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Theoretical methane production generated by the co-digestion of organic fraction municipal solid waste and biological sludge

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ABSTRACT

The co-digestion of two problematic and available wastes, namely Organic Fraction Municipal Solid Waste (OFMSW) and biological sludge, was carried out in this work. Biochemical Methane Potential (BMP) tests are a useful tool for determining the best substrate and co-digestion configurations, however there are some methodologies destined to save costs and time from this process by using the theoretical final methane potential of a substrate from its organic composition. Besides there are some models capable not only of reproducing the methane curve behavior, but also of predicting final methane productions from the first days of experimentation. Methodologies based in the elemental composition for the determination of theoretical production fit better with the experimental results and behavior, nevertheless the Gompertz model was capable of predicting the final productivity within the 7th day of experiment, selecting at the same time the co-digestion of 80% OFMSW and 20% Biological sludge as the optimum.

1. Introduction

In Spain about 18 million tons per year of organic fraction municipal solid waste (OFMSW) were produced during the year 2011 [20]. At the same time, the amount of biological sludge from waste water treatment plants (WWTP) is growing with the increase in the volume of treated wastewater, and the management of biological sludge has thus become an environmental and economic issue [29].

The anaerobic digestion (AD) of biological sludge and OFMSW contributes not only towards achieving the aim of the European directive [29], but also provides a route by which some of the energy inherent in this material can be recovered [28]. Moreover, the AD process offers the possibility to recycle nutrients, reduce greenhouse emissions, reduce odors and controlled waste disposal [2].

The anaerobic co-digestion of organic wastes has several advantages: the economical scale can increase as the quantity of waste increases; inhibitory compounds are diluted; the diversity of bacterial species increases due to the nutrition from a wide variety of organic wastes and helps stabilize a digester ecosystem [10,18]. The numbers of co-digestion plants are continuously increasing in many European countries and have become a standard practice [7].

Besides, researchers have been studying the co-digestion of OFMSW and biological sludge with different waste and mixture proportions; Hartmann et al. [19], consider the co-digestion of OFMSW and manure, establishing a mixture ratio of 50% VS as optimum, while Fernandez et al. [16], compare the co-digestion of OFMSW with fats from vegetable and animal origin. For biological sludge, its co-digestion with tanning residues were studied by Di Berardino and Martinho [14], revealing this to be technically feasible and economically advantageous and Komatsu et al. [23] obtained increases from 66% to 82% with the co-digestion of sewage sludge and rice straw using a mixture ratio of 1:0.5 based in TS.

Biological sludge and OFMSW are two available wastes with a high methane potential due to their high VS solid content, especially OFMSW, whose inherent problems derived from landfilling or incineration could be solved by the co-digestion process. Several studies had determined the optimum mixture ratio for these two substrates: Kim et al. [22] determine an optimum ratio of 50% VS for both substrates, Sosnowski et al. [33] define a 75% dw biological sludge and 25% dw for OFMSW as optimum, La Cour jansen et al. [25] explain how the mixture of 80% VS for sewage sludge and 20% for OFMSW is the best option and Cabbai et al. [9] studied ratios in volatile solids (VS) of 0.23 and 2.09 gVS/gVS for biological sludge with good results. Then, a depth study is needed, in order to optimize the substrates mixture ratio, the parameters involve in the biodegradation process and the kinetic parameters.

The biochemical methane potential (BMP) tests are applicable when used to expose which types of substrates, from a variety of

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Nomenclature

λ	Lag-phase parameter (days) from Gompertz model
γ	Maximum volume accumulated (mlCH_4/gVS) from Gompertz model
μ	Specific microorganisms growing speed (d^{-1})
α	Synergistic effect
AD	Anaerobic digestion
BD	Biodegradability
BMP	Biological methane potential
BMP_{th}	Theoretical BMP
bmp_{exp}	Experimental BMP
COD	Chemical oxygen cemand
COD_t	Total chemical oxygen demand
K	Kinetic parameter (mLCH_4/gVS/d) from Gompertz model
n_{CH_4}	Amount of molecular methane (mol)
OFMSW	Organic fraction municipal solid waste
P	Maximum biogas production parameter (mLCH_4/gVS) from Gompertz model
p	Atmospheric pressure (atm)
R	Gas constant (atm L/mol K)
T	Temperature (K)
t	Time (days) from Gompertz model
TS	Total solids
UVa	University of Valladolid
VS	Volatile solids
WWTP	Waste water treatment plant

possibilities, have the highest biochemical potential. In addition BMP assays can be used to estimate the optimum ratios between co-substrates when co-digestion is intended [24].

Waste has a complex composition which is difficult to describe in detail but can be readily analyzed by bulk chemical processes [2]. Some works have concluded that the organic matter composition in the substrates has a strong impact on AD performances, showing the existence of a relationship between the quantity of methane produces and the organic matter used, not only the biodegradable fraction but also the non-biodegradable fraction [27]. Examples of approaches for obtaining quick BMP results include the use of empirical relationships based on the chemical and biochemical composition of the material [34]. The theoretical methane potential is widely recognized in order to give an indication of the maximum methane production expected from a specific waste [2], although the experimental methane yields are often much lower than theoretical yield due to the difficulty in degrading tightly lignocellulosic material [30]. Several methods could help to determine theoretical methane potentials based on chemical oxygen demand (COD) characterization [35]; elemental composition [32] or organic fraction composition [27]; however, these methods do not provide any information about the kinetic parameters involved in the process.

It is commonly known that well-controlled batch degradation follows certain patterns that can be modeled using a mathematical expression. Therefore, another way to obtain quick BMP results, which includes the kinetic information, is the use of mathematical prediction models [34].

The objective of this research paper is to present and evaluate strategies for predicting the BMP of the co-digestion of OFMSW and biological sludge using several approaches and two mathematical models, to save time and costs derived from the BMP tests, and to optimize the co-digestion ratios for these two substrates for subsequent experiments in full scale digesters.

2. Materials and methods

Several experiments were carried out using BMP tests at mesophilic conditions in order to evaluate the optimum ratio for the co-digestion of OFMSW and biological sludge, and thus estimate the increase or diminution of productivity from the sole substrates. A variety of co-digestion mixtures were selected for this work in order to cover all the possibilities that allow co-digestion in both real WWTP or waste treatment plants, in order to achieve the optimum conditions for obtaining the best productivity and kinetics.

2.1. Substrates and co-digestion mixtures

A synthetic substrate simulating the OFMSW and a biological sludge from the WWTP were used for the assays. In order to avoid the heterogeneity that real OFMSW can offer and thus evaluate the optimum mixture ratio for these two substrates, a synthetic OFMSW was considered. This synthetic fraction was composed of several organic and inorganic materials. The proportions of mixture were determined from previous studies in which the use of synthetic mixture obtained good results [6]. A typical characterization of a real OFMSW can be observe in Table 1.

The co-digestion of biological sludge and OFMSW has been considered by some authors without existing an agreement according to the optimum mixture, then a large range of ratios have been considered in this study using weight percentages to get the desired mixtures. The concentration of each co-digestion has not being modified in order to study the problems derived of the TS concentration.Table 2 shows the four different co-digestion mixtures that were considered in this work.

A full characterization of the substrates, co-digested mixtures and the inoculum used for the experiments are presented in Tables 3 and 4. The characterization of the co-digestion mixtures was obtained from the theoretic mixture of the sole substrates OFMSW and biological sludge.

2.2. Analytical methods

The main characterization of the inoculum and the co-substrates was accomplished following an internal method of the University of Valladolid (UVa) based on standard methods [3]. Total and volatile solids (TS, VS) and total chemical oxygen demand (CODt) were determined.

To calculate the theoretical potential using several methodologies, an extended characterization is necessary performed by external laboratories. Gravimetric techniques were used to determine grease content [15,12] and gross fiber (Weende Method), volumetric procedures [12] for carbohydrate content, and elemental analyses [31] for protein content and elemental composition.

2.3. Experimental biochemical methane potential (BMP) tests

The BMP assays were performed following an internal method from the UVa based on standardized assays for research purposes

Table 1
MSW typical characterization.

CODt	g/kg	542
CODs	g/kg	92
TS	g/kg	468
VS	g/kg	394
pH[a]		7.8
Phosphorus[a]	dw%	0.002
Sodium[a]	dw%	4.8
Potassium[a]	dw%	0.35

[a] Source: [38].

Table 2
Substrates for BMP and ratios of mixture.

SUBSTRATES	OFMSW/biological sludge % weight	OFMSW/biological sludge % VS
Biological sludge	–	–
OFMSW	–	–
Co-digestion 1	80/20	96/4
Co-digestion 2	60/40	91/9
Co-digestion 3	40/60	82/18
Co-digestion 4	20/80	63/37

[1]. The substrate and the inoculum were placed in a glass bottle of 2 L capacity at mesophilic conditions following a substrate/inoculum ratio of 1/1 in terms of VS. Micronutrients and macronutrients were added in order to ensure the activity of the inoculum [17]. Mesophilic inoculum coming from a reactor fed with mixed sludge was used for all the assays and finally the bottles were closed and placed in a rotational stirrer which mixed the substrate and inoculum perfectly.

Triplicates were carried out for these experiments including a blank, which indicated the productivity of the inoculum, in order to obtain the production of the sole substrate, and a control with cellulose to verify the activity of the inoculum. Periodical monitoring analyses of biogas production and composition were performed during the assays using a pressure meter and gas chromatography. The BMP were finished when a dairy production of less than 1% of the whole production occurred as it is indicated in Eq. (1) where "*n*" represents the day of the experiment.

$$\text{Production}\% = \left(\left(\frac{\text{Gross prod(ml)}_n - (\text{Gross prod(ml)}_{n-1})}{\text{Gross prod(ml)}_n}\right) \times 100 \right. \quad (1)$$

The results provided by the BMP assays were obtained from the triplicate average for each bottle and were expressed as the net volume of methane per g of VS added (mlCH4/gVSadded). A standard deviation is also calculated in order to identify the error among triplicates.

2.4. Theoretical BMP

The methods described below are designed to easily determine the methane productivity of a specific substrate from its COD characterization, elemental composition or organic fraction composition in order to obtain reliable results quickly and get an economic advantage. These methods are applied considering that all the organic material is degraded; therefore a proper adjustment of this value is necessary, using the biodegradability obtained from the experimental BMP tests. The methane potential is expressed as $mlCH_4$ at standard temperature and pressure conditions per amount of organic material added (VS).

2.4.1. Chemical oxygen demand (COD)

The maximum methane potential can be calculated from the amount of material and the COD concentration of the test using Eq. (2), assuming that this equation is valid for any substance or product [35]. This equation gives the theoretical value of methane at laboratory conditions:

$$\text{BMP}_{\text{thCOD}} = \frac{n_{CH_4}RT}{pVS_{\text{added}}} \quad (2)$$

where $\text{BMP}_{\text{thCOD}}$ is the theoretical production at laboratory conditions, R is the gas constant (R = 0.082 atm L/mol K), T is the temperature of the glass bottle(308 K), p is the atmospheric pressure (1 atm), VS_{added} (g) are the volatile solids of the substrate and n_{CH_4} is the amount of molecular methane (mol) determined from Eq. (3)

$$n_{CH_4} = \frac{\text{COD}}{64(\text{g/mol})} \quad (3)$$

2.4.2. Elemental composition analysis (C, O, H and N)

The stoichiometric equation based on the atomic composition of the waste material ($\text{BMP}_{\text{thAtC}}$), is also used to calculate the theoretical methane composition by taking into account the elements C, O, H and N (Table 3). The presence of proteins and ammonia are considered in Boyles Eq. (4) ([32]):

$$C_nH_aO_bN_c + \left(n - \frac{a}{4} - \frac{b}{2} + \frac{3c}{4}\right)H_2O \rightarrow \left(\frac{n}{2} + \frac{a}{8} - \frac{b}{4} - \frac{3c}{8}\right)CH_4 + \left(\frac{n}{2} - \frac{a}{8} + \frac{b}{4} + \frac{3c}{8}\right)CO_2 + cNH_3$$

$$\text{BMP}_{\text{thAtC}} = \frac{22.4(n/2 + a/8 - b/4 - 3c/8)}{12n + a + 16b + 14c} \quad (4)$$

The determination of the elemental composition is relatively fast for all the compounds, although this equation does not differentiate between biodegradable and non-biodegradable matter, and part of the biodegradable organic matter used by the bacteria to grow does not contribute to the BMP theoretical value [27].

2.4.3. Organic fraction composition (OFC) analysis (grease, carbohydrate, protein and fiber content)

The use of the organic fraction composition to calculate the theoretical production ($\text{BMP}_{\text{thOFC}}$) is a good method in which the

Table 3
Substrates and co-digestions main characterization. dw: dry weight.

	TS g/kg	VS g/kg	CODt g/kg	C dw%	H dw%	O dw%	N dw%	C/N
Biological sludge	69.8	56.9	77.1	5.4	9.1	36.4	0.6	8.9
OFMSW	467.9	393.5	542.2	20.3	7.8	31.0	0.4	51.8
Co-digestion 1	388.3	326.2	449.2	17.3	8.0	32.1	0.4	39.8
Co-digestion 2	308.6	258.9	356.2	14.4	8.3	33.2	0.5	29.9
Co-digestion 3	229.0	191.5	263.2	11.4	8.6	34.3	0.5	21.7
Co-digestion 4	149.4	124.2	170.1	8.4	8.8	35.3	0.6	14.8
Inoculum	31.78	19.72	31	–	–	–	–	–

Table 4
Substrates and co-digestion organic characterization.

	Lipid dw%	Carbohydrate dw%	Protein dw%	Fiber dw%
Biological sludge	0.18	0.00	6.44	0.35
OFMSW	0.47	6.95	4.23	35.13
Co-digestion 1	0.41	5.55	4.71	28.14
Co-digestion 2	0.36	4.16	5.19	21.16
Co-digestion 3	0.30	2.76	5.66	14.18
Co-digestion 4	0.24	1.37	6.10	7.22

easily biodegradable compounds such as carbohydrates, lipids and proteins and the poorly biodegradable compounds as fiber are taken into account. Bushwell's formula indicates the amount of methane provided by the different compounds which follow the next general Eq. (5) [27]:

$$BMP_{thOFC} = 415 \times \%carbohydrates + 496 \times \%proteins + 1014 \times \%lipids \quad (5)$$

Even though this method can predict the ultimate methane yield, the chemical composition is obtained using chemical methods, taking less time than a full BMP test but still being time-consuming, requiring anything from several hours to several days.

2.4.4. Experimental biodegradability and relative error

The previously explained methods worked under the consideration that all the organic material was degraded, thus a proper adjustment of this value was needed, using the biodegradability obtained from the experimental BMP tests. Then, once the experimental assays had finished the biodegradability of the substrates and co-digestions were analyzed in order to evaluate the level of anaerobic biodegradability under the defined test conditions. To calculate the experimental biodegradability (BD_{exp}) the next Eqs. (6) and (7) have been established, using the initial and final volatile solids and chemical oxygen demand added (VS_0,VS_f, COD_0 and COD_f) for each substrate or co-digestion. The BD_{expCOD} based on the COD will be applied to the COD methodology and the BDexpVS based on the VS will be applied for the elemental and organic fraction composition methodologies.

$$BD_{expVS}(\%) = \left(\frac{(VS_0 - VS_f)}{VS_0}\right) \times 100 \quad (6)$$

$$BD_{expCOD}(\%) = \left(\frac{(COD_0 - COD_f)}{COD_0}\right) \times 100 \quad (7)$$

Finally, to evaluate the consistency of the methods describe below, the deviation between the experimental production BD_{exp} and the theoretical production with the adjustment of the experimental BMP_{thBD} is calculated to obtain the relative error according to Eq. (8):

$$error = \frac{BMP_{exp} - BMP_{thBD}}{BMP_{exp}} \quad (8)$$

2.5. BMP mathematical models

Mathematically, the degradation rate of each group of compounds can be described by a differential kinetic equation. The knowledge of the biodegradation kinetics and methane production could be helpful for the methane prediction of a specific substrate [11]. In this work, the ability to predict the methane potential of the co-substrates and co-digested mixtures was evaluated by two mathematical models applied to the experimental BMP tests.

The prediction models consider the experimental biodegradability of the substrate during the process, but there is also a relative error that should be calculated (Eq. (8)) in order to establish the perfect conditions and models which fit with the experimental results.

2.5.1. First-order model

This simplified model assumes that the gas production follows first order kinetics in which biogas accumulation was simulated using exponential rise to a maximum [5]:

$$P = \gamma * (1 - \exp(-\mu t)) \quad (9)$$

Two parameters are necessary for the prediction of the methane production (P); the maximum volume accumulated at an infinite digestion time (t) γ ($mlCH_4/gVS$) and the specific microorganisms growing speed μ (d^{-1}).

2.5.2. Modified Gompertz model

Assuming that the biogas production is proportional to the microbial activity, the following modify Gompertz Eq. (10) is used to predict the methane production. This model was originally set to describe the growth of bacteria in batch mode [26].

$$P = \gamma \exp\left(-\exp\left(\frac{K(\lambda - t)e^1}{\gamma} + 1\right)\right) \quad (10)$$

Three parameters are needed for the prediction of the methane production (P); the maximum volume accumulated at an infinite digestion time (t) γ ($mlCH_4/gVS$), the specific rate constant K ($mlCH_4/gVS/d$) and the lag phase time constant λ (d).

2.6. Synergistic effects

BMP prediction methodologies could give an idea of the results obtained by the experimental process but there will always be inner reactions produced by the co-digestion of the different components. These reactions are called synergistic effects. To evaluate the influence of each substrate in the different mixtures and calculate the possible synergistic effects that could be produced during the biodegradation process the subsequent Eq. (11) was used:

$$\alpha = \frac{\text{Experimental production}}{\text{Theoretical production}} \quad (11)$$

The "experimental production" is the result of the BMP tests for each co-digestion mixture while the "theoretical production" is the theoretical value obtained from the BMP of the sole substrates considering the VS of each substrate contained in the final mixture. The result of α indicates:

- $\alpha > 1$; the mixture has a synergistic effect in the final production.
- $\alpha = 1$; the substrates work independently from the mixture.
- $\alpha < 1$; the mixture has a competitive effect in the final production.

3. Results and discussion

3.1. Experimental BMP

The experimental results were obtained after a period of 39 days when the BMP assays ended with a dairy production of less than 1%:

Fig. 1 shows the productivity during all the experiment for the sole substrates (OFMSW and biological sludge) and its co-digestion mixtures. The standard deviation calculated from the results of the triplicates is also represented showing the consistency of the experiments.

Similar final productivities were obtained for all the co-digestions of biological sludge and OFMSW. Co-digestion 1 obtained the best productivity values (221 $mlCH_4/gVS$) for the BMP tests followed by the next co-digestion configurations 2 and 3 with 217 $mlCH_4/gVS$ and 212 $mlCH_4/gVS$ respectively. All these mixtures obtained higher values than the sole substrates OFMSW and biological sludge, while co-digestion 4 just achieved a 22% increase from the biological sludge production as sole substrate. Although biological sludge achieves the lowest production, the

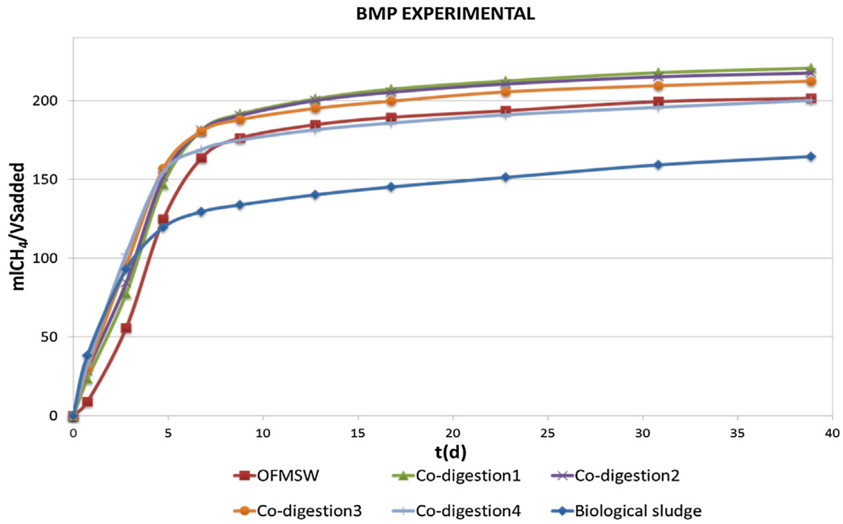

Fig. 1. BMP results for all the substrates and co-digestions.

methane content is higher than in both OFMSW and the co-digestions, obtaining values of over 60% for methane composition from the third day while the other substrates did not achieve 60% methane during the whole experiment.

One of the objectives of this work is to find the optimum mixture for the co-digestion of biological sludge and OFMSW, which will be the co-digestion that increases its productivity from both sole substrates (OFMSW and biological sludge) to the maximum. Co-digestions 1, 2 and 3 increase the productivity of OFMSW and biological sludge, even though co-digestion 1 achieve the best results with an increase of 9% for OFMSW and 34% for biological sludge. Then we can confirm that the configuration used for co-digestion 1 (80% OFMSW and 20% biological sludge) is the optimum, however all the co-digestion mixtures achieve productivities over the sole substrates indicating that the co-digestion of OFMSW and biological sludge could be a good opportunity to enhance both substrates.

3.2. Theoretical BMP

The ability of the theoretical methodologies to accurately estimate methane yields of complex substrates was evaluated by comparing the experimental productivity from the BMP tests with the theoretical productivity obtained from the different methodologies. Table 5 represents the experimental BMP results and biodegradability (BMP_{exp} and BD_{exp}), the theoretical results obtained for each methodology (BMP_{th}) and the theoretical results previously corrected using the experimental biodegradability (BMP_{thBD}). However the experimental biodegradability cannot be applied to the COD methodology as it was determine from de VS of the. Also the relative error is obtained from the Eq. (8) comparing the BMP_{exp} and BMP_{thBD}.

For the COD Eq. (2) the theoretical production (BMP_{th}) follows the same behavior for biological sludge and OFMSW as the experimental results, where higher productivity was achieved by the OFMSW with a COD of 542 g/kg than the biological sludge (77.1 g/kg COD). In the co-digestion mixtures the productivity decreases with the COD content and the co-digestion mixture productivities do not surpass the productivity of the sole substrates, although when applying the experimental biodegradability (BMP_{thBD}) the behavior changes, increasing the productivity for all the co-digestion mixtures from the sole substrates as occurs in the experimental results. The highest errors are obtained for this method with agreements lower than 90%.

Despite the fact that the theoretical results obtained for the elemental composition equation method follows behavior similar to the previous method and the experimental results, the values are lower, but it gets agreements higher than 90%. However the co-digestion mixtures get similar increases from the sole substrates OFMSW and biological sludge for co-digestion 1, while co-digestions 2, 3 and 4 increase only from the sole biological sludge. In this case the theoretical productivity decreases in those substrates with higher hydrogen and nitrogen presence, which can produce toxic concentration of ammonia and hydrogen sulfide [8]. It is also observed that the productivity increases with the rise of the COD and with the increase of the C/N ratio (Table 3). Some researchers have suggested that the C/N ratio for optimum digestion performance is in the range of 20–30, while many have demonstrated that digestion can be successfully performed using a wider range of C/N ratios [13,37].

The organic fraction composition Eq. (5), obtains prediction results with a relative error % below 10%. The productivity increases with the proportion of lipids, as lipids exhibit a much higher biogas potential (1 m^3 per kg of volatile solids) than carbohydrates, proteins

Table 5
Experimental and theoretical results based on different methodologies. E: error; BS: biological sludge; Co-d: Co-digestion.

	Experimental results			COD composition			Elemental composition			Organic fraction composition		
	BMP_{exp} mlCH4/gVS	BD_{expCOD} %	BD_{expVS} %	BMP_{th} mlCH4/gVS	BMP_{thBD}	E %	BMP_{th} mlCH4/gVS	BMP_{thBD}	E %	BMP_{th} mlCH4/gVS	BMP_{thBD}	E %
BS	164.5 ± 4	36	45	535.8	193.0	−17	333.9	150.2	9	338.2	152.2	7
OFMSW	201.5 ± 11	43	42	544.3	234.0	−16	494.3	207.6	-3	546.1	229.3	−14
Co-d1	220.6 ± 6	48	45	543.9	261.0	−18	465.8	209.6	5	506.3	227.8	−3
Co-d2	217.5 ± 1	47	45	543.5	256.1	−18	435.6	196.0	10	466.2	209.8	4
Co-d3	212.3 ± 4	45	48	542.8	244.6	−15	403.7	193.8	9	425.8	204.4	4
Co-d4	200.2 ± 2	44	48	541.2	239.6	−20	369.8	177.5	11	384.3	184.5	8

or cellulose [36], nevertheless their kinetics are slower with higher fiber percentages (Table 4). Applying the biodegradability of the experimental results, none of the co-digestion mixtures exceed the productivity of the sole OFMSW. Otherwise the experimental results showed a different behavior, meaning that the synergistic effects could play an important role in the biodegradability of the co-digestion of these two substrates.

In summary it is apparent that the use of methods based on the stoichiometric composition or organic fraction composition with biodegradability information are able to produce reasonable estimations of specific methane yields with lower error. For these complex wastes the use of COD methods to estimate anaerobic digestion does not fit with the experimental results, although this method outlines co-digestion 1 as the optimum mixture for obtaining higher productivities as is indicated in the experimental results while the other methodologies practically do not show any increases for the co-digestions. Labatut et al. [24] obtained similar results studying the BMP of complex substrates such as dairy manure or corn silage.

3.3. BMP mathematical models

Two different models first-order model (FO) and Gompertz model (GM) were applied to the experimental BMP results to determine the optimum equation to fit with these kind of wastes and evaluate the parameters that had influence on the anaerobic digestion process. Both models were studied and the maximum methane production was predicted in diverse points of the experiment (3, 7, 13, 23 and 39 days). The final methane production achieved from the experimental BMP assays was then compared with the maximum methane production (γ) obtained by applying both models to the different points of the experiment (Table 6).

Generally the Gompertz model fits better than the first-order equation for the experimental values, with the exception of biological sludge and co-digestion 4, which has a high biological sludge content (80%) that is better suited with the first-order model. These models can explain 99% of the BMP results.

Similar kinetics are observed between the sole substrates and mixtures in both models, although it is noticed a growth of K and μ was noted with the increase in the proportion of biological sludge in the co-digestion mixtures. The same behavior occurs with the lag phase parameter that decreases with the diminution in the proportion of biological sludge. In this manner the model results indicate co-digestion 4 is the substrate that is more easily biodegradable and has quicker biodegradability periods.

During the first 3 days the kinetics and productivities are better for biological sludge, and the methane production of the mixtures increases with the proportion of biological sludge.

Table 6
Results of the prediction models at different days. The numbers in bold indicate % error less than 10%. BS: biological sludge; Co-d: Co-digestion.

Time (d)	γ(ml/gVSadded)		Error (%)		r^2		Kinetic parameters		
	FO	GM	FO	GM	FO	GM	FO	GM	
							$\mu(d^{-1})$	$K(mlCH_4/gVS/d)$	$\lambda(d)$
BS	BMP experimental: 164.49 ml/gVS added								
3	125.24	134.75	23.86	18.08	1.00	0.99	0.48	35.86	0.00
7	138.13	134.75	16.02	18.08	1.00	0.99	0.41	35.86	0.00
13	151.54	134.75	**7.87**	18.08	0.99	0.99	0.32	35.86	0.00
23	144.48	140.96	12.17	14.30	1.00	0.98	0.36	33.74	0.00
39	151.54	148.11	**7.87**	**9.96**	0.98	0.96	0.32	31.42	0.00
OFMSW	BMP experimental: 201.46 Nml/gVS added								
3	2035.38	57.61	−910.31	71.41	0.99	1.00	0.01	140.39	0.56
7	3604.65	192.98	−1689.26	**4.21**	0.99	1.00	0.01	36.08	1.20
13	230.96	185.62	−14.64	**7.86**	0.97	1.00	0.15	37.19	1.25
23	203.11	189.27	**−0.82**	**6.05**	0.97	1.00	0.19	35.89	1.18
39	201.86	193.70	**−0.20**	**3.85**	0.98	1.00	0.19	34.40	1.10
Co-d1	BMP experimental: 220.62 Nml/gVS added								
3	272.47	78.09	−23.50	64.61	1.00	1.00	0.12	73.11	0,43
7	581.40	211.71	−163.53	**4.04**	0.99	1.00	0.06	36.53	0,58
13	229.80	202.47	**−4.16**	**8.23**	0.98	1.00	0.19	37.39	0,59
23	217.36	206.97	**1.48**	**6.19**	0.99	1.00	0.22	36.27	0,55
39	218.36	211.76	**1.02**	**4.01**	0.99	0.99	0.21	35.04	0,49
Co-d2	BMP experimental: 217.52 Nml/gVS added								
3	170.69	84.77	21.53	61.03	1.00	1.00	0.24	82.51	0.40
7	371.96	206.68	−71.00	**4.98**	0.99	0.99	0.10	36.74	0.39
13	221.79	200.63	**−1.96**	**7.76**	0.99	1.00	0.22	37.27	0.40
23	213.58	204.95	**1.81**	**5.78**	0.99	1.00	0.23	36.22	0.36
39	214.11	209.33	**1.57**	**3.76**	0.99	0.99	0.23	35.12	0.31
Co-d3	BMP experimental: 212.32 Nml/gVS added								
3	267.42	96.06	−25.95	54.75	1.00	1.00	0.16	90.89	0.42
7	279.11	203.00	−31.46	**7.69**	1.00	1.00	0.16	39.69	0.30
13	209.77	194.51	**1.20**	**8.39**	0.99	1.00	0.26	39.81	0.30
23	205.92	198.87	**3.02**	**6.33**	0.99	1.00	0.27	38.61	0.27
39	208.14	203.27	**1.97**	**4.26**	0.99	0.99	0.26	37.34	0.22
Co-d4	BMP experimental: 200.15 Nml/gVS added								
3	265.24	103.16	−32.52	48.46	1.00	1.00	0.18	97.84	0.42
7	214.85	176.86	**−7.35**	11.63	1.00	0.99	0.24	41.51	0.19
13	189.10	178.98	**5.52**	10.58	0.99	1.00	0.31	40.90	0.18
23	189.07	183.63	**5.54**	**8.26**	1.00	0.99	0.31	39.40	0.15
39	192.74	188.63	**3.70**	**5.76**	0.99	0.99	0.29	37.69	0.10

However after the 7th day the behavior changes and the co-digestion mixtures' productivity increases with the proportion of OFMSW. This performance could be explained by the fact that biological sludge contains easily biodegradable material while OFMSW has less readily biodegradable material, such as fiber, which makes the process slower at the beginning. Therefore, we can confirm that the lag phase of the Gompertz equation is related to the fiber content, increasing with the proportion of this material as is the case of OFMSW, which has a higher lag phase but is still negligible.

For the OFMSW and the co-digestion mixtures, the Gompertz Eq. (10), is capable of predicting the final productivity in the first 7 days with a relative error of less than 8% and less than 5% in some of the cases (OFMSW, co-digestion 1 and 2) (Table 6). Otherwise, the first order model can predict the BMP experimental results just from day 23 but with a relative error below 5%. There is also a point for the OFMSW substrate where the first order model can predict the productivity at 23 days with 0.8% of error, even though the r^2 for this model is 0.97 which made the results slightly uncertain.

Considering the Gompertz productivity results for the sole substrates and co-digestion mixtures at the seventh day, it is noticeable that the increase in the productivity for the co-digestion mixtures from the OFMSW is the same as in the final production.

3.4. Synergistic effects

Co-digestion of certain substrates can produce synergistic or antagonistic effects. The synergism would be seen as an additional methane yield for co-digestion samples over the weighted average of the individual substrates. Similarly, evidence of antagonism would be translated into a lower methane yield in the co-digestion samples when compared with the expected ones. The synergistic effects may appear from the contribution of additional alkalinity, trace elements, nutrients, enzymes, or any other improvement which a substrate by itself may lack, and could result in an increase in substrate biodegradability and therefore methane potential. Competitive effects can come from several factors such as pH inhibition, ammonia toxicity or high volatile acid concentration. Table 7 shows the synergistic and antagonistic effects produced by the co-digestion of biological sludge and OFMSW. The theoretical productions of the co-digestion mixtures are obtained from the productivity of the sole substrates taking into account the VS of each substrate.

While similar co-digestion studies were found with antagonistic effects for mixtures with 5%, 15% and 25% weight of biological sludge [4], the results of the BMP tests for this research work indicate a synergism between the two substrates increasing the effect with the addition of OFMSW. These results may explain the theoretical productivities obtained by the prediction methodologies, in which the experimental results did not follow the same behavior as the experimental ones. The use of co-substrates as biological sludge and OFMSW together are a good option to obtain an increase in the productivity of the sole substrates and take advantage of easily available wastes.

Table 7
Results of the synergistic or antagonistic effects produced by the co-digestion.

	Experimental production	Theoretical production	α
Biological sludge	164.49 ± 4	164.49	–
OFMSW	201.46 ± 11	201.46	–
Co-digestion 1	220.62 ± 6	200.17	1.102
Co-digestion 2	217.52 ± 1	198.21	1.097
Co-digestion 3	212.32 ± 4	194.87	1.090
Co-digestion 4	200.15 ± 2	187.92	1.065

4. Conclusions

The experimental results indicate that all the co-digestion mixtures increased the productivity from the sole substrates, offering the opportunity of co-digestion of these two wastes in different circumstances. Nevertheless, co-digestion 1 (80% OFMSW and 20% biological sludge) obtained the highest increase, for OFMSW sole substrate in 9% and 34% for biological sludge.

In-depth knowledge of the organic composition of a substrate could be helpful for the prediction of the methane potential and biodegradability of different substrates. Otherwise, the prediction models could explain the final behavior and kinetics in just seven days using the Gompertz model, determining the kinetics of the process, pointing out the best co-digestion configuration and saving time and costs, with great reliability.

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