Biochemical Methane Potential (BMP) of Market Wastes from Nairobi Inoculated With Dagoretti Slaughterhouse Waste

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Biochemical Methane Potential (BMP) of Market Wastes from Nairobi Inoculated With Dagoretti Slaughterhouse Waste

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ABSTRACT

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Background: Anaerobic degradation entails the conversion of substrate organic matter to biogas. A wide variety of substrate has been employed. The biochemical methane potential of twenty market wastes was investigated using rumen fluid inoculum.

Experimental: The proximate properties like carbohydrates, crude proteins, crude lipids, fibre, and moisture levels were determined using standard procedures. The physio-chemical analysis was done to investigate the ash, total solids and volatile matter content. The substrates biogas production capacity based on elemental composition, COD, organic fraction composition was investigated. However, the BMP experiments were carried out at mesophillic conditions.

Results: The total biogas production was in the range of 1000 to 3500ml, with a methane composition of 56 – 60%. The biodegradability of the substrates ranges from 71 to 94%, subject to the lignin levels.

Conclusion: The BMP studies are vital in assessing the methane potential of the substrate without carrying out the experiments.

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Keywords : Biogas, Methane, rumen fluid, market wastes.

List of abbreviations and symbols

AD	-	Anaerobic Digestion
BMP	-	Biochemical Methane Potential
BD	-	Bio-degradability
COD	-	Chemical Oxygen Demand
OFC	-	Organic Fraction Composition
STP	-	Standard Temperature and Pressure
TS	-	Total Solids
VS	-	Volatile Solids

I. INTRODUCTION

The hypothetical CH_4 potential is broadly utilized to simulate the CH_4 generation of a particular degradable matter. The unit of BMP is milliliters of CH_4 at STP (mL CH_4 g^{-1}VS) conditions per amount of degradable matter or chemical oxygen demand added or removed. The BMP is calculated in numerous ways (Angelidaki and Sanders, 2004). The theoretical (BMP_{Th}) can be evaluated based on atomic composition or the organic fraction compositions (Angelidaki and Sanders, 2004). The general breakdown of substrate with carbon, hydrogen and oxygen content is shown in equation 1.

$$C_nH_aO_b + \left(n - \frac{a}{4} - \frac{b}{2}\right)H_2\vec{O}\left(\frac{n}{2} + \frac{a}{8} - \frac{b}{4}\right)CH_4 + \left(\frac{n}{2} + \frac{a}{8} - \frac{b}{4}\right)CO_2 \ldots\ldots\ldots\ldots\ldots..(1)$$

Buswell and Mueller, 1952 proposed a method of BMP determination based on the elemental composition analysis as shown in equation 2. The method entails empirical formulae ($C_aH_bO_cN_dS_e$) which can be designed from experimental elemental determination. The main assumption in this procedure is that substrates are converted to methane and carbon dioxide only (Buswell and Mueller, 1952).

$$B_{(ThAtc)} = \frac{\left(\left(\frac{a}{2}\right) + \left(\frac{b}{8}\right) - \left(\frac{c}{4}\right)\right) * 22400}{12a + b + 16c} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots.(2)$$

Where a,b,c,d are the mole coefficients. Whenever there is protein in the substrate, NH_3 and H_2S are among the products of anaerobic digestion as shown in equation 3 and therefore, Boyle's equation 4 is used instead of equation 2 (Boyle, 1976).

$$C_nH_aO_bN_xS_y + \left(n - \frac{a}{4} - \frac{b}{2} + \frac{3x}{4} + \frac{y}{2}\right)H_2O \rightarrow \left(n + \frac{a}{4} - \frac{b}{2} - \frac{3x}{4} - \frac{y}{2}\right)CH_4 + \left(n - \frac{a}{4} + \frac{b}{2} + \frac{3x}{4} + \frac{y}{2}\right)CO_2 + xNH_3 + yH_2S \ldots\ldots\ldots\ldots\ldots\ldots\ldots..(3)$$

$$B_{(ThAtc)} = \frac{22400 * \left(\frac{a}{2} + \frac{b}{8} - \frac{c}{4} - \frac{3d}{8} - \frac{e}{4}\right)}{12a + b + 16c + 14d + 32e} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots.(4)$$

The examination of the elemental content is moderately quick for all the substrates, in spite of the fact that this condition does not separate between biodegradable and non-biodegradable matter. A portion of the degradable matter is utilized by microbes for growth and, therefore, does not contribute to the BMP theoretical value (Lesteur et al., 2010).

Another method of BMP calculation is based on the organic fraction composition (OFC) analysis. In this case, the general equation 5 is employed:

$$BMP_{CHNO(OFC)} = 415 * \%carbohydrates + 496 * \%proteins + 1014 * \%lipids \ldots\ldots.(5)$$

The fractions of proteins, carbohydrates and crude fats are quantified as per the analytical procedures. The coefficients in equation 3 are obtained stoichiometrically and therefore, the general formula for carbohydrates, protein and lipids are $C_6H_{10}O_5$, $C_5H_7O_2N$ and $C_{57}H_{104}O_6$ respectively as described by Angelidaki and Sanders, 2004. Amon et al., 2007; Gunaseelan, 2007 and Schievano et al., 2008 have proposed some advanced regression models to calculate the BMP of a substrate from its chemical composition.

Based on the chemical oxygen demand (COD), 0.350 L CH_4 at STP or 0.395 L at 35^{0}C and 1atm can be generated from 1g COD depletd (COD_{rem}). The maximum methane potential can be calculated from the amount the COD concentration of the substrate using equation 6 (Tarvin and Buswell, 1934).

$$BMP_{thCOD} = \frac{n_{CH_4}RT}{PVS_{added}} \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots (6)$$

where BMP_{thCOD} is the theoretical production at laboratory conditions, R is the universal gas constant (R = 0.082 atm L/mol K), T is the temperature of the glass bottle (308K), p is the atmospheric pressure (1atm), VS_{added} (g) are the volatile solids of the substrate and nCH_4 is the amount of molecular methane (mol) determined from equation 7.

$$n_{CH_4} = \frac{COD}{64\left(\frac{g}{mol}\right)} \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots (7)$$

Raposo et al., 2009 reported that direct determination of COD in wastes is mostly erroneous. Studies have been carried out by comparing the proficiency tests of COD by inter-laboratory tests (Raposo et al., 2019). The COD analysis is vital in designing a digester as it helps in normalizing the results regardless of the volatile solid composition (Batstone et al., 2002). Equation 8 is applied to calculate the methane yield based on theoretical oxygen demand:

$$B_{o-ThCOD} = VSadded \cdot \left(g\frac{COD}{g}VS\right) \cdot 350 \dots\dots\dots\dots\dots\dots\dots\dots . (8)$$

The degradable matter in any given substrate can simply be estimated by calculating its theoretical oxygen demand (Th_{OD}) to obtain its methane potential. The same can be achieved using the empirical formula as described in VDI 4630 (2006) as illustrated in equation 9.

$$Th_{OD}(gO2 \cdot g^{-1}VS) = \frac{16\left((2a) + \left(\frac{b}{2}\right) - c - \left(\frac{3d}{2}\right)\right)}{12a + b + 16c + 14d} \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots (9)$$

The ISO/DIS 10 707(ISO/DIS, 10707(1994) is applied in calculating the Th_{OD}. Regardless of how Th_{OD} is estimated, the methane potential is obtained using equation 10.

$$B_{(0-ThOD)} = VSadded \cdot \left(g\frac{ThOD}{g}VS\right) \cdot 350 \dots\dots\dots\dots\dots\dots\dots\dots . . (10)$$

This research work investigates the BMP of twenty fruit and vegetable wastes calculated and compared to the experimentally obtained results. Two different mathematical models have been applied to simulate the expected methane yield from the market wastes.

II. Methodology

2.1 Analytical methods

Twenty market waste substrates were sampled from Wakulima and/or Kangemi market in Nairobi County. Size reduction was done by chopping with a kitchen knife and blending. Total solids (TS), volatile solids (VS) and ash content were determined by gravimetric method (Spellman, 2013). The ultimate composition (C, H, O, N, and S) of each substrate was investigated using an elemental (CHNS/O) analyzer. The modified Maynard methods of food analysis (Faithfull, 2002) was used to examine the crude fiber levels. Other proximate properties were as per the standard method in AOAC (1990) and Pearson (1976) and described by Onwuka (2005).

2.2 Calculations

Buswell and Mueller equations 1 and 2 were used to determine the theoretical methane yields (Buswell and Mueller, 1952). The proximate matter fraction used to calculate the theoretical CH_4 yields (BMP_{OFC}) were carbohydrate, lipids and crude proteins using equation 5 (Lesteur et al., 2010). Elemental anaerobic biodegradability (BD_{ele}) of the feedstock was calculated based on experimental BMP_{exp} and BMP_{CHNO} using as described by Raposo et al., 2011. Similarly, the experimental biodegradability (BD_{exp}) of the substrates was calculated based on initial and final VS values according to Nielfa et al., 2015.

2.2 Statistical analyses

All experiments were carried out in triplicate. All the measurable analysis was done using MS office Excel 2016 while plots were made using Minitab Statistical software and/or origin 8.0.

III. RESULTS AND DISCUSSION

3.1 BMP studies

The theoretical BMP of the individual market wastes was computed using equations 2, 4, 5 and 11 and the results given in Table 3.1

$$TBMP_{mlCH_4gVS^{-1}} = \frac{22.4 * \left(\frac{a}{2}+\frac{b}{8}-\frac{c}{4}-\frac{3d}{8}-\frac{e}{4}\right)}{12.017a+1.0079b+15.999c+14.0067d+32.065e} \dots\dots\dots (11)$$

The results obtained for BMP_{CHNO} and BMP_{OFC} are almost the same with slight variation. **TBMP $_{mlCH4gVS^{-1}}$** is highest compared to other methods employed in BMP calculations.

Table Error! No text of specified style in document..**1: Table of Experimental and theoretical BMPs**

SAMPLE	% CARB.	% PROTEIN	% FAT	BMP_{CHNO} (ml/g.VS)	BMP_{OFC} (ml/g.VS)	TBMP $mlCH4gVS^{-1}$	BMP_{thCOD}
Kales	31.12	21.68	3.22	269.33	236.7135	449.6350	67.30139
Cabbage	57.71	16.12	0.96	329.18	319.4614	491.6115	109.9541

Pumpkin Leaves	28.54	25.99	2.12	268.84	247.3729	452.9704	77.29398
Cucumis ficifolia	29.46	26.11	2.46	276.70	251.7895	492.8013	50.34303
Pigweed	20.39	22.98	1.83	217.15	198.6179	494.8469	66.33125
Erucastrum arabicum	26.38	26.57	1.85	260.02	241.283	502.3386	64.26722
Coriander	19.56	33.01	1.19	256.97	244.9157	494.5887	94.49666
A. nightshade	23.45	22.69	2.23	232.47	209.8825	503.2272	57.0536
Spinach	28.54	22.8	2.52	257.08	231.5546	501.9992	111.3876
Comfrey	24.37	21.71	1.98	228.89	208.8372	495.7319	47.94584
Tomato	55.42	11.89	2.57	315.02	288.9935	490.9395	116.9625
Potato	62.51	8.73	3.34	336.58	302.7512	454.7203	33.25288
Sweet Potato	46.76	4.42	4.07	257.24	216.0185	454.5800	14.28796
Pawpaw	62.9	6.36	3.15	324.52	292.6125	467.3760	49.55236
Banana	49.06	11.89	1.97	282.54	262.5934	451.7274	21.39028
Avocado	2.36	7.69	52.64	581.70	48.47017	456.3218	64.28575
Courgette	36.5	22.92	5.48	320.72	265.2138	930.5539	145.2442
Cucumber	48.13	12.65	5.19	315.11	262.5361	508.9576	325.9308
Mango	61.91	6.61	5.23	342.74	289.7651	1065.510	41.40575
Watermelon	49.34	12.72	4.63	314.80	267.8991	467.7762	84.05076
Waste Mixture	38.2205	17.277	5.43	299.38	244.3641	478.3047	51.14803

3.2 Biodegradability studies

The digestibility methods that had been indicated earlier, assumed that all the degradable matter is broken-down; as a consequence, a compensation of this assumption is made by the experimental BMP examination. The elemental biodegradability (BD_{ele}) of the substrate was estimated by equation 12 as described by Raposo, et al., 2011

$$BD_{ele} = \frac{BMP_{exp}}{BMP_{CHNO}} \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots (12)$$

Similarly, the BD_{exp} was determined by employing equation 13 based on the values of VS as previously highlighted by Nielfa, 2015.

$$BD_{expVS} = \frac{VS_i - VS_f}{VS_i} * 100 \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots (13)$$

The digestibility of the substrates based on the lignin levels (BD_{LB}) was calculated using equation 14 as described by Chandler et al., 1980.

$$LB = \left(0.83 - (0.028 * X_i)\right) * 100 \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots (14)$$

Where LB represents the digestible portion of VS which is in the range of 0<B<1, X_i is initial lignin in VS ($0<X_i<20\%$) for the model to be applied accurately. The results of biodegradability of the sample are shown in table 3.2.

Table Error! No text of specified style in document..**2 :** Table of biodegradability of the feedstocks.

Substrate	BD_{exp}	BD_{LB}	BD_{ele}
Kales	86.24±2.34	77.40±1.09	83.91±2.11
Cabbage	83.19±1.00	73.90±1.20	80.50±1.53
Pumkin Leaves	84.64±2.19	75.72±3.01	79.60±1.00
Cucumis ficifolia	77.36±3.99	71.81±3.00	81.98±1.54
Pigweed	85.88±0.99	68.36±1.26	81.51±1.64
Erucastrum arabicum	76.85±5.87	72.08±2.78	73.07±1.88
Coriander	85.43±0.89	69.28±2.89	77.83±1.93
A. nightshade	80.77±2.33	74.04±1.66	76.57±1.07
Spinach	80.00±1.50	74.88±2.06	77.80±0.87
Comfrey	86.96±7.00	71.80±1.96	78.64±1.90
Tomato	82.19±3.33	72.92±2.00	79.36±1.98
Potato	84.10±2.12	76.56±1.19	80.22±1.22
Sweet Potato	84.82±7.88	70.43±2.36	77.75±0.68
Pawpaw	84.73±5.63	76.56±1.88	77.04±0.89
Banana	86.27±5.73	74.04±2.05	75.74±1.45
Avocado	84.08±0.82	76.56±2.76	77.36±0.95
Courgette	77.16±1.26	68.16±1.33	74.83±1.55
Cucumber	78.26±3.56	69.28±1.25	76.16±1.67
Mango	81.95±0.99	77.12±2.89	79.07±1.88
Water Melon	76.61±.32	71.82±1.22	74.65±1.00
Mix	93.48±1.11	77.76±1.26	83.51±1.78

BD_{ele} describes the degree to which biomass is degraded and categorized into biodegradable and non-biodegradable. Due to undigested VS and chemical oxygen demand, the BD_{exp} was determined using equation 13. Similarly, in comparison with BD_{exp} and BD_{ele} as described in table 3.2, lignin-based (BD_{LB}) has shown the least degradability of the substrate. The BD order depended heavily on the fiber content of the lignin matter of the substrate. Lignin's existence determines the degree of BD andbiogas yields. This further implies that other organic content relates directly to biogas generation. It is observed that BD_{ele} was lower than BD_{exp} and BD_{LB}. The high levels of BD_{exp} means that some volatile matter is utilized for microbial growth and metabolism. The relationship between BD and lignin has shown that 1 percent of lignin reduces biomass degradability by about 3 fold. Slight differences in BD and BMP results are also observed, which may vary due to different plant conditions appropriate for AD i.e. temperature, flask gas-space size, inoculum, inoculum substrate ratio.

The obtained BMP experimental results were used to plot the time series plot in figure 3.1, which shows that wastes rich in carbohydrates have the highest biochemical methane potential.

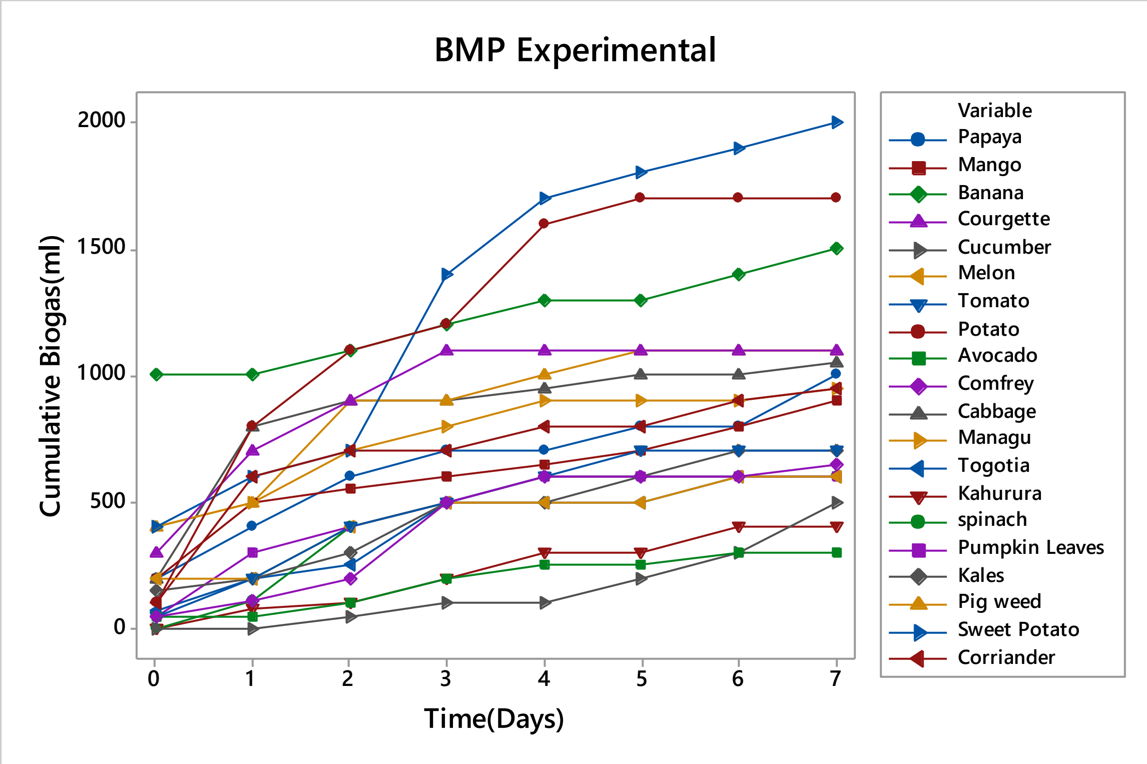

Figure Error! No text of specified style in document..**1:** The biochemical methane potential experimental results

3.3 BMP mathematical models

Different mathematical equations have been employed in the description of the kinetics of substrates digestion. Cecchi, et al., 1991 suggested that understanding the substrate conversion to methane capacity is based on its kinetics studies. In this section, two mathematical models were used in fitting the resultant data.

3.3.1 First-order model

The major assumption I this model is that gas production obeys 1st-order kinetics and therefore, exponential rise to a maximum as shown in equation k.1.

$$P = \gamma * (1 - exp(-\mu t)) \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots.(K.1)$$

Where P is methane production, γ is the accumulated biogas at time (t) (mlCH4/gVS) and μ the specific microorganisms growing speed m (d^{-1}).

3.3.2 Modified Gompertz model

This model is used to predict methane production on the assumption that biogas production is proportional to the microbial activity, as shown in equation (k.2). The kinetic data obtained from digestion of market wastes inoculated with rumen, blank rumen and blank mix were checked for their fitness on the modified Gompertz equation. The modified Gompertz equation is given by

$$P = \gamma_m . exp\left\{-exp\left[\frac{u.e}{\gamma_m}(\lambda - t) + 1\right]\right\} \ldots \ldots \ldots \ldots (K.2)$$

Where P is biogas production rate in ml/gm/day, t is digestion time in day, γ_m is the methane production potential in ml CH_4/g VS^{-1}; λ is the lag phase period(d), e is the Euler's number (2.71828), μ_m is the maximum biogas production rate (ml CH_4/g $VS^{-1}d^{-1}$). The parameters P, μ_m and γ_m were estimated for each of the digester using Excel solver software or Minitab statistical software. These parameters were determined for best fit.

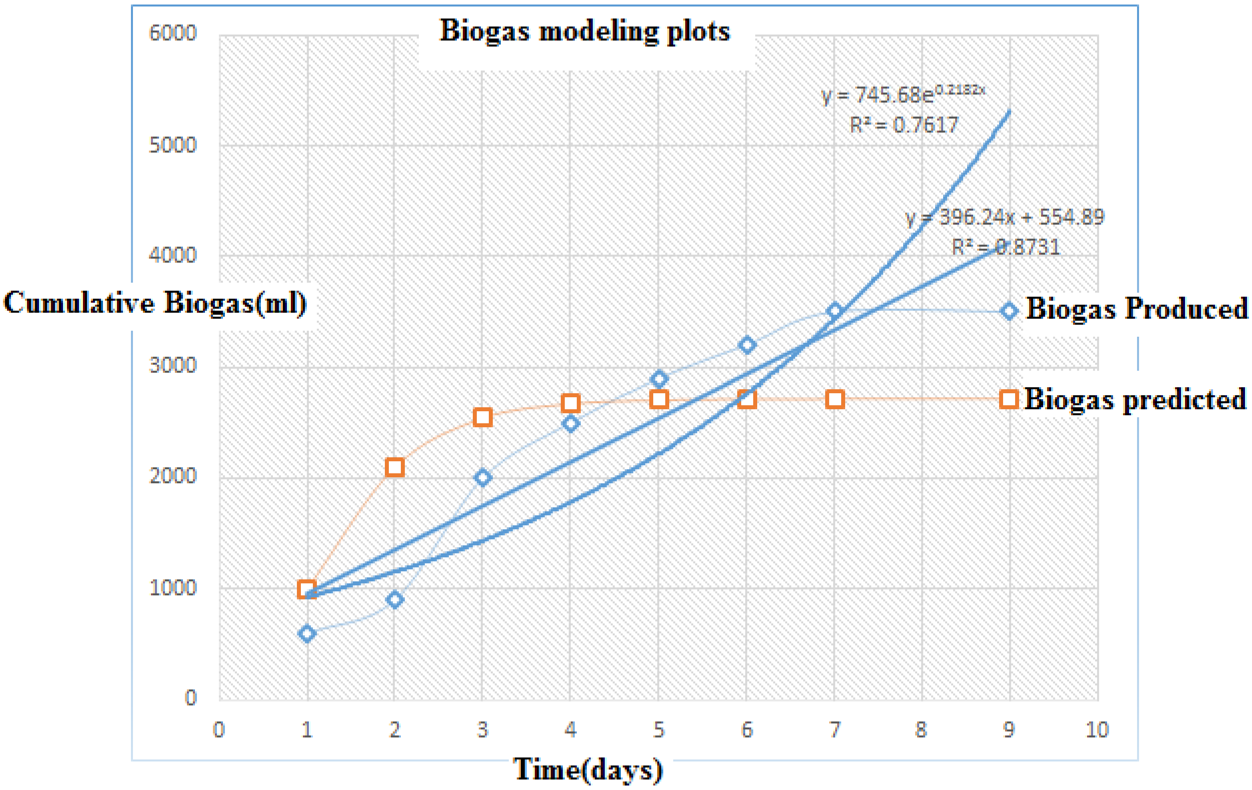

Figure Error! No text of specified style in document.**.2: Plots of biogas production models**

The two models were applied to the experimental results BMP to determine the best fitting equation for the market wastes and assess the parameters that influenced the AD process. The models were tested and at various points of the experiment the peak output of methane was expected. The final production of methane obtained from the experimental BMP assays was then compared to the peak output of methane (g) obtained by applying both models to the specific experiment points. Generally speaking, the Gompertz model fits the experimental values better than the first-order equation. Such models will account for 99 percent of the outcome of BMP.

IV. CONCLUSIONS

To sum up, utilization of strategies based on stoichiometric composition or organic fraction levels with data on biodegradability will provide reasonable estimates of different yields of methane with a lower error. For complex waste, utilization of COD methods to investigate biogas generation from waste is not comparable with the experimental results, though this approach describes co-digestion as the optimal mixture of obtaining higher productivity, as shown in the experimental results, while the other techniques don't show any increment for co-digestion. Similar results were obtained by Labatut et al., 2010 who study the BMP of complex substrates such as milk manure or maize silage.

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