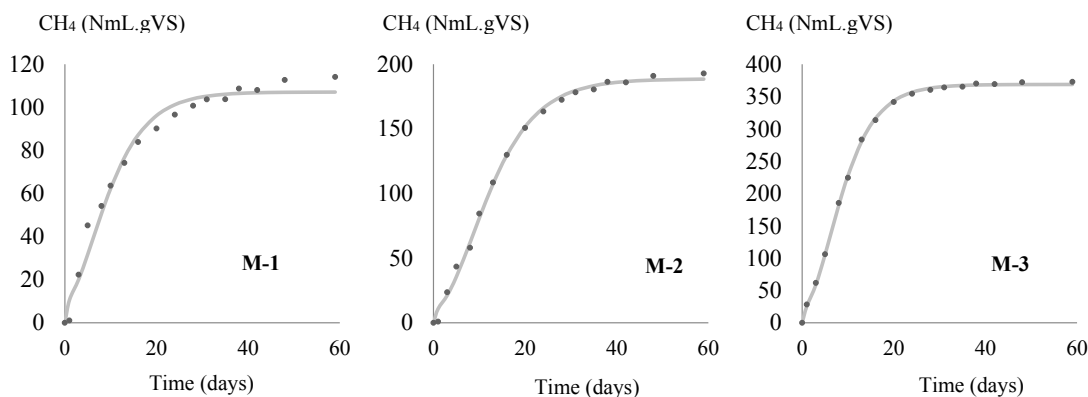
3.1. Kinetic of biogas production

We can see in Figure 1 that the fine elements have the highest methane production per mass of VS with 613 NmL/gVS followed by the fermentable wastes with 541 NmL/gVS. That can be due to their high easily biodegradable content, and a good C/N ratio.

Table 3: Summary of BMP performance

Mix	K _{h1}	K _{h2}	R ²	RMSE	R _m	λ	M(t)	R ²	RMSE	Experimental production	α
M-1	0.094	-	0.99	2.755	6.359	1.40E-07	107.1	0.978	6.083	114	-
M-2	0.077	0.005	0.99	3.055	9.397	1.39E+00	188.7	0.9962	4.662	193	-
M-3	0.11	1.16e-6	0.99	14.61	25.86	0.9336	368.7	0.9989	4.733	373	-
M-4	0.096	-	0.99	14.61	24.13	0.419	281.5	0.9933	8.684	283	-
M-5	0.122	0.002	0.99	0.644	9.027	2.472E-09	237.1	0.9423	15.22	96	-
M-6	0.087	-	0.99	15.2	16.58	0.581	94.55	0.9917	1.58	252	-
M-7	0.14	4.28e-8	0.99	4.854	20.5	1.11	210.4	0.9921	4.425	214	1.16
M-8	0.129	-	0.987	12.06	22.86	0.5454	211.7	0.9928	6.754	93	0.50
M-9	0.167	0.0001	0.99	5.586	19.83	1.653	201.8	0.9921	7.12	213	0.94
M-10	0.173	-	0.997	4.534	22.48	3.164	353.8	0.9973	5.322	196	0.94
M-11	0.089	-	0.996	3.778	20.91	2.174	282.7	0.9962	4.841	161	1.09
M-12	0.174	3.6e-5	0.99	4.063	9.23	2.91E-10	161.8	0.9225	10.79	75	1.00

Observations can be made from figure 1 that the Gompertz model has some difficulties to describe the hydrolysis phases for the mixes 5 and 12. It is due to the hydrolysis of the non-easily biodegradable matter contains in green wastes and mix of green wastes and fermentable wastes. Table 3 presents the parameters determined for the Gompertz and the modified first order models. We can see from this table that the mixes M1, M5 and M12 show shorter lag period λ (close to 0) while the mix M7, M9, M10, M11 has a longer lag period (>1 days). That can be interpreted by a difficulty encountered by the biological consortium to hydrolyze the wastes mixtures. Theses mixtures include mainly green wastes or cardboard. The Gompertz model performs well on the main mixtures.



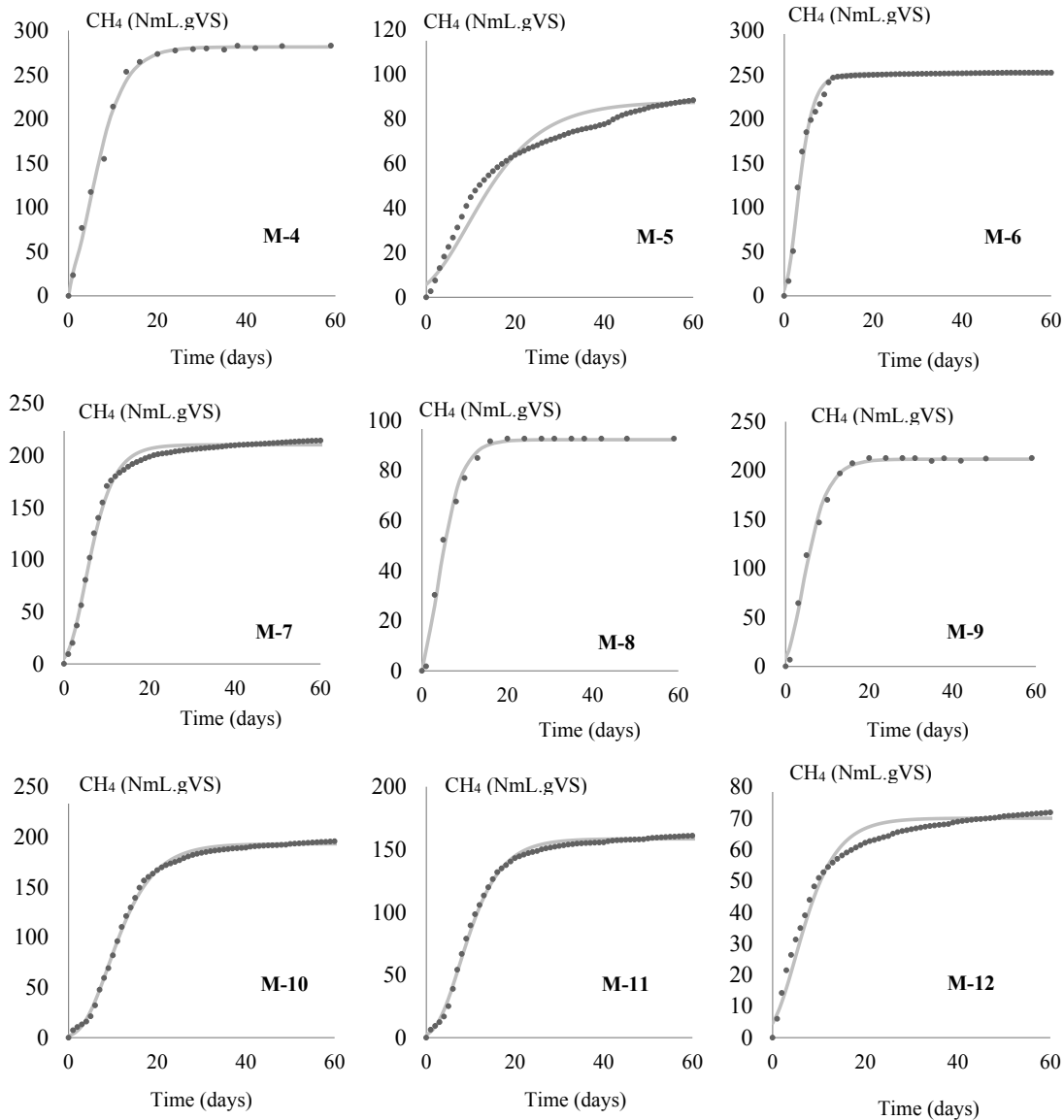


Figure 1: Comparison between measured data (points) and calculated data (full line) for cumulative biogas production using modified Gompertz equation

It can describe more than 92 % of the variations of $M(t)$. However, as shown in figure 1, model could be improved for example for M5 and M12. The results for the modified first order model are then presented also in table 3. The K_{b2} coefficient is not detailed when it is not necessary, and the results shows that the Gompertz model can be optimized for some mixtures (M2, M5, M12, M9) in terms of RMSE. Table 4 presents also the special quartic model defined for the biogas prediction of a specific mixture of wastes like green wastes, cardboard, paper, fermentable [13] and fine elements obtained from the experimental plan. The objective was to model the alpha coefficient or Y_{max} coefficient as a pondered sum of polynomial combinations of the pure waste proportions. The results show that even for some mixes of 5 elements, this kind of model can give satisfying results.

Table 4: Coefficients of the α and Y_{max} as a function of wastes combination

Term	Coefficients (alpha model)	Coefficients (Y_{max} model)
Fine elements (EF)	0,99	409.16
Fermentescible (Ferm)	0,99	367.26
Carboard (Ca)	0,97	107.51
Paper (Pa)	1,05	203.49
Green Wastes (GW)	1,00	64.05

EF*Ferm	-0,06	R ² : 0.88	-6.84	R ² : 0.97
EF*Ca	0,62	RMSE	178.46	RMSE
EF*Pa	-0,21		-53.47	
EF*GW	-0,69		-149.21	
Ferm*Ca	0,37		101.84	
Ferm*Pa	0,26		81.84	
Ferm*GW	-1,21		-252.21	
Ca*Pa	0,17		43.77	
Ca*GW	0,08		13.21	
Pa*GW	2,69		370.24	

4. Conclusions

In this study, it was found that the household waste bin contains mainly fermentable waste, plastics and paper. Besides, it was shown that about 55% of the bins contain could undergo methanogenesis and 25 % could be reused. We showed that 80 % of the waste bins contents could avoid landfilling. Regarding the BMP tests, results have shown that the fine elements produce the highest amount of CH₄ (373 NmL/gVS) followed by fermentable waste 283 (NmL/gVS), and some mixtures can reach also a good yield in methane. Simulated results have shown that the modified Gompertz models can be applied to our BMP results and are adapted to the hydrolysis of the easily biodegradable matter. Nevertheless, simulated results have also shown the limit of the model. Indeed, we proposed a modified superimposed first order model that give better results for wastes like paper, green wastes, and mixes of these elements. We have shown that co-digestion of all the wastes have a significant synergistic effect. However, the co-digestion of paper and cardboard shown a significant antagonistic effect. The experimental plan allowed to propose polynomial models to predict the efficiency of mixtures of influent in AD. Further work will allow us to evaluate the sensitivity of ADM1 model in evaluating the performances of anaerobic codigestion.

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