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Biochemical potential of methane (BMP) of camelid waste and the Andean region agricultural crops

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ABSTRACT

This paper evaluates the anaerobic digestion of agricultural waste, manure and slaughterhouse residues of species typical of the Andes, such as llama, vicuña and guinea pig; quinoa, amaranth and wheat straw in order to be able to use them as a renewable energy source and boost rural development in the region. Has been used sludge from a WWTP as inoculum, evaluating the effect of two relationships between the substrate and inoculum (RSI) for both livestock and agricultural waste. The highest cumulative maximum methane production rate was obtained for the residues of flame manure and quinoa straw for an RSI of 1:2 with productions of 376.08 ml CH_4/g SV and 377.02 ml CH_4/g SV respectively. In these materials an RSI of 1:2 obtained increases of 22.56% and 37.54% compared to the RSI 1:1. Also, the kinetic analysis showed that the modified Gompertz model is the one that best fits performance, with constant differences of 7.06% between the experimental and predicted values. On the other hand, the modified Gompertz model was adjusted to the experimental results with an r^2 of (0.998) and an RMSE of 4.09 ml/g SV at 17.12 ml/g SV.

1. Introduction

In recent years, waste management and renewable fuels demand are important challenges that need study and analysis [1,2]. Manure and slaughterhouse livestock residues, as well as agricultural residue from various crops generate large amounts of waste with enormous energy potential if treated through anaerobic digestion as a methane production source [3].

The Andean mountainous area of Latin America covers Colombia, Ecuador, Peru and Bolivia, eminently comprising a large cattle and agricultural area. In this zone, livestock production is made up of autochthonous animals such as vicuñas and guanacos (whose management is not barn), and llamas, bobbins and guinea pigs that are managed on farms. Despite livestock production being supplemented with amaranth, quinoa and wheat crops, the area lacks of an efficient energy supply. That is the reason why anaerobic digestion seems to be one of the most promising bioenergy technologies for rural development [4].

Anaerobic digestion (AD) is a process that involves the transformation of organic matter into biogas (60–70% methane and 30–40%) carbon dioxide [5,6]. Despite the fact that this process has been known for a long time, nowadays, there are still new raw materials, susceptible to fermentation, that need to be evaluated through the biochemical potential of methane (BMP) to obtain methane [7,8].

The present study addresses the AD through the BMP tests of three agricultural residues that are produced in the Andean area: amaranth straw (AS), quinoa straw (QS) and wheat straw (WS); and four livestock residues: manure of llama (LM), vicuña (VM) and guinea pig (GPM), and slaughterhouse waste (SW). These resources are easily accessible in this area. The excrements of the stable's animals were periodically removed from the farms for sanitary reasons. They usually pile up in free areas where compost is formed. On the other hand, even though vicuñas are not established and live free in the Andean area, they deposit their droppings in specific well-located areas where farmers can easily pick them up with shovels or even mechanical means. However, despite their availability, the fermentative potential of these resources as a source of energy has not been sufficiently evaluated.

Since there are more than 3 million camelid heads spread throughout the Andean region (CM), mainly LM (domesticated

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species) and VM (wild species) [9] its manure becomes a potential source for AD. Besides, CM manure has traditionally served as energy source in the Andean countries, being used for cooking instead of firewood. Further, in the Bolivian antiplane 89% of its inhabitants use manure as fuel, of which 92% is llama manure [10] easily collected since CM defecate in established identifiable places [11]. It should be noted that the AD of cattle manure depends greatly on the type and ratio of materials added to the biodigester [12]. Hence a specific analysis is required when new raw materials are explored.

Similarly, SW is of great interest as raw material for AD because most meat industries generate large amounts 45–53% live animal's weight, organic by-products considered industrial organic waste [13]. Comparable, SW residues are characterized by having a high animal protein and fat content [14] becoming an attractive raw material for AD, because of its methane high yield [15].

Although, AS, QS and WS crops are abundant in the Andean regions, only a portion of WS wheat waste is used as animal feed, many AS and QS traces of straw are burned or unused causing a tremendous loss of energy potential.

Given that very few studies have addressed methane's biochemical potential (BMP) from residues obtained under appropriate conditions as those from the Andes, this study aimed to characterize agricultural and livestock residues fermentation process in the Andean region through the addition of a sewage sludge microbial inoculum in batch biodigesters. The amount of methane obtained the degree of biodegradability of the substrates and the modelling of the kinetics of the process were measured.

2. Materials and methods

2.1. Origin of substrates and inoculum

Livestock waste samples were collected from three different areas within close proximity. First, llama manure was primarily collected from farms surrounding the capital city of Guaranda in Bolivar Province whereas VM manure was collected at the Chimborazo province—both located in central Ecuador—volcano pastures and plains, where the animals live freely and wildly. Alternatively, GPM manure was obtained from farms at "Bolivar State University". Finally, SW was collected from the Guaranda Municipal slaughterhouse. The latter was extracted from cattle stomachs as it is a complex substrate composed of manure remains contained inside the intestines like blood, rumen and grass detritus not being completely degraded. Such samples were collected in polyethylene bags obtaining significative manure samples produced on farms or waste sites. Subsequently, they were stored in the laboratory at 6 °C for 72 h before being added to the biodigesters.

On the other hand, AS, QS and WS straw were obtained from plots at the Bolivar State University. This waste was collected from the stubble produced during the summer months (August and September). Once the straw was collected it was stored in the laboratory and dried at room temperature before performing a mechanical pretreatment in two stages. The mechanical pretreatment was aimed at increasing the surface area of the material to improve the reaction rate, accelerating the hydrolysis stage, increasing the biogas yield in the AD according to the studies by Ariunbaatar et al. [16]. First, the particle size was reduced to approximately 3 and 4 cm by a mass mill. Then a second milling was carried out with a smaller mill to reduce its size to a diameter of less than 1 mm to obtain a better homogenization of the size. According to Sharma et al. [17], the particle size of agricultural and forestry residues that produces the maximum amount of biogas is between 0.088 and 0.40 mm.

The inoculum used in all the tests comes from the urban wastewater treatment station (WWTP) in the city of San Miguel de Ibarra (Ecuador). It is extracted from the primary sludge of the anaerobic digester that worked in mesophilic conditions (temperature between 35 and 37 °C approximately).

2.2. Characterization of raw materials and biogas

The materials were characterized by proximal analysis and elemental analysis.

The total solids (ST) of the substrates were determined by the methodology proposed by the standards UNE-EN 18134-1: 2016, UNE-EN 18134-2: 2017 and UNE-EN ISO 18134-3, 2016 [18–20]. Volatile solids percentage (VS) with respect to total solids was determined following the procedure proposed by the standard UNE-EN ISO 18123: 2016 [21], while the ashes were determined according to the standard UNE-EN ISO 18122: 2016 [22].

Similarly, for the proximal analysis of the inoculum, whose composition was mostly liquid, a more proper methodology of wastewater proposed by the American Public Health Association (APHA) [23] sections 2540A-2540G was used, determining the TS, VS and ashes.

The elementary analysis from which the percentages of N, C, O, H, S and C/N ratio of the substrates and the inoculum are obtained were determined through the VARIOUS MACRO CUBE elemental analyzer, following the guidelines proposed by the standard UNE ISO16948 15104. The pH was determined at room temperature using a HACH HQ 40D digital multimeter meter potentiometer.

The biogas production was calculated from the pressure exerted by the biogas inside the biodigester. The pressure was measured daily by the manometer (Delta OHM HD 2124.2) equipped with a sensor (Delta TP 704 with a capacity of 100 bar). After the daily pressure measurement, the biogas accumulated in the upper space of the biodigester was completely released; this caused the pressure exerted by the biodigester to be reduced to a pressure close to atmospheric pressure. After releasing the biogas, the pressure in the head space of the biodigester was again measured as an initial condition for the next day measurement. The biogas components (CH_4, H_2S, CO_2 and O_2) were determined with the Geotech BIOGAS GA-5000 analyzer. The biogas estimate was evaluated daily from each biodigester by daily extraction of all the generated biogas.

2.3. Experimental methodology

BMP tests were performed on a laboratory scale and in batch digesters, through which the maximum CH_4 production of different substrates was determined. All BMP tests for the test were performed in glass digesters of 310 ml of total volume (V_T) sealed tightly throughout the digestion process. The reactors were filled occupying a useful volume (V_U) of 60% of the total volume, while the gas or head volume (V_G) was set at 40%. All batch tests were performed in triplicate. Biodigesters were kept at 38 °C within a 40-day retention time. Finally, the measurement was carried out daily until the accumulated biogas production stabilized. During data collection, all biodigesters were shaken with an orbital shaker for a period of 120 s at 100 rev/min before taking biogas volume and pressure measurements generated in the biodigester.

BMP evaluation was performed with two substrate/inoculum ratios (SIR): 1:1 g/g VS and 1:2 g/g VS. To obtain these proportions, the amount of inoculum in each test was kept constant at 18g VS/l, while the amount of substrate varied according to the respective SIR value. Only sewage sludge was used as inoculum in these experiments. The process was evaluated at mesophilic temperature, with a C/N ratio determined by the elementary analysis of the combination of raw materials. The influence of the inoculum was evaluated by subtracting between the total accumulated volume of the substrate and the total accumulated volume of the inoculum; for this, the volume of biogas and methane produced solely by the inoculum was determined and at the end of the experiment mathematically the total inoculum production was subtracted from the total production of the substrates. Finally, biogas volume in each of the tests was expressed in ml/g VS and normalized under standard conditions (P = 1atm, T = 25 °C) through (**Eq. (1)**).

$$V_{BIOGAS}(STP) = \frac{\Delta P V_G T_{STP}}{P_{STP} T_1} \tag{1}$$

where.

V_{BIOGAS} (STP) total methane volume under standard conditions.

ΔP represents the difference between the daily pressure exerted by the biogas in the biodigester and the pressure after the gas was released the day before (atm)

T_{STP} temperature in standard conditions (298 K)

T_1 experiment test temperature (311 K)

P_{STP} pressure under standard conditions (1 atm)

V_G volume of the digester head space (0.124 l)

2.4. Kinetic modeling

To describing the AD process, the different kinetic models were adjusted to the observed values and thus managed to predict methane production, as a function of time, in the different BMP tests. Once the kinetic parameters were obtained by parameterizing the kinetic equations, they were compared with each other to see their relationship with the observed values. In total, five different kinetic models were evaluated (Mc 1- Mc 5): Mc 1 - modified Gompertz model [24] (**Eq. (2)**), Mc 2 - transfer function model [25] (**Eq. (3)**), Mc 4 - logistic function model [25] (**Eq. (4)**), Mc 5 - cone model [26] (**Eq. (5)**), Mc 5 -model of Richards [27] (**Eq. (6)**).

$$\mathrm{Mc}\cdot 1\cdot M = M_\mathrm{e}.exp\left\{-exp\left[\frac{\nu_\mathrm{max}{*}exp}{M_\mathrm{e}}\left(t_{lag}-\mathrm{t}\right)+1\right]\right\} \tag{2}$$

$$\mathrm{Mc}\cdot 2\cdot M = M_\mathrm{e}\left\{1-exp\left[-\frac{\nu_\mathrm{max}}{M_\mathrm{e}}\left(t-\mathrm{t_{lag}}\right)\right]\right\} \tag{3}$$

$$\mathrm{Mc}\cdot 3\cdot M = \frac{M_\mathrm{e}}{1+exp\left[\frac{4\nu_\mathrm{max}\left(t_{lag}-t\right)}{M_\mathrm{e}}+2\right]} \tag{4}$$

$$\mathrm{Mc}\cdot 4\cdot M = \frac{M_e}{1+(k.t)^{-n}}\mathrm{Ec.} \tag{5}$$

$$\mathrm{Mc}\cdot 5\cdot M = M_e\left\{1+d.exp(1+d)exp\left[\frac{\nu_{max}{*}exp}{M_e}(1+d)\left(1+\frac{1}{d}\right)\left(t_{lag}-1\right)\right]\right\}^{\frac{1}{d}}\mathrm{Ec} \tag{6}$$

where.

M accumulated specific methane yield over time t (ml CH_4. g^{-1} VS)

M_e maximum methane yield (ml CH_4. g^{-1} VS)

t digestion time (d)

k first order decomposition constant (d^{-1})

ν_{max} maximum specific rate of methane production (ml CH_4. g^{-1} VS. d^{-1})

t_{lag} lag phase parameter (d)

d dimensionless factor

n factor order

exp 2.71828.

Methane production was modeled by adjusting the data from the five kinetic models by nonlinear regression, using the STATISTICA 10 tool. To evaluate the efficiency of the models, the coefficient of determination (r^2) and the mean square error (RMSE) were used. The RMSE reveals the average error in the cross-validation method or set of predictions. The model is considered good when there is a greater correlation between the experimental values of the BMP test and the predicted values, that is, when the RMSE values are 0 and the coefficient r^2 is as close as possible to 1 [28].

2.5. Calculation of theoretical performance and biodegradability

The maximum theoretical methane yield (TMY) was estimated based on the elemental compositions of organic elements, such as C, H, O and N, based on the Buswell equation [29] (**Eq. (7)**).

$$C_aH_bO_cN_d + \left(\frac{4a-b-2c+3d}{4}\right)H_2O \rightarrow \left(\frac{4a+b-2c-3d}{8}\right)CH_4 + \left(\frac{4a+b+2c+3d}{8}\right)CO_2 + dNH_3 \tag{7}$$

where.

a, b, c and d are the stoichiometric coefficients of biodegradable molecules.

However, all the analyzed substrates had ammonia and H2S, so the considerations of using the Boyle equation [30] (**Eq. (8)**).

$$TMY = \frac{22\,400{*}(4a+b-2c-3d-2e)}{(12a+b+16c+14d+32e){*}8} \tag{8}$$

According to Sobotka et al. [31], the biological efficiency of the anaerobic process is defined as the relationship between experimental and theoretical performance. In this way, knowing the values of experimental yield γ(exp) and theoretical γ(th), the biological efficiency was estimated from (Eq. (9)) [24].

$$\varepsilon = \frac{\gamma_{(exp)}}{\gamma_{(th)}} \tag{9}$$

3. Results and discussion

3.1. Characterization of substrates and inoculums

Table 1 demonstrates proximal and elementary analyzes results from the different raw materials studied. Livestock waste substrates

Table 1
Characterization of substrates and inoculums.

Parameters	Units	LM	VM	GPM	SW	AS	QS	WS	IN
TS	%	50.6 (1.0)	57.4 (0.5)	33.9 (1.7)	9.6 (1.3)	88.2 (0.1)	87.0 (0.1)	92.6 (0.1)	3.9 (0.1)
VS (% ST)	%	61.6 (0.4)	41.2 (1.6)	72.6 (1.1)	70.7 (0.1)	74.8 (0.3)	58.4 (1.5)	77.2 (0.9)	58.5 (0.5)
Ashes	%	25.5 (0.3)	27.6 (1.8)	13.1 (0.1)	12.8 (0.2)	8.4 (0.1)	30.3 (1.4)	11.8 (0.1)	55.6 (0.2)
N	%	2.2 (0.1)	2.6 (0.4)	2.3 (1.0)	0.4 (0.1)	3.3 (0.9)	2.2 (0.9)	1.7 (0.7)	3.4 (0.1)
C	%	40.7 (1.2)	40.3 (1.1)	39.5 (1.2)	42.2 (1.1)	42.9 (1.9)	30.7 (1.7)	48.9 (1.6)	25.0 (1.2)
H	%	4.5 (0.2)	5.1 (0.3)	4.6 (0.5	6.3 (0.9)	6.5 (0.8)	6.4 (0.9)	6.1 (0.5)	2.1 (0.1)
O	%	27.0 (1.2)	23.9 (1.1)	39.7 (1.2)	38.3 (1.1)	38.6 (1.9)	29.8 (1.7)	31.1 (1.6)	12.9 (1.2)
S	%	0.2 (0.0)	0.4 (0.0)	0.4 (0.0)	0.0 (0.0)	0.2 (0.0)	0.6 (0.1)	0.5 (0.0)	0.7 (0.0)
C/N	–	17.4 (0.9)	15.4 (0.7)	15.3 (0.8)	101.9 (0.9)	12.9 (0.8)	12.0 (0.9)	29.6 (0.8)	7.5 (0.7)

NOTE: LM (Llama manure), VM (Vicuña manure), GPM (Guinea pig manure), SW (Slaughterhouse waste), WS (Wheat straw), AS(Amaranth straw), QS (Quinoa straw) and IN (inoculum, WWTP sludge). The data in brackets are the standard deviations.

(LM, GPM, VM and SW) have several important differences in TS and VS content. Particularly, SW and GPM VS content is remarkably much higher than VM and LM residues. Nonetheless, LM residues have a very competitive VS content compared to other studies. For instance, LM residues has 61.58% of VS compared to the results obtained by other authors [[9,32–34]] hat is 74.4%; 70.9%; 70.3 and 66.1% VS respectively. The fact that the LM and VM residues has a low VS content is justified, to a large extent, by the high ash content of 25.51 and 27.6%% respectively. On the other hand, the SW and the GPM have a high moisture content of 90.44% and 66.10% respectively. However, despite the greater dilution of the SW and GPM residues used in the trials, they have a high VS content on a dry basis (70.74% and 72.63% respectively).

Agricultural residues (WS, QS and AS) had a high TS content, around 87–93%. This is because they are stubble residues collected in summer. However, they presented significant differences in the percentage of volatile (VS) solids with respect to total solids. The substrates with the highest amount of VS are the residues of QS and WS (77.26% and 74.79% respectively) residues due to a high protein and lipid content. AS residues have a significantly lower volatile content with 58.37% on average and contain a high ash content (8.4%). Volatile solids obtained in quinoa are lower than those reported by Ref. [9], which indicated an average of 95.3% of VS compared to total solids. That there are differences between the characteristics of two equal materials may reflect the different cultivation systems used in each of them.

Regarding inoculum, WWTP sludge was used in all the trials, in accordance with the recommendations of many studies in the literature [[35–39]]. The inoculum used was the same for all the tests performed and was degassed by incubation for 4 days. The TS were 3.9%; while the wet-based VS were 2.3%, which makes it possible to have an VS/TS ratio of 0.59 typical of WWTP sludge. The VS/TS ratio is an indirect measure of the activity of microorganisms in biomass [40]. In this case, the value obtained from the VS/TS was much higher than the values obtained by Shen et al. and Liu et al. [40,41], who obtained values of 0.49 and 0.38, respectively. The VS obtained were consistent with the results of [[42–45]] who obtained 38.01%; 44.89%; 45.5% and 65.5% of VS respectively. The C/N ratio of the substrates (LM, VM and GPM) and the residues of (AS and QS) is around 12–17.41, which is low, since for a better methanogenic activity, the C/N ratio should be around 20–30. The low C/N ratio expects some type of inhibition of microorganisms, due to an excess accumulation of ammonia due to protein degradation [46].

3.2. Cumulative production of biogas and methane from agricultural and livestock waste

The total biogas and methane production accumulated in the digesters was obtained by adding the daily biogas production throughout the experimental period. Fig. 1 shows the total accumulation during the 40 days of AD of all monodigestion residues, with the average yield of all trials. In general, all cumulative performance curves have a similar behavior, which implies that the test material is easily biodegradable. In this sense, according to Fig. 1a, biogas is produced immediately once the biodegradation process has begun, which makes the initial lag phase very fast and the biogas yield curve stabilizes quickly [47]. When the amount of inoculum varies from 50% to 66.67% (Fig. 1b), the biogas production of WS, QS, LM and SW residues increases by 2.19; 23.61; 20.65 and 17.01% respectively. This evidences that the WS residues did not undergo major changes as the amount of inoculum increased. However, with the increase in inoculum, they showed a greater production of biogas in the first days and a quick stabilization in the days after its biodegradation. On the other hand, the residues of QS, LM and AS did undergo significant changes as the amount of inoculum increased. According to Bouallagui et al. [48], there is a direct relationship between soluble organic matter and hydrolysis, since, at a higher content of soluble organic matter, times for substrate formation are reduced and cumulative production is increased. In this sense, when the amount of inoculum is increased, the lag phase is decreased, and the hydrolysis process is accelerated during the first days of AD.

Regarding methane production, its yields are in Fig. 1c and d. When the inoculum amount was increased from 50% to 66.67%, the digesters with residues of WS, QS, LM and SW increased by 1.54; 22.56; 37.54 and 16.32% respectively. On the contrary, with the increase in inoculum, digesters containing residues of AS, GPM and VM decreased their total methane production by 5.05; 17.43 and 9.93% respectively. The fact that some residues decreased their production with the increase of inoculum agree with other fermentation studies by Zhou et al. and Boulanger et al. [49,50], who experimented with bean residues. They found that SIR greater than 2 can negatively affect the AD process, especially methane yield and substrate biodegradability. In this sense, Raposo et al. [51] considers that the decrease in methane yield with the increase of the inoculum is associated with the inhibition of anaerobic microorganism activity due to the accumulation of volatile fatty acids (VFA). The increase in methane in the QS, LM and SW residues was very significant unlike the WS residues, in which it was not very effective. In this sense, for the residues of QS, LM and SW as the inoculum increases, there is a greater adaptation of the microorganisms to the substrate, which means that the delay phase is deduced.

Generally speaking, the highest amount of methane was obtained when the amount of inoculum was increased from 50% to 66.67% for the residues of LM and QS, with results of 377.02 and 376.08 ml of CH_4/g VS. Along the same lines, WS and SW residues also improved their methane production with productions of 268 and 283 ml CH_4/g VS. However, AS, GPM and VM residues reduced

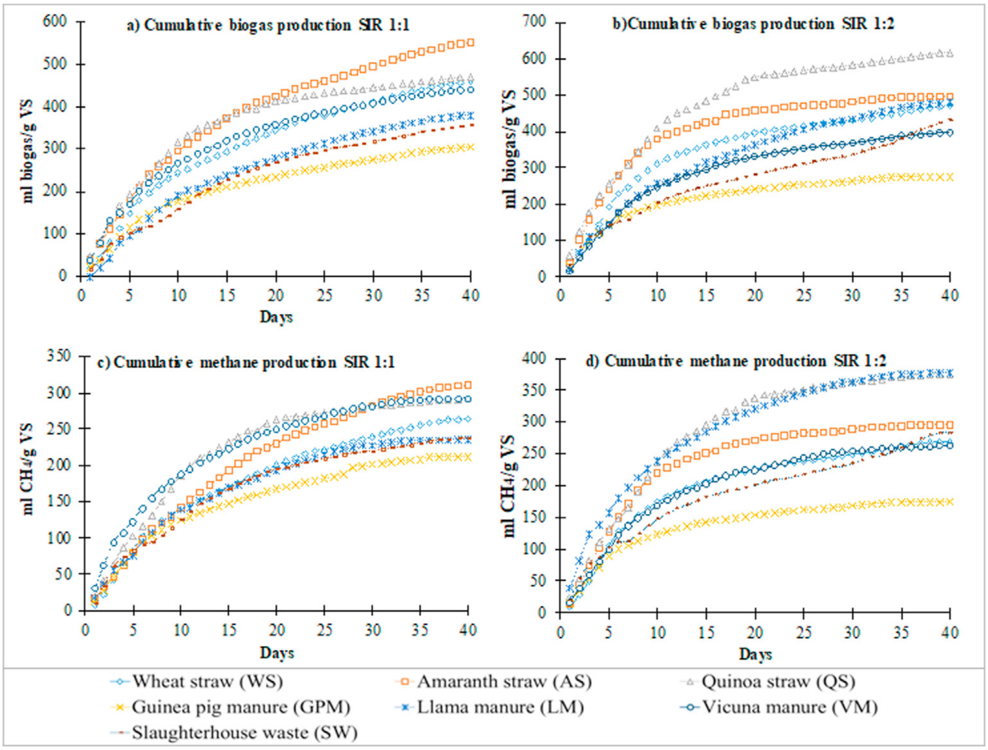

Fig. 1. Daily production of biogas and methane from agricultural and livestock waste.
NOTE: LM (Llama manure), VM (Vicuña manure), GPM (Guinea pig manure), SW (Slaughterhouse waste), WS (Wheat straw), AS (Amaranth straw), QS (Quinoa straw).

their methane production by 5%, 17% and 9%, respectively. On the other hand, all the residues with the highest percentages of CH_4 were those of animal origin, that is, the residues of LM and VM (78.76% and 66.34% respectively). These results suggest that increases in the inoculum to camelid residues stimulate bacterial activity, increasing biodegradability and the production of biogas and methane.

Many authors [30,52,54] conclude that one of the most important parameters affecting BMP tests is the inoculum, both the source, and the amount of inoculum added. It is clearly demonstrated that SIR can affect not only biodegradability but also the production rate of CH_4 [30]

If the residue with the highest yield obtained in both biogas and methane (LM) is compared, with other previous studies in the literature the production obtained is in the same ranges. The amount of biogas from the LM residue obtained in this investigation is 379.89 ml of biogas/g VS with a methane percentage of 78.76%. For their part Alvarez et al. [32], obtained results between 20 and 550 ml of biogas/g VS with 50–57% of CH_4, Alvarez and Lidén [9] achieved an average between 150 and 450 ml of biogas g VS with 50–60% of CH_4, Alvarez and Lidén [34] generated 10 and 690 ml of biogas/g VS with 27–55% of CH_4, finally Alvarez and Lidén [53] obtained averages between 30 and 480 ml of biogas/g VS with 47–55% CH_4. It should be noted that the studies carried out by these authors were carried out in continuous flow stirred-tank reactors (CFSTR), with volumes between 1.8 and 9.3 ml and temperature ranges between 11 and 25 °C.

3.3. Kinetic model analysis

Table 2 summarizes the results of the kinetic study using the different models. As you can see, all the models fit well with the experimental data. The kinetic constants were calculated during 40 days of digestion, which was the time necessary to obtain more than 95% biogas. All kinetic models adequately described the cumulative biogas production of the biodigesters. Kinetics is a very sensitive process, which makes biogas production related to bacterial growth [55]. In general, the kinetic parameters determined from modeling provided additional valuable information on the results of BMP tests on the biodegradation patterns of the substrates.

The lag phase (t_{lag}) yielded mostly negative values for both biogas and methane production. GPM and QS residues decrease as inoculum amount is increased. In contrast, SW residues increase their t_{lag} when SIR increases. The negative periods of the lag phase of some substrates indicates the high bioavailability of organic compounds within the substrates [27]. On the other hand, the residues of AS, QS and VM have positive values for the transfer model, which suggests that these residues present a more complex degradation of fats in their initial process. However, the model that presents more irregular values with respect to the other models is the transfer. In this sense, it is worth noting that this irregularity of the transfer model overestimated the t_{lag} to a higher degree than the rest of the models.

The amount of M_e predicted by the 5 models evaluated have the same trend in their behavior. For its part, the cone model is the one that overestimates this parameter and moves it away from the rest of the models. Thus, for example, when the amount of inoculum is increased in both methane and biogas, the SW residue has values of 716.77 ml CH_4/g VS and 2136.53 ml biogas/g VS respectively, causing it to overestimate me by more than 200%. The performance values modeled with the Gompertz, logistics and Richards models are the ones that have more similarity to each other and at the same time are the ones that have less error difference with the experimental performance. In principle, the Richards model is a generalization of the logistic model, since it introduces a fourth

Table 2
Kinetic parameters of methane and biogas for different models.

SIR	Models	Parameters	Units	METHANE							BIOGAS						
				WS	AS	QS	GPM	LM	VM	SW	WS	AS	QS	GPM	LM	VM	SW
(1:1)	**GOMPERTZ**	$\mathbf{M_e}$	ml CH_4/g VS	262.500	317.470	286.540	211.050	238.240	290.560	235.360	456.384	542.385	454.540	295.771	384.279	432.137	358.203
		v_{max}	ml CH_4/g VS day	10.600	11.960	17.820	8.970	10.790	14.150	10.630	17.605	22.153	27.561	12.737	14.663	19.321	13.884
		$\mathbf{t_{lag}}$	days	−2.090	−1.400	−0.460	−3.020	−2.150	−3.210	−1.890	−2.714	−2.727	−1.646	−3.175	−2.642	−3.456	−1.640
	TRANSFER	$\mathbf{M_e}$	ml CH_4/g VS	235.360	358.380	297.510	221.400	251.570	300.130	250.320	490.490	580.579	467.855	309.615	410.357	449.964	400.147
		v_{max}	ml CH_4/g VS day	10.630	18.580	30.520	16.400	18.890	26.740	18.160	30.480	38.288	50.401	23.488	30.259	35.963	21.811
		$\mathbf{t_{lag}}$	days	−1.890	0.130	0.640	−0.420	−0.140	−0.740	−0.080	−0.277	−0.458	0.016	−0.509	−0.488	−0.830	−0.082
	LOGISTIC	$\mathbf{M_e}$	ml CH_4/g VS	255.450	304.860	282.320	206.890	233.260	286.200	229.440	443.666	527.776	448.545	290.084	372.658	424.206	344.246
		v_{max}	ml CH_4/g VS day	9.740	11.460	16.610	7.990	9.830	12.500	9.940	16.113	20.340	24.960	11.298	13.553	17.183	13.362
		$\mathbf{t_{lag}}$	days	−2.710	−1.480	−0.660	−4.060	−2.800	−4.250	−2.230	−3.448	−3.399	−2.190	−4.288	−3.241	−4.506	−1.676
	CONE	$\mathbf{M_e}$	ml CH_4/g VS	361.620	454.470	318.930	284.220	303.430	366.300	304.650	662.804	760.744	521.633	399.074	563.041	576.185	513.611
		k	1/day	0.060	0.050	0.120	0.070	0.080	0.100	0.080	0.055	0.063	0.136	0.076	0.053	0.085	0.053
		n	dimensionless	1.090	1.140	1.550	1.020	1.140	1.020	1.140	1.005	1.016	1.287	0.998	1.007	0.968	1.104
	RICHARDS	$\mathbf{M_e}$	ml CH_4/g VS	263.390	317.410	286.640	211.440	239.080	290.540	235.470	457.486	542.281	454.630	*	386.659	433.024	358.336
		d	dimensionless	0.000	0.010	0.000	0.000	0.030	0.010	0.010	0.005	0.005	0.006	*	0.005	0.006	0.007
		v_{max}	ml CH_4/g VS day	9.990	13.550	20.950	10.760	12.750	17.220	12.490	20.710	26.060	33.200	*	18.860	23.380	15.820
		$\mathbf{t_{lag}}$	days	−2.230	−1.420	−0.510	−3.110	−2.280	−3.230	−1.920	−2.757	−2.717	−1.663	*	−2.801	−3.576	−1.669
(1:2)	**GOMPERTZ**	$\mathbf{M_e}$	ml CH_4/g VS	254.654	287.603	370.254	168.703	376.477	258.092	282.461	440.958	480.989	598.180	266.590	484.336	380.589	459.354
		v_{max}	ml CH_4/g VS day	16.157	23.192	22.571	10.984	17.666	14.807	8.580	27.910	38.870	35.023	16.106	18.212	21.240	10.598
		$\mathbf{t_{lag}}$	days	−0.801	−0.236	−0.492	−2.070	−3.459	−1.393	−5.962	−1.238	−0.891	−1.847	−3.003	−2.919	−1.435	−7.536
	TRANSFER	$\mathbf{M_e}$	ml CH_4/g VS	263.161	293.954	384.972	171.942	389.468	266.949	307.942	454.409	489.269	615.680	264.220	524.671	394.615	541.916
		v_{max}	ml CH_4/g VS day	28.866	41.232	38.593	21.402	33.387	26.796	15.009	50.743	72.611	32.391	30.979	30.979	38.423	16.878
		$\mathbf{t_{lag}}$	days	0.657	0.765	0.633	−9.137	−0.877	0.305	−2.420	0.353	0.405	−7.996	−0.554	−0.554	0.348	−3.844
	LOGISTIC	$\mathbf{M_e}$	ml CH_4/g VS	251.166	284.803	364.602	167.125	370.543	254.503	272.158	435.098	476.940	590.336	264.222	469.446	374.846	431.519
		v_{max}	ml CH_4/g VS day	14.678	21.339	21.050	9.560	15.610	13.320	7.815	25.224	34.949	31.567	13.745	16.830	19.129	10.005
		$\mathbf{t_{lag}}$	days	−1.289	−0.497	−0.692	−2.994	−4.532	−2.022	−7.164	−1.799	−1.347	−2.451	−4.253	−3.544	−2.083	−8.328
	CONE	$\mathbf{M_e}$	ml CH_4/g VS	287.830	308.304	414.295	191.515	485.454	297.860	716.768	502.322	520.264	693.638	311.057	729.282	446.560	2136.533
		k	1/day	0.130	0.167	0.121	0.164	0.098	0.122	0.012	0.137	0.187	0.132	0.164	0.050	0.115	0.002
		n	dimensionless	1.431	1.670	1.530	1.230	0.985	1.328	0.655	1.347	1.494	1.247	1.084	0.968	1.291	0.607
	RICHARDS	$\mathbf{M_e}$	ml CH_4/g VS	254.782	287.577	370.212	168.674	376.392	257.997	283.035	441.212	481.655	598.086	266.598	483.751	380.657	459.302
		d	dimensionless	0.002	0.004	0.006	0.004	0.004	0.005	0.004	0.002	0.003	0.005	0.003	0.006	0.005	0.009
		v_{max}	ml CH_4/g VS day	19.260	27.670	26.520	13.530	21.500	17.720	10.130	33.510	47.240	31.930	19.620	21.300	25.420	12.090
		$\mathbf{t_{lag}}$	days	−0.843	−0.243	−0.497	−2.067	−3.475	−1.407	−6.132	−1.276	−1.001	−1.854	−3.033	−2.900	−1.455	−7.556

NOTE: LM (Llama manure), VM (Vicuña manure), GPM (Guinea pig manure), SW (Slaughterhouse waste), WS (Wheat straw), AS (Amaranth straw), QS (Quinoa straw) and IN (inoculum, WWTP sludge). (*) Predicted data does not converge with that observed in this model.

parameter d, which allows some flexibility in the shape of the curve. For d = 0 and 1, the Richards model is reduced to the Gompertz and logistic model respectively [56]. In this sense, the three and four parameter sigmoidal kinetic models better describe the methane production kinetics. On the other hand, the data of the Richards model are more similar to those of Gompertz, since in all the tests carried out the parameter d tends more to 0 than to 1, with which Richard's model has the tendency to be reduced to the model from Gompertz. The asymptotes calculated for the model that best adjusts the specific performance (Gompertz) causes them to vary by no more than 7.06% with respect to the experimental data. On the other hand, the best adjustments are in the residues of GPM (−0.01%) and LL (−0.15%). According to these results according to Zahan et al. and Raposo et al. [57,58], low deviations reached between predicted and measured values (almost equal to or less than 10%) in LM and GPM residues suggest that the proposed model predicts digesters role more accurately.

The maximum rate of methane production (ν_{max}) shows that the highest peaks are obtained with the transfer model, especially in the residues of QS (30.52 ml/g VS day) and VM (26.74 ml/g VS day) in the SIR (1:1), and in the residues of AS (41.23 ml/g VS day) and QS (38.59 ml/g VS day) in the SIR (1:2). With regard to biogas production, the highest results were obtained in the residues of QS (50.40 ml/g VS day) and VM (35.96 ml/g VS day) for SIR(1:1), and in WS (50.74 ml/g VS day) and AS (72.61 ml/g VS day) for SIR (1:2). The highest values of ν_{max} were obtained in the exponential phases and when the amount of inoculum to the tests was increased since a better dissolution of the organic matter was obtained.

3.4. Evaluation of the different kinetic models

For the evaluation of the models, two statistics have been used (Table 3); a) the coefficient of determination of the adjustment r^2 and b) the root of the mean of the squares of the errors (RMSE). In the table, it is observed that the highest values of r^2 were recorded in the cone and transfer models for both methane and biogas measurements in their different SIR. Thus, the cone model had the best fit of $r^2 = 0.999$ for residues of VM (CH_4 SIR of 1:1 and 1:2), AS (CH_4 SIR 1:1 and 1:2), VM (biogas SIR 1:1 and 1:2) and AS (biogas SIR 1:1). At the same time, the transfer model recorded values of $r^2 = 0.996$–0.999 for residues of VM (CH_4 SIR of 1:1 and 1:2), AS (CH_4 SIR 1:1 and 1:2), VM (biogas SIR 1:1 and 1:2) and AS (biogas SIR 1:1 and 1:2). Similarly, the Gompertz model and the Richards model provide the same results of r^2 since the parameter d, of the Richards model, tends to 0. However, the Gompertz model comprises r^2 values between 0.969 and 0.998 for GPM residues (biogas SIR 1:2), LM and VM (CH4 SIR 1:2). Regarding the logistics model, r2 values range from 0.954 to 0.990 for GPM (biogas SIR 1: 2) and QS (CH4 SIR1:1,1:2) waste. Regarding the logistics model, r^2 values range from 0.954 to 0.990 for GPM (biogas SIR 1: 2) and QS (CH_4 SIR1:1,1:2) waste.

Regarding RMSE statistic performance, it is observed that the behavior of this statistic is much lower in the cone and transfer models. Thus, the transfer model ranges its RMSE between 1.96 ml CH_4/g VS (SIR 1:1) and 17.18 ml biogas/g VS (SIR 1:2) for AS and WS residues, respectively. On the other hand, in the cone model RMSE was recorded between 0.61 ml CH_4/g VS (SIR 1:1) and 10.68 ml biogas/g VS (SIR 1:2) for WS and SW residues, respectively. In the RMSE analysis for the Gompertz model, values between 4.09 ml CH_4/g VS (SIR 1:1) and 17.12 ml biogas/g VS (SIR 1:2) were obtained for the residues of QS and SW, respectively. Finally, the logistic model is the one that had the greatest difference between the observed and estimated values. In this model, RMSE values of 7.49 ml CH_4/g VS (SIR 1:1) and 21.84 ml biogas/g VS (SIR 1:2) were recorded for the residues of QS and WS, respectively. In general, for all models the residues that best approximated the observed data were those of QS and AS and those that were least adjusted were those of WS and SW.

The best estimates of r^2 and RMSE were obtained for cone and transfer models, however, these models have more extreme values

Table 3
Evaluation of the kinetic models for methane and biogas.

SIR	Parameters	Feedstock	r^2					RMSE				
			Gompertz	Transfer	Logistic	Cone	Richards	Gompertz	Transfer	Logistic	Cone	Richards
(1:1)	**Methane**	Wheat straw (WS)	0.981	0.992	0.968	0.996	0.981	9.7	17.08	12.52	4.23	9.72
		Amaranth straw (AS)	0.994	0.999	0.986	0.999	0.994	6.53	1.96	10.19	2.04	6.56
		Quinoa straw (QS)	0.997	0.997	0.99	0.997	0.997	4.09	4.06	7.49	4.24	4.11
		Guinea pig manure (GPM)	0.977	0.991	0.963	0.995	0.977	8.15	5.02	10.21	3.65	8.15
		Llama manure (LM)	0.991	0.998	0.982	0.998	0.991	5.75	2.83	8.25	3.06	5.87
		Vicuña manure (VM)	0.989	0.997	0.979	0.999	0.989	7.33	3.5	10	2.36	7.35
		Slaughterhouse waste (SW)	0.992	0.996	0.985	0.995	0.992	5.56	3.76	7.57	4.17	5.57
	Biogas	Wheat straw (WS)	0.979	0.993	0.983	0.996	0.979	16.99	9.78	21.6	7.28	17.03
		Amaranth straw (AS)	0.987	0.997	0.976	0.999	0.987	15.93	7.64	21.66	4.25	15.97
		Quinoa straw (QS)	0.992	0.998	0.983	0.998	0.992	9.89	4.84	14.56	4.91	9.92
		Guinea pig manure (GPM)	0.973	0.989	0.958	0.995	–	12.16	7.73	15.1	5.22	–
		Llama manure (LM)	0.987	–	0.976	0.998	0.987	11.36	–	15.28	3.85	11.4
		Vicuña manure (VM)	0.984	0.995	0.973	0.999	0.984	13.15	7.20	17.16	3.19	13.19
		Slaughterhouse waste (SW)	0.993	0.997	0.987	0.996	0.993	7.8	5.65	11.02	6.02	7.82
(1:2)	**Methane**	Wheat straw (WS)	0.977	0.993	0.961	0.996	0.977	10.15	5.66	13.27	0.61	10.16
		Amaranth straw (AS)	0.991	0.998	0.979	0.999	0.991	7.07	3.02	10.6	4.3	7.09
		Quinoa straw (QS)	0.997	0.997	0.99	0.997	0.997	5.47	5.34	9.73	1.67	5.5
		Guinea pig manure (GPM)	0.975	0.991	0.96	0.997	0.975	6.25	3.74	7.92	5.74	6.26
		Llama manure (LM)	0.988	0.997	0.979	0.998	0.988	9.67	4.99	12.96	1.98	9.69
		Vicuña manure (VM)	0.988	0.998	0.976	0.999	0.988	7.25	2.79	10.37	3.46	7.27
		Slaughterhouse waste (SW)	0.969	0.982	0.957	0.991	0.969	11.39	8.78	13.35	1.89	11.4
	Biogas	Wheat straw (WS)	0.977	0.992	0.962	0.996	0.977	16.91	10.19	21.84	7.07	16.93
		Amaranth straw (AS)	0.986	0.997	0.974	0.999	0.986	13.3	6.2	18.38	3.36	13.34
		Quinoa straw (QS)	0.993	0.998	0.985	0.997	0.993	12.23	6.25	18.01	7.9	12.26
		Guinea pig manure (GPM)	0.969	0.997	0.954	0.996	0.969	10.42	7.02	12.74	3.51	10.43
		Llama manure (LM)	0.987	0.997	0.977	0.999	0.987	14.06	7.03	18.78	4.69	14.09
		Vicuña manure (VM)	0.982	0.996	0.968	0.998	0.982	13.29	6.32	17.83	4.02	13.31
		Slaughterhouse waste (SW)	0.969	0.98	0.959	0.988	0.969	17.12	13.83	19.59	10.68	17.15

in the calculation of Me with error differences of 20.55 (transfer model) and 79.85% (cone model). In this sense, in these models the value of Me is overestimated with respect to sigmoidal model models. In addition, the transfer model is the only one that registered positive values on the lag phase. On the other hand, in the cone model the lag phase cannot be compared with the other models since this model does not provide this parameter.

The Gompertz and Richards models adjusted better since they did not oversize the estimated M_e of the performance observed in the digesters. In addition, these models presented a high coefficient of determination and a low value in the RMSE for all the analyzed residues. This showed that these two proposed models can accurately describe the variation of methane and biogas yield curves. On the other hand, the low t_{lag} value observed for methane and biogas in these models demonstrated the low inhibition of AD and the high biodegradability of the residues. According to the results obtained, it shows that these models, in particular the Gompertz, are the most used kinetic model in the literature due to their good adjustments [59].

The fact that sigmoidal models do not overestimate M_e as the cone model does is because all models are based on functions that increase monotonously (that is, the function always assumes that the growth rate increases and is never the same to zero or decrease) [60]. However, sigmoidal models have a turning point, where the sign of the curvature changes from concave to convex or vice versa, that is, ν_{max} [61]. Thus, for example, the logistic and Gompertz functions have fixed inflection points. On the one hand, the logistic function is symmetric with respect to its inflection point that exists when growth reaches half of its final growth (maximum asymptote) [60,61]. While Gompertz's function is asymmetric about its inflection point that occurs at a much earlier point than that of the logistic model, approximately 1/e of its final growth (maximum asymptote) [62].

3.5. Biodegradability and theoretical yield

The biological efficiency was calculated considering the experimental performance of the biodigesters and the theoretical performance of the elemental analysis of the substrates. The results estimated a biodegradability between 44% and 70% for all the substrates tested. This is because the theoretical yield was much higher than the experimental one. In general, the reactions that take place in AD are not completely terminated during the assay process, which makes the experimental performance have discrepancies with the theoretical performances. The fact that reactions do not occur completely in experimental trials is due to the presence of toxins, insufficient mixing, establishment of the microbial population, lignin complexity and other effects of the process condition (pH, temperature and redox) [63]. The theoretical values are very optimistic and do not coincide with the experimental ones since in practice there is no complete reaction and there is no 100% decomposition of the cellulosic materials. On the other hand, the theoretical performance does not consider the non-degradable material or the energy demand of microorganisms. Thus, the equations of Buswell and Müller (1952) and Boyle (1976) imply a complete conversion of biomass, which results in an overestimation of methane yields. The determination of the elemental composition is relatively rapid for all compounds, although this equation does not differentiate between biodegradable and non-biodegradable matter, and part of the biodegradable organic matter used by bacteria to grow does not contribute to the theoretical value of BMP [64,65].

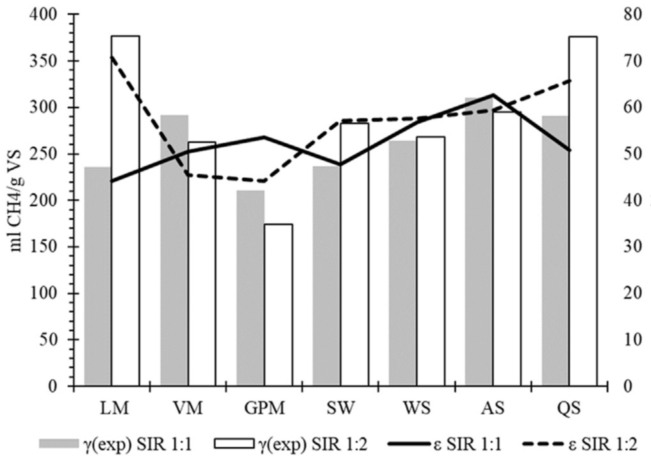

Fig. 2. Production of experimental methane and biodegradability of the substrates used for SIR 1:1 and 1:2.

Fig. 2 shows that of all the residues analyzed, the SW and GPM residues have the lowest ε; this decrease is due to the fact that these substrates contain a greater presence of hydrogen and nitrogen, which makes it possible to produce a toxic concentration of ammonia and hydrogen sulfide [66]**.** On the contrary, it is observed that the productivity of CH_4 increases with the increase of the C/N ratio to 30 as in the case of the residue of WS (C/N = 29.61). In this regard, some researchers have suggested that the C/N ratio for optimal digestion performance is in the range of 20–30, while many have shown that digestion can be performed successfully using a wider range of the ratio C/N [67,68].

When the amount of inoculum was increased from 50% to 66.67%, the LM and QS residues had a biological efficiency (ε) of 70.74 and 65.65%, respectively, followed by AS, SW and RM (59.41; 57.68 and 57.13%), and the lowest ε was obtained for GPM and VM (44.17 and 45.54%). In addition, with the addition of inoculum, the LM, SW, WS and QS residues increased the values of ε, while the residues of VM, GPM and AS experienced a slight decrease in their ε. A possible reason for the increase in ε after the addition of more inoculum is that it is possible to avoid further inhibition of high VFA concentration and acidic pH in methane production [69]. On the other hand, lignocellulosic residues such as those of QS and WS increased ε with the increase of the inoculum since it is achieved that the mixture of cellulose and hemicellulose has a better balance of nutrients and facilitates the optimal growth of the microorganisms responsible for the process of AD [24].

4. Conclusions

This study investigated the impact on the addition of inoculum in agricultural and livestock waste treatments. On the whole, findings showed that the addition of an inoculum to treatments can reinforce degradation performance. More specifically, an SIR 1:2 yielded the highest methane in the residues of QS and LM providing 376.08 ml CH4/g VS and 377.02 ml CH_4/g VS, respectively. Althoguh an adequate amount of mud is required for efficient operation, higher SIR improves methane production except AS, GPM and VM residues which exhibited a yield decrease by 5.32%; 21.12% and 11.02%.

With respect to prediction models, sigmoidal models with three and four parameters are the ones that best estimate BMP. Thus, the asymptotes calculated with the Gompertz model adjust very precisely specific performance which causes them to vary by no more than 7.06% with respect to the experimental data. Also, the best adjustments are in the GPM and LM residues whose yield varied by 0.01% and 0.15% with respect to those observed. In short, he modified Gompertz model was better adjusted to the experimental results than the rest of the kinetic models with the highest r^2 (0.998) and RMSE of 4.09 ml/g VS and 17.12 ml/g VS.

Finally, theoretical yield proved to be higher than experimental values for both SIR 1:1 and 1:2 although the highest efficiency and the greatest biodegradability was obtained in the LM and QS residues with 70.74% 65.65%.

CRediT authorship contribution statement

W.O. Meneses-Quelal: Investigation, Data curation, Writing - original draft. **B. Velázquez-Martí:** Conceptualization, Methodology, Investigation, Writing - review & editing. **J. Gaibor-Chávez:** Visualization, Investigation. **Z. Niño-Ruiz:** Supervision, Software, Validation.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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References

[1] P. Weiland, Biogas production: current state and perspectives, Appl. Microbiol. Biotechnol. 85 (2010) 849–860, https://doi.org/10.1007/s00253-009-2246-7.

[2] P. Abdeshahian, J. Lim, WHo, H. Hashim, C. Lee, Potential of biogas production from farm animal waste in Malaysia, Renew. Sustain. Energy Rev. 60 (2016) 714–723, https://doi.org/10.1016/j.rser.2016.01.117.

[3] L. Cuiping, Yanyongjie, W. Chuangzhi, H. Haitao, Study on the distribution and quantity of biomass residues resource in China, Biomass Bioenergy 27 (2004) 111–117, https://doi.org/10.1016/j.biombioe.2003.10.009.

[4] S.R. Paudel, S.P. Banjara, O.K. Choi, K.Y. Park, Y.M. Kim, J.W. Lee, Pretreatment of agricultural biomass for anaerobic digestion: current state and challenges, Bioresour. Technol. 245 (2017) 1194–1205, https://doi.org/10.1016/j.biortech.2017.08.182.

[5] M. González-Sánchez, S. Pérez-Fabiel, A. Wong-Villarreal, R. Bello-Mendoza, G. Yañez-Ocampo, Residuos agroindustriales con potential para la producción de metano mediante la digestión anaerobia, Rev. Argent. Microbiol. 47 (2015) 229–235, https://doi.org/10.1016/j.ram.2015.05.003.

[6] M. Balat, H. Balat, Biogas as a renewable energy source. A review, energy sources, Part A recover, Util. Environ. Eff. 31 (2009) 1280–1293, https://doi.org/10.1080/15567030802089565.

[7] I. Angelidaki, M. Alves, D. Bolzonella, L. Borzacconi, J.L. Campos, A. Guwy, S. Kalyuzhnyi, P. Jenicek, J. van Lier, Defining the biomethane potential (BMP) of solid organic wastes and energy crops: a proposed protocol for batch assays, Water Sci. Technol. 59 (2009), https://doi.org/10.2166/wst.2009.040, 927 LP – 934.

[8] G. Kafle, L. Chen, Comparison on batch anaerobic digestion of five different livestock manures and prediction of biochemical methane potential (BMP) using different statistical models, Waste Manag. 48 (2016) 492–502, https://doi.org/10.1016/j.wasman.2015.10.021.

[9] R. Alvarez, G. Lidén, Anaerobic co-digestion of aquatic flora and quinoa with manures from Bolivian Altiplano, Waste Manag. 28 (2008) 1933–1940, https://doi.org/10.1016/j.wasman.2007.11.002.

[10] D. Avilés-Esquivel, M. Barros-Rodríguez, M. Montero-Recalde, Los camélidos sudamericanos: productos y subproductos usados en la región andina south american camelids: products and sub-products used in the andean region, vol. 11, 2018, pp. 30–38.

[11] S. White, No Alpacas y llamas como herramientas de conservación del páramo, J. Ef F. Archaeol. 17 (2010) 49–68.

[12] A.G. Hashimoto, Methane from cattle waste: effects of temperature, hydraulic retention time, and influent substrate concentration on kinetic parameter (k), Biotechnol. Bioeng. 24 (1982) 2039–2052, https://doi.org/10.1002/bit.260240911.

[13] A. Naska, M. Berg, C. Cuadrado, H. Freisling, K. Gedrich, M. Gregorič, C. Kelleher, E. Leskova, M. Nelson, L. Pace, Food balance sheet and household budget survey dietary data and mortality patterns in Europe, Br. J. Nutr. 102 (2008) 166–171, https://doi.org/10.1017/S000711450809466X.

[14] S. Bayr, M. Rantanen, P. Kaparaju, J. Rintala, Mesophilic and thermophilic anaerobic co-digestion of rendering plant and slaughterhouse wastes, Bioresour. Technol. 104 (2012) 28–36, https://doi.org/10.1016/j.biortech.2011.09.104.

[15] J. Palatsi, M. Viñas, M. Guivernau, B. Fernandez, X. Flotats, Anaerobic digestion of slaughterhouse waste: main process limitations and microbial community interactions, Bioresour. Technol. 102 (2011) 2219–2227, https://doi.org/10.1016/j.biortech.2010.09.121.

[16] J. Ariunbaatar, A. Panico, G. Esposito, F. Pirozzi, P. Lens, Pretreatment methods to enhance anaerobic digestion of organic solid waste, Appl. Energy 123 (2014) 143–156, https://doi.org/10.1016/j.apenergy.2014.02.035.

[17] S.K. Sharma, I.M. Mishra, M.P. Sharma, J.S. Saini, Effect of particle size on biogas generation from biomass residues, Biomass 17 (1988) 251–263, https://doi.org/10.1016/0144-4565(88)90107-2.

[18] European Standard. UNE-EN 18134-1, No TitlSolid Biofuels - Determination of Moisture Content - Oven Dry Method - Part 1: Total Moisture - Reference Method, 2016 (ISO 18134-1:2015).

[19] European Standard. UNE-EN 18134-2, Solid Biofuels - Determination of Moisture Content - Oven Dry Method - Part 2: Total Moisture - Simplified Method, 2017 (ISO 18134-2:2017).

[20] European Standard. UNE-EN ISO 18134-3, Solid Biofuels - Determination of Moisture Content - Oven Dry Method - Part 3: Moisture in General Analysis Sample, 2016 (ISO 18134-3:2015).

[21] European Standard. UNE-EN ISO 18123, Solid Biofuels - Determination of the Content of Volatile Matter, 2016 (ISO 18123:2015).

[22] European Standard. UNE-EN ISO 18122, Solid Biofuels - Determination of Ash Content, 2016 (ISO 18122:2015).

[23] A.P.H. Association, A.W.W. Association, W.P.C. Federation, W.E. Federation, Standard Methods for the Examination of Water and Wastewater, American Public Health Association, Washington, DC, USA, 2005.

[24] W. Li, H. Khalid, Z. Zhu, R. Zhang, G. Liu, C. Chen, E. Thorin, Methane production through anaerobic digestion: participation and digestion characteristics of cellulose, hemicellulose and lignin, Appl. Energy 226 (2018) 1219–1228, https://doi.org/10.1016/j.apenergy.2018.05.055.

[25] M. Ali, D. Nourou, B. Bilal, M. Ndongo, Theoretical models for prediction of methane production from anaerobic digestion: a critical review, Int. J. Phys. Sci. 13 (2018) 206–216, https://doi.org/10.5897/ijps2018.4740.

[26] S. Achinas, J. Krooneman, G. Euverink, Enhanced biogas production from the anaerobic batch treatment of banana peels, Engineering 5 (2019) 970–978, https://doi.org/10.1016/j.eng.2018.11.036.

[27] A. Ware, N. Power, Modelling methane production kinetics of complex poultry slaughterhouse wastes using sigmoidal growth functions, Renew. Energy 104 (2017) 50–59, https://doi.org/10.1016/j.renene.2016.11.045.

[28] T. Fitamo, J. Triolo, A. Boldrin, C. Scheutz, Rapid biochemical methane potential prediction of urban organic waste with near-infrared reflectance spectroscopy, Water Res. 119 (2017) 242–251, https://doi.org/10.1016/j.watres.2017.04.051.

[29] G.E. Symons, A.M. Buswell, The methane fermentation of Carbohydrates1,2, J. Am. Chem. Soc. 55 (1933) 2028–2036, https://doi.org/10.1021/ja01332a039.

[30] F. Raposo, V. Fernández-Cegrí, M. De la Rubia, R. Borja, F. Béline, C. Cavinato, G. Demirer, B. Fernández, M. Fernández-Polanco, J. Frigon, R. Ganesh, P. Kaparaju, J. Koubova, R. Méndez, G. Menin, A. Peene, P. Scherer, M. Torrijos, H. Uellendahl, I. Wierinck, V. de Wilde, Biochemical methane potential (BMP) of solid organic substrates: evaluation of anaerobic biodegradability using data from an international interlaboratory study, J. Chem. Technol. Biotechnol. 86 (2011) 1088–1098, https://doi.org/10.1002/jctb.2622.

[31] M. Sobotka, J. Votruba, I. Havlik, I. Minkevich, The mass energy balance of anaerobic methane production, Folia Microbiol. (Praha) 28 (1983) 195–204, https://doi.org/10.1007/BF02884083.

[32] R. Alvarez, S. Villca, G. Lidén, Biogas production from llama and cow manure at high altitude, Biomass Bioenergy 30 (2006) 66–75, https://doi.org/10.1016/j.biombioe.2005.10.001.

[33] J. Martí-Herrero, R. Alvarez, R. Cespedes, M.R. Rojas, V. Conde, L. Aliaga, M. Balboa, S. Danov, Cow, sheep and llama manure at psychrophilic anaerobic co-digestion with low cost tubular digesters in cold climate and high altitude, Bioresour. Technol. 181 (2015) 238–246, https://doi.org/10.1016/j.biortech.2015.01.063.

[34] R. Alvarez, G. Lidén, The effect of temperature variation on biomethanation at high altitude, Bioresour. Technol. 99 (2008) 7278–7284, https://doi.org/10.1016/j.biortech.2007.12.055.

[35] C. Holliger, M. Alves, D. Andrade, I. Angelidaki, S. Astals, U. Baier, C. Bougrier, P. Buffière, M. Carballa, V. De Wilde, Towards a standardization of biomethane potential tests, Water Sci. Technol. 74 (2016) 2515–2522, https://doi.org/10.2166/wst.2016.336.

[36] L. Pearse, J. Hettiaratchi, S. Kumar, Towards developing a representative biochemical methane potential (BMP) assay for landfilled municipal solid waste – a review, Bioresour. Technol. 254 (2018) 312–324, https://doi.org/10.1016/j.biortech.2018.01.069.

[37] A. Rozzi, E. Remigi, Methods of assessing microbial activity and inhibition under anaerobic conditions: a literature review, Re/Views Environ. Sci. Bio/

Technology. 3 (2004) 93–115, https://doi.org/10.1007/s11157-004-5762-z.

[38] E. Elbeshbishy, G. Nakhla, H. Hafez, Biochemical methane potential (BMP) of food waste and primary sludge: influence of inoculum pre-incubation and inoculum source, Bioresour. Technol. 110 (2012) 18–25, https://doi.org/10.1016/j.biortech.2012.01.025.

[39] D.P. Chynoweth, C.E. Turick, J.M. Owens, D.E. Jerger, M.W. Peck, Biochemical methane potential of biomass and waste feedstocks, Biomass Bioenergy 5 (1993) 95–111, https://doi.org/10.1016/0961-9534(93)90010-2.

[40] P.O. Alexis, T.L. Patricia, M.R. Fernando, C.C. Marcela, V.F. Carlos, T.L. Alexander, O.A. Abdón, Efecto de la relación sustrato-inóculo sobre el potencial bioquímico de metano de biorresiduos de origen municipal, Ing. Invest. Tecnol. 16 (2015) 515–526, https://doi.org/10.1016/j.riit.2015.09.004.

[41] P. Torres, A. Cardoso, O. Rojas, Mejoramiento de la Calidad de Lodos anaerobios. Influencia de la Adición de Cloruro férrico, Ing. Y Compet. 5 (2011), https://doi.org/10.25100/iyc.v5i2.2293.

[42] H. Zhang, L. Luo, W. Li, X. Wang, Y. Sun, Y. Sun, W. Gong, Optimization of mixing ratio of ammoniated rice straw and food waste co-digestion and impact of trace element supplementation on biogas production, J. Mater. Cycles Waste Manag. 20 (2018) 745–753, https://doi.org/10.1007/s10163-017-0634-0.

[43] F. Shen, H. Yuan, Y. Pang, S. Chen, B. Zhu, D. Zou, Y. Liu, J. Ma, L. Yu, X. Li, Performances of anaerobic co-digestion of fruit & vegetable waste (FVW) and food waste (FW): single-phase vs. two-phase, Bioresour. Technol. 144 (2013) 80–85, https://doi.org/10.1016/j.biortech.2013.06.099.

[44] X. Liu, R. Li, M. Ji, L. Han, Hydrogen and methane production by co-digestion of waste activated sludge and food waste in the two-stage fermentation process: substrate conversion and energy yield, Bioresour. Technol. 146 (2013) 317–323, https://doi.org/10.1016/j.biortech.2013.07.096.

[45] M. Kawai, N. Nagao, N. Tajima, C. Niwa, T. Matsuyama, T. Toda, The effect of the labile organic fraction in food waste and the substrate/inoculum ratio on anaerobic digestion for a reliable methane yield, Bioresour. Technol. 157 (2014) 174–180, https://doi.org/10.1016/j.biortech.2014.01.018.

[46] J.L. Ramos Suárez, Producción de biogás a partir de biomasa de la microalga *scenedesmus sp.* procedente de diferentes procesos, Thesis (Doctoral), E.T.S.I. Agronomists (UPM), 2014.

[47] J. Filer, H. Ding, S. Chang, Biochemical methane potential (BMP) assay method for anaerobic digestion research, Water 11 (2019) 921, https://doi.org/10.3390/w11050921.

[48] H. Bouallagui, Y. Touhami, R. Ben Cheikh, M. Hamdi, Bioreactor performance in anaerobic digestion of fruit and vegetable wastes, Process Biochem. 40 (2005) 989–995, https://doi.org/10.1016/j.procbio.2004.03.007.

[49] Y. Zhou, Z. Zhang, T. Nakamoto, Y. Li, Y. Yang, M. Utsumi, N. Sugiura, Influence of substrate-to-inoculum ratio on the batch anaerobic digestion of bean curd refuse-okara under mesophilic conditions, Biomass Bioenergy 35 (2011) 3251–3256, https://doi.org/10.1016/j.biombioe.2011.04.002.

[50] A. Boulanger, E. Pinet, M. Bouix, T. Bouchez, A.A. Mansour, Effect of inoculum to substrate ratio (I/S) on municipal solid waste anaerobic degradation kinetics and potential, Waste Manag. 32 (2012) 2258–2265, https://doi.org/10.1016/j.wasman.2012.07.024.

[51] F. Raposo, C.J. Banks, I. Siegert, S. Heaven, R. Borja, Influence of inoculum to substrate ratio on the biochemical methane potential of maize in batch tests, Process Biochem. 41 (2006) 1444–1450, https://doi.org/10.1016/j.procbio.2006.01.012.

[52] F. Vedrenne, F. Béline, P. Dabert, N. Bernet, The effect of incubation conditions on the laboratory measurement of the methane producing capacity of livestock wastes, Bioresour. Technol. 99 (2008) 146–155, https://doi.org/10.1016/j.biortech.2006.11.043.

[53] R. Alvarez, G. Lidén, Low temperature anaerobic digestion of mixtures of llama, cow and sheep manure for improved methane production, Biomass Bioenergy 33 (2009) 527–533, https://doi.org/10.1016/j.biombioe.2008.08.012.

[54] F. Pellera, E. Gidarakos, Effect of substrate to inoculum ratio and inoculum type on the biochemical methane potential of solid agroindustrial waste, J. Environ. Chem. Eng. 4 (2016) 3217–3229, https://doi.org/10.1016/j.jece.2016.05.026.

[55] S. Pommier, D. Chenu, M. Quintard, X. Lefebvre, A logistic model for the prediction of the influence of water on the solid waste methanization in landfills, Biotechnol. Bioeng. 97 (2007) 473–482, https://doi.org/10.1002/bit.21241.

[56] L. Altaş, Inhibitory effect of heavy metals on methane-producing anaerobic granular sludge, J. Hazard Mater. 162 (2009) 1551–1556, https://doi.org/10.1016/j.jhazmat.2008.06.048.

[57] Z. Zahan, M. Othman, T. Muster, Anaerobic digestion/co-digestion kinetic potentials of different agro-industrial wastes: a comparative batch study for C/N optimisation, Waste Manag. 71 (2018) 663–674, https://doi.org/10.1016/j.wasman.2017.08.014.

[58] F. Raposo, R. Borja, M. Martín, A. Martín, M. de la Rubia, B. Rincón, Influence of inoculum–substrate ratio on the anaerobic digestion of sunflower oil cake in batch mode: process stability and kinetic evaluation, Chem. Eng. J. 149 (2009) 70–77, https://doi.org/10.1016/j.cej.2008.10.001.

[59] J.H. Patil, M.A. Raj, P.L. Muralidhara, S.M. Desai, G.K. Raju, Kinetics of anaerobic digestion of water hyacinth using poultry litter as inoculum, Int. J. Environ. Sustain Dev. 3 (2012) 94.

[60] S. Vieira, R. Hoffmann, Comparison of the logistic and the Gompertz growth functions considering additive and multiplicative error terms, J. R. Stat. Soc. Ser. C (Applied Stat. 26 (1977) 143–148, https://doi.org/10.2307/2347021.

[61] A.T. Goshu, P.R. Koya, Derivation of inflection points of nonlinear regression curves-implications to statistics, Am. J. Theor. Appl. Stat. 2 (2013) 268–272, https://doi.org/10.1016/j.procbio.2004.03.007.

[62] C.P. Birch, A new generalized logistic sigmoid growth equation compared with the Richards growth equation, Ann. Bot. 83 (1999) 713–723, https://doi.org/10.1006/anbo.1999.0877.

[63] S. Achinas, G. Euverink, Theoretical analysis of biogas potential prediction from agricultural waste, Resour. Technol. 2 (2016) 143–147, https://doi.org/10.1016/j.reffit.2016.08.001.

[64] M. Lesteur, V. Bellon-Maurel, C. Gonzalez, E. Latrille, J. Roger, G. Junqua, J. Steyer, Alternative methods for determining anaerobic biodegradability: a review, Process Biochem. 45 (2010) 431–440, https://doi.org/10.1016/j.procbio.2009.11.018.

[65] A. Nielfa, R. Cano, M. Fdz-Polanco, Theoretical methane production generated by the co-digestion of organic fraction municipal solid waste and biological sludge, Biotechnol. Reports. 5 (2015) 14–21, https://doi.org/10.1016/j.btre.2014.10.005.

[66] D.A. Burke, Dairy Waste Anaerobic Digestion Handbook: Options for Recovering Beneficial Products from Dairy Manure, Environmental Energy Company, 2001, pp. 17–27.

[67] E. Demirekler, G. Anderson, Effect of sewage sludge addition on the start-up of the anaerobic digestion of OFMSW, Environ. Technol. 19 (1998) 837–843, https://doi.org/10.1080/09593331908616740.

[68] P. Zhang, G. Zeng, G. Zhang, Y. Li, B. Zhang, M. Fan, Anaerobic co-digestion of biosolids and organic fraction of municipal solid waste by sequencing batch process, Fuel Process. Technol. 89 (2008) 485–489, https://doi.org/10.1016/j.fuproc.2007.11.013.

[69] P. Eronen, M. Österberg, S. Heikkinen, M. Tenkanen, J. Laine, Interactions of structurally different hemicelluloses with nanofibrillar cellulose, Carbohydr. Polym. 86 (2011) 1281–1290, https://doi.org/10.1016/j.carbpol.2011.06.031.