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Modeling of sludge and flax anaerobic co-digestion based on combination of first order and modified Gompertz models: influence of C/N ratio and headspace gas volume

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ABSTRACT

The goal of this study is to improve biogas yields from the co-digestion of primary sludge (PS) and flax, based on their carbon-to-nitrogen (C/N) ratio, and the effects of the headspace gas volume fraction (HSVF) in the batch reactor. The work was carried out in two stages. First, five mixtures of PS and flax at different C/N ratios were prepared for biogas production. The highest biogas production was observed at a C/N ratio of 20, and the lowest at a C/N ratio of 10. In the second stage, the optimum C/N ratio of 20 was used in batch reactor experiments to test five different HSVFs. The highest biogas productions were obtained at an HSVF of 2.33. However, the highest methane content was recorded at an HSVF of 1.5 (62.33%). The theoretical and stoichiometric methane yields of the feedstock used were estimated. Biochemical Methane Potential (BMP) tests showed the presence of two fractions: one immediately biodegradable to methane and another, less biodegradable, which required a lag phase to transform into biogas. A new kinetic model representing these two phases was proposed to accurately describe the results of the experiment.

Keywords: Sludge; Flax; Anaerobic co-digestion; Headspace gas volume fraction (HSVF); C/N ratio

1. Introduction

The disposal of sludge in a sustainable, environmentally acceptable manner is a major challenge facing many countries. With the rapid advancement of urbanization, greater amounts of sewage sludge (SS) are being produced at waste treatment plants (WWTPs), which increases the overall cost; sludge treatment now accounts for over 60% of the total cost of wastewater treatment [1]. Recent works have therefore focused on improving the digestion of SS, which would reduce SS handling costs. Anaerobic digestion (AD) has been put forward as the best technique for producing renewable energy from organic waste [2].

Enormous amounts of waste are also created with agricultural crops, which are mainly disposed of via incineration or landfill; methods which are not environmentally sound. Agricultural waste contains important resources that can be recuperated for many and varied financial, social and physical purposes. Flax, for example, is considered an important textile crop. It is grown in many parts of the world, but the best quality flax is grown in Ukraine and some Western European nations. Europe and Asia are the top worldwide producers of flax [3].

Anaerobic co-digestion of SS and agricultural waste is the best solution for enhancing the properties of the feedstock tested, improving gas production [4], enhancing the carbon-to-nitrogen proportion (C/N) ratio [5] and reducing the chance of ammonia inhibition [6]. There have been few reports on the co-digestion of SS and flax in previous works. Elsayed et al. [7], reported the improvement of methane production from the co-digestion of sludge and agricultural waste with different C/N ratios; the results concluded

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that the greatest methane production was obtained at a C/N ratio of 10. Wu et al. [8] showed significant methane production from the co-digestion of swine manure and three crops (depending on the C/N ratio) at a C/N ratio of 20.

The headspace conditions have a significant influence on the fermentation process, as demonstrated in the two-stage anaerobic digestion study; their effects were observed on both the volume (and therefore pressure) of the headspace and the composition of the gas it comprises [9].

The effect of the ratio of working volume to head space on biogas production using the BMP test has not been widely enough investigated. Valero et al. [10] studied the effects of headspace pressure in a BMP test, and the results concluded that headspace overpressure affects biogas production and composition, based on the type of feedstock. Himanshu et al. [11] demonstrated the role of the pressure in the gaseous headspace on the composition of the biogas. Hua et al. [12] studied the effect of acidogenic headspace pressure on gas production using four different headspace pressures in a two-stage anaerobic digestion processes, the results demonstrating that a headspace pressure of 3 to 6 psi is best for improving the hydrolysis process. Yan et al. [13] studied the effect of acidogenic headspace pressure on gas production using four different headspace pressures in a two-stage anaerobic digestion processes, the results demonstrating that a headspace pressure of 3 to 6 psi is best for improving the hydrolysis process.

The influence of the batch reactor's HSVF on biogas production has not yet been investigated and the anaerobic co-digestion of PS and flax has been insufficiently documented in previous studies. For this work, the co-digestion of SS and flax based on C/N ratios was investigated first of all, then the influence of HSVF on gas production was examined. A kinetic analysis of methane production was carried out using a proposed new model to reveal the easily biodegradable fraction in the mixture and the lag phase time required for degradation of the fraction less easy to convert into biogas. The Buswell equation was used to provide a stoichiometric calculation of the products from anaerobic breakdown of the generic organic material present in each batch. The results were compared with those of the experiment, to identify the parts of the organic matter used in the production of biogas and those used in the maintenance of bacterial activity. The aim was to discover the effect of each parameter studied on the production of methane.

2. Methodology

2.1. Preparation of substrates

Primary sludge (PS) obtained from the Nantes wastewater treatment plant (France) was used as a substrate. PS was recovered from a wastewater treatment plant by coagulation–flocculation. The settled sludge was partially dehydrated in a screw press up to a moisture content of 80 wt.% and dried up to a moisture of 30 wt.% in a steam dryer (scan ship). Before use, these wastes were stored in closed bags. Flax was obtained from a farm in Normandy (France) and dried at ambient temperature (for 3 d). The flax sample was ground to reduce its size.

2.2. Inoculum

Digested cow manure was obtained from a semi-continuous reactor at IMT Atlantique, Nantes (France). The total solids (TS) of the inoculum were found to be 5.59% of the dry weight, and volatile solids (VS) amounted to 73.18% of the total solids.

2.3. Analytical techniques

The elemental analysis was carried out using a FLASH EA 1112 Series CHN Analyzer. VS, TS and pH were estimated using APHA Standard methods [14]. The biogas yields were collected using the water displacement method then analyzed using the G2801A (Agilent Technologies, China). The cumulative biogas yields were estimated to STP values (10^5 Pa and 273.15 K). The characteristics of the substrate and inoculum used in the BMP tests are shown in Table 1.

The VS removal efficiency was calculated from the following equation:

$$\mathrm{VS}_{\mathrm{removal}} = \frac{\mathrm{VS}_{\mathrm{in}} - \mathrm{VS}_{\mathrm{exit}}}{\mathrm{VS}_{\mathrm{in}}} \times 100 \quad (1)$$

2.4. Experimental design and set-up

The BMP test was carried out in triplicate following a method described by Elsayed et al. [7] (Fig. 1). In the initial experiments, five mixtures of anaerobic co-digested PS and flax at different C/N ratios were used in BMP reactors,

Table 1
Characteristics of feedstock components used in batch tests

Characteristics	Primary sludge (PS)	Flax	Inoculum
Volatile solids (TS %)	82.50 ± 0.10	98.20 ± 0.10	81.97 ± 0.08
Total solids (dry wt.%)	81.70 ± 0.15	88.42 ± 0.15	4.123 ± 0.36
Carbon (dry wt.%)	39.90 ± 0.44	48.64 ± 0.44	ND
Nitrogen (dry wt.%)	6.70 ± 0.25	0.59 ± 0.25	ND
Oxygen (dry wt.%)	28.30 ± 0.19	28.30 ± 0.19	ND
Hydrogen (dry wt.%)	5.40 ± 0.09	5.98 ± 0.09	ND
C/N ratio	5.96	82.44	ND
pH	ND	ND	6.90 ± 0.09

Notes: ND: Not determined, C/N = nitrogen-to-carbon (data represent the means ± SD, $n = 4$).

designated D1 to D5 (Table 2). Two digestion reactors, one containing only PS and the other only flax, were also prepared, designated D6 and D7 respectively.

In the second phase, anaerobic digestion of the five PS and flax mixtures was carried out in batch reactors designated G1 to G5 (Table 3), corresponding to different headspace gas volume factions. The optimal C/N ratio of 20, identified in the initial experiments, was used in all the reactors.

2.5. Stoichiometric methane (BMP_{th}) yield of substrates

The stoichiometric equation based on the atomic composition of each mixture was used to calculate the theoretical methane production and composition. The substrate is described by the empirical formula $C_aH_bO_cN_dS_x$ according to the C, H, N, S and O composition [15]. The theoretical methane, carbon dioxide and ammonium yields were calculated with the following formula adapted from Symons and Buswell [16]:

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

However, this theoretical approach does not differentiate between biodegradable and non-biodegradable matter and not take into account the need for methanogen cell maintenance and anabolism. The specific stoichiometric CH_4 yield (BMP_{th}) expressed as mL_{CH_4}/g VS at normal temperature and pressure conditions can therefore be subsequently calculated using Eq. (3) [17,18]:

$$BMP_{th} = \frac{V_m}{8}\left(\frac{4a + b - 2c - 3d}{12a + b + 16c + 14d}\right) \quad (3)$$

Table 2
Different C/N ratios of co-digested PS and flax

Reactor number	D1	D2	D3	D4	D5	D6	D7
PS_{added} (g VS/400 mL)	4.25	2.65	1.85	1.37	1.04	7.50	0.00
$Flax_{added}$ (g VS/400 mL)	3.25	4.85	5.65	6.14	6.46	0.00	7.50
C/N ratio	10.0	15.0	20.0	25.0	30.0	5.96	82.44

where V_m is the molar volume of CH_4 under normal pressure and temperature conditions.

However, the theoretical methane production based on the atomic composition of each batch reactor considers all organic material as being degraded, so a proper adjustment of this value is needed, using the biodegradability (BD_{VS} [%]), calculated using the VS content before ($VS_{initial}$) and after (VS_{final}) the experimental BMP tests:

$$BD_{VS}(\%) = \frac{VS_{initial} - VS_{final}}{VS_{initial}} \times 100 \quad (4)$$

The deviation between experimental and theoretical production involving the biodegradability rate (BMP_{thBD}) was calculated [Eq. (5)] in order to identify the presence of inhibitory or accelerator factors for biogas production. This parameter was calculated using the relationships given by Nielfa et al. [19].

$$\text{Error} = \frac{BMP_{exp} - BMP_{thBD}}{BMP_{exp}} \quad (5)$$

2.6. Kinetic analysis of cumulative biogas production

In this part, a parametrization operation was carried out with functions able to predict a fairly accurate methane production profile, involving a certain number of parameters. The main reason for this type of modeling was to establish a comparable basis for the various profiles that could be transposed from one experiment to another. A prediction algorithm was therefore used to estimate the final BMP and the time needed to reach this state. The kinetic prediction was done by minimizing the difference between the output from a kinetic model and the experimental gas profile production of the target sample. The two main functions used in the literature are the model derived from the general solution of a first-order differential equation [20] and the Gompertz model [21, 22].

2.6.1. First-order model

The first-order model is often used to characterize BMP measurements for high I/S (Inoculum/Substrate) ratios. This type of profile, without a methanogenic activity latency phase, is characterized by the apparent first-order kinetics and the structurally-identifiable global constant k (d^{-1}) associated with it.

Table 3
Different ratios of batch reactor HSVF to anaerobic co-digested PS and flax

Reactor number	G1	G2	G3	G4	G5
PS_{added} (g VS/L)	1.85	1.85	1.85	1.85	1.85
$Flax_{added}$ (g VS/L)	5.65	5.65	5.65	5.65	5.65
HSVF	9 (450/50 mL)	4 (400/100 mL)	2.33 (350/150 mL)	1.5 (300/200 mL)	1 (250/250 mL)
C/N ratio	20.0	20.0	20.0	20.0	20.0

Note: PS = primary sludge; HSVF = headspace gas volume fraction; C/N = carbon-to-nitrogen.

In this case, the AD kinetics are generally reduced to the hydrolytic reaction of organic matter, which is considered a limiting stage of the AD, the products of which would be almost instantaneously metabolized by methanogenic organisms [23].

$$\text{BMP}(t) = \text{BMP}^{\text{1st}}_{t\to\infty}\left(1-\exp(-k\times t)\right) \tag{6}$$

where BMP (t) is the accumulative methane production (mL/g VS), $\text{BMP}^{\text{1st}}_{t\to\infty}$ the methane production potential (mL/g VS) obtained by the first order model, and k the rate constants for the first-order equation (d^{-1}).

2.6.2. Modified Gompertz equation

Production profiles similar to a sigmoid are characterized by a methanogenic activity lag time. This lag time is caused by an organic charge responsible for the reduction in I/S ratio. The reduction in the amount of active AD biomass vs substrate to be degraded consequently induces lower apparent methanogenic kinetics. The microbial digestion consortium undergoes an 'organic shock' under these conditions [24]. The modified Gompertz equation, proposed by Jiunn-Jyi et al. [25], was used to predict this adaptation phase prior to methane production.

$$\text{BMP}(t) = \text{BMP}^{G}_{t\to\infty}\cdot\exp\left[-\exp\left[\frac{R_m\cdot e}{\text{BMP}^{G}_{t\to\infty}}(\lambda-t)+1\right]\right] \tag{7}$$

where R_m is the maximum methane production rate (mL/g VS d), $\text{BMP}^{G}_{t\to\infty}$ is the methane production potential (mL/g VS) obtained from the modified Gompertz equation, λ is the length of the lag-phase (days) and e is 2.718281828.

2.6.3. Mixed production profiles: combination of first-order and modified Gompertz models

The disadvantage of the first-order and modified Gompertz models is that they are limited to a strict production profile description. However, it is not uncommon for mixed methane production profiles to be obtained when degrading a complex substrate, which may contain both easily-digested and poorly-biodegradable organic components, so a model must be proposed that takes into account the different forms of organic matter.

Consequently, a mixed-parameter model based on the work of Strömberg et al. [26] and Bassard [27] was used to counteract the limitations of the two models described above. The simple method used consisted of combining the two models to benefit from the advantages of each. However, the kinetics of the two models share the coefficient x_{eb}, the 'easily-biodegradable' fraction of the substrate or mixture under consideration. In this model, the AD of the easily-biodegradable fraction was carried out according to the first-order rate model, while the less-biodegradable fraction contributed to the BMP profile after the lag phase time λ. This coefficient therefore corresponded to the ratio of potential methane production obtained with the first-order model and modified Gompertz equation: $x_{eb} = \text{BMP}^{\text{1st}}_{t\to\infty} / \text{BMP}^{G}_{t\to\infty}$

Eq. (8) gives the developed model:

$$\text{BMP}(t) = \text{BMP}^{\text{1st}}_{t\to\infty}\cdot\left(1-\exp(-k\times t)\right)+\left(\text{BMP}^{G}_{t\to\infty}-\text{BMP}^{\text{1st}}_{t\to\infty}\right)\cdot\exp\left[-\exp\left[\frac{R_m\cdot e}{\left(\text{BMP}^{G}_{t\to\infty}-\text{BMP}^{\text{1st}}_{t\to\infty}\right)}\cdot(\lambda-t)+1\right]\right] \tag{8}$$

In the first phase, the less-biodegradable fraction was hydrolyzed to prepare for the second phase of biogas production. Kinetic prediction was carried out by minimizing the difference between the output from a kinetic model and the gas profile of the target sample. Root mean square error (RMSE) was used to ascertain the experimental and predictive values.

3. Results and discussion

3.1. Co-digestion study of PS and flax at different C/N ratios

3.1.1. Daily and cumulative methane yield

According to Hartmann and Ahring [28], the main problem with co-digestion lies in the C/N ratio (by mass),

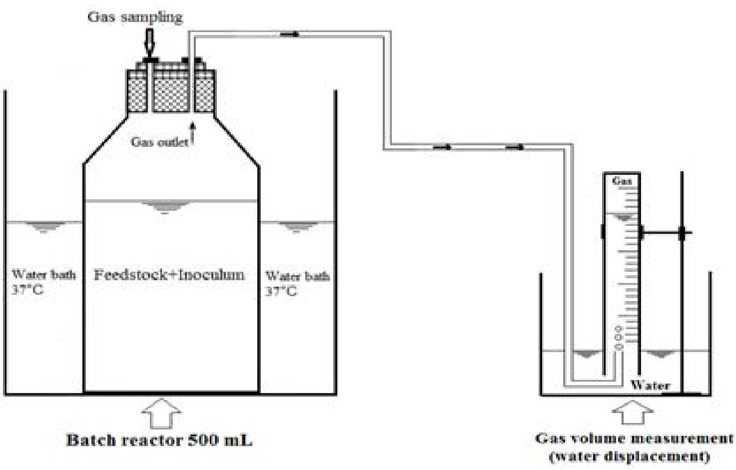

Fig. 1. BMP test set-up.

but there are several other substrate parameters that affect it, such as macro/micronutrients, pH, inhibitory/toxic compounds and organic and dry matter. Given this large number of variables, identifying the optimal parameters for biogas production requires a combination of experimental and predictive theoretical approaches.

The daily methane production for different C/N ratios is given in Fig. 2. For the different batches studied, the production of biogas was very low over the early days of the BMP test, which can be explained by the low fraction of easily-biodegradable organic matter capable of being converted into biogas [7]. An increase in daily production was observed from day 10 and remained until day 20, with a peak observed for the C/N ratio of 20 on day 14. This increase in production occurred after a latency period corresponding to preparation of the biogas production stages via enzymatic hydrolysis. This lag phase has often been observed when agricultural waste is treated by anaerobic digestion and has always been explained by the presence of lignocellulosic compounds in the composition of this type of waste. The daily biogas production decreased greatly over the last 5 d of the BMP test, reaching lower levels than those observed in the initial trial and for the different C/N ratios.

The cumulative methane yields (CMYs) from the co-digestion of PS and flax are shown in Fig. 3. The different C/N ratios were compared with STATGRAPHICS Centurion XV software (Virginia, USA). There was a statistically significant difference between the mean cumulative methane yields from one C/N ratio and another at the 95.0% confidence level. At C/N ratios of 10.0, 15.0, 20.0, 25.0 and 30.0, the CMYs were recorded as 172.5, 247.6, 297.3, 229.3 and 194.3 mL/g VS respectively. The highest value was at the C/N ratio of 20 and the lowest at the C/N ratio of 10. Comparisons of all cases revealed greater CMYs than those for the individual digestion of PS and flax. The low CMY with PS can be explained by the low level of organic matter in the mixture with a C/N ratio of 6. With flax, a high C/N ratio was measured (82.44), which could cause an increase in the concentration of volatile fatty acids (VFAs). This overproduction can lead to the 'acid-crash' phenomenon where the pH drops due to an accumulation of VFAs, hindering biogas production [29]; this could explain the CMY value observed for this substrate.

It is clear that a peak in biogas production is obtained at C/N = 20 and either a limitation or excess of organic carbon is observed on either side of this value, which causes inhibition by acidification of the medium via the accumulation of VFAs. To counteract this low-biodegradable carbon content in the PS substrate, co-digestion with flax enabled a C/N ratio that would give high biogas yields, as with batches D1, D2 and D3, but without reaching carbon concentrations that would impede the activity of methanogenic bacteria. The use of vegetable waste or waste from agricultural activity has always been used in anaerobic digestion processes to assist primary sludge as a co-substrate, since this type of waste is rich in biodegradable organic matter [30]. Indeed, Elsayed et al. [31], studied the anaerobic co-digestion of primary sludge, buckwheat husk, and wheat straw.

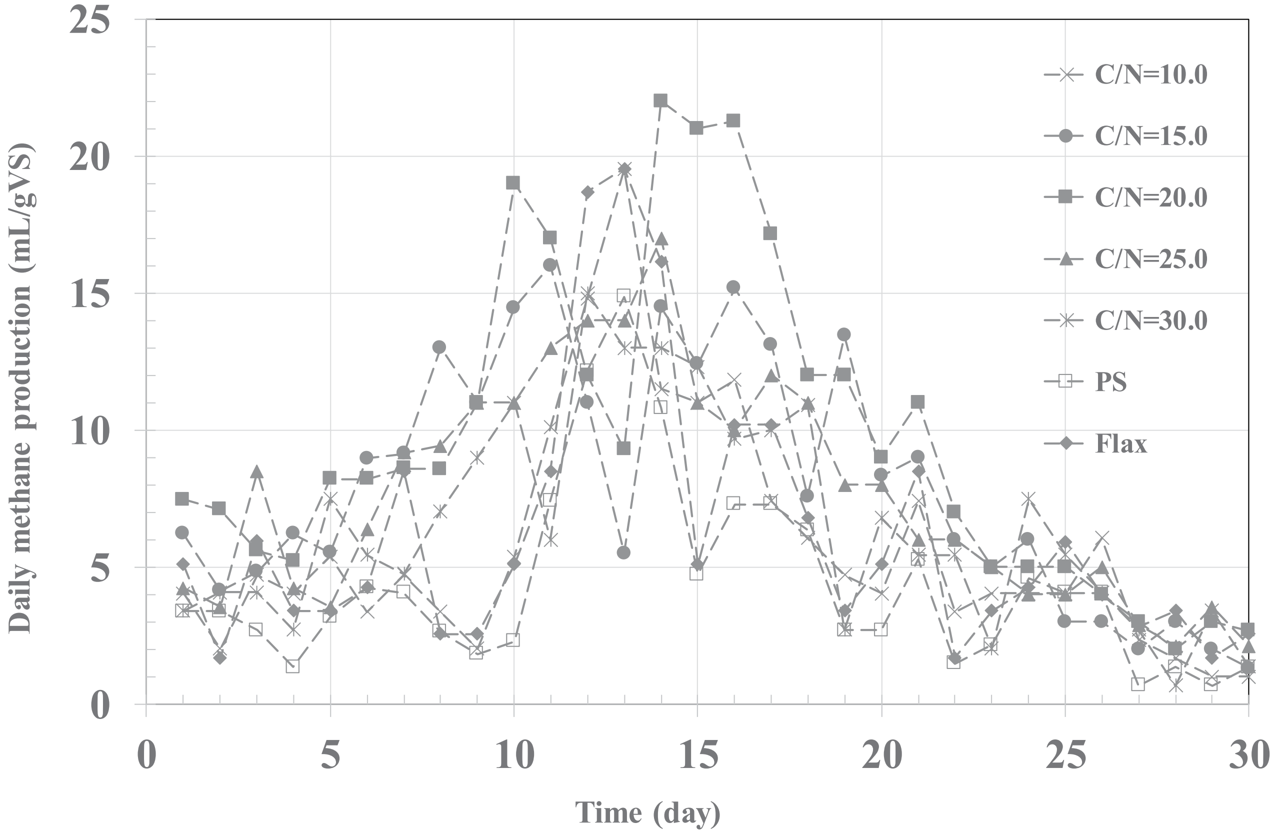

Fig. 2. Daily methane production at different C/N ratios.

These authors showed that the organic loads and the I/S ratio play an important role in the anaerobic digestion of theses agricultural wastes. In the current study, only flax is used as co-substrate in the anaerobic co-digestion with primary sludge, which could explain the different in the biogas production yield compared to that of Elsayed et al. [31].

3.1.2. Methane content and VS removal

Fig. 4a shows the daily evolution in CH_4 content for the different C/N ratios. The maximum methane content was observed for batch D3 (C/N = 20) at a rate of 59.3% methane. Note that this rate was not constant and varied throughout the BMP test for all batches. However, the variation was insignificant for batch D3 (C/N = 20) from day 15, with values fluctuating around 58%. The lowest values were observed with C/N = 10, accounted for by the low level of organic carbon in the mixture. Note that with flax only (D7), higher methane levels were observed than for D1 until day 25, due in particular to the high C/N ratio (80). A decrease was subsequently observed, probably due to the effect of the high C/N level on bacterial activity. In all cases,

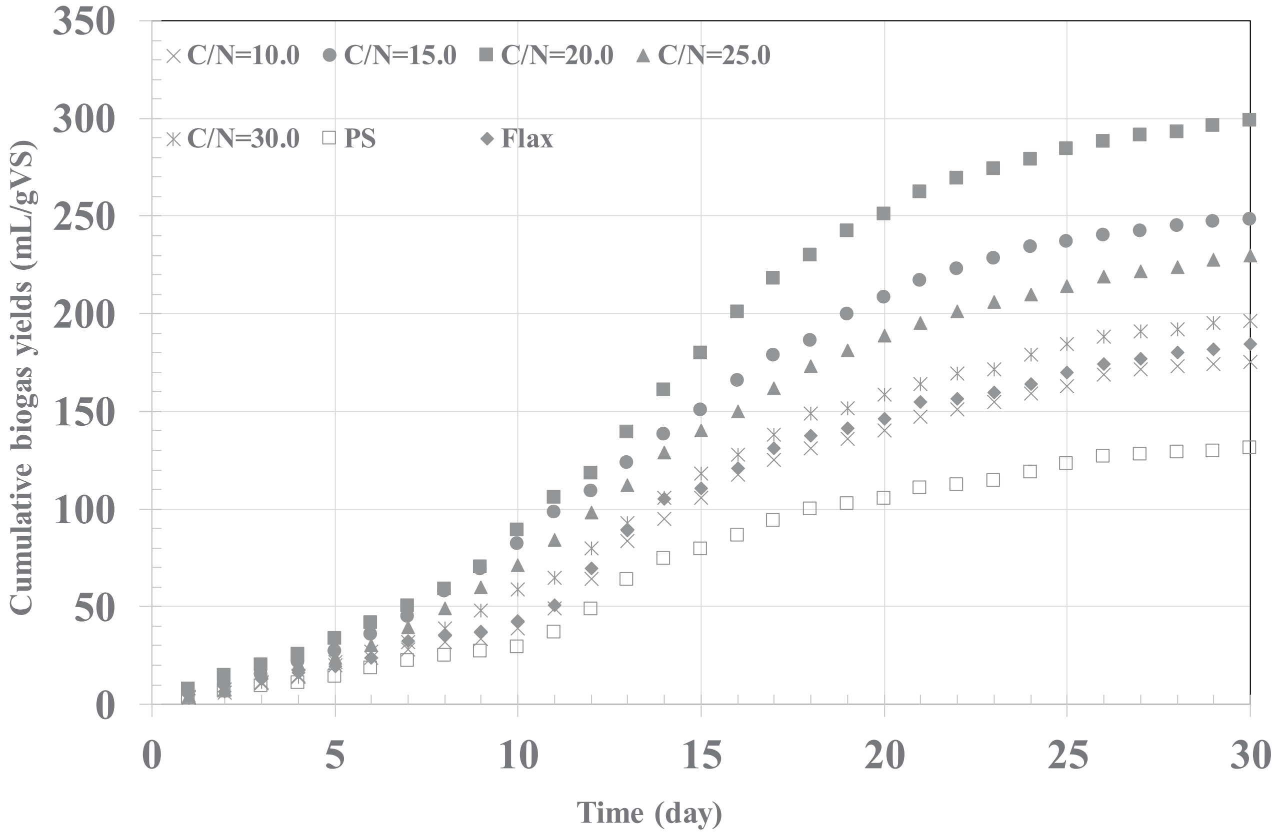

Fig. 3. CMY from co-digestions of PS and flax at different C/N ratios.

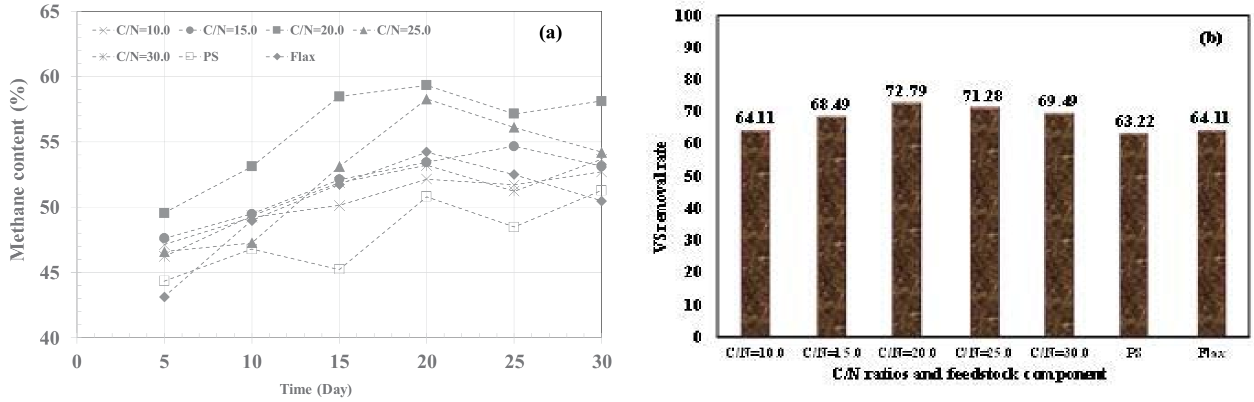

Fig. 4. Average CH_4 content (a) and VS removal efficiency (b) for PS and flax co-digestion.

the methane levels obtained correspond to those given in the literature for the anaerobic digestion of agricultural waste without pre-treatment [32].

Fig. 4b shows that the VS removal efficiency is also slightly higher at a C/N ratio of 20 compared to other cases; the rate was about 72.8% compared to 64%, 68.5%, 71.3% and 69.5% respectively for batches D1, D2, D4 and D5. This parameter also provides confirmation that the C/N = 20 batch is the most suitable for a co-digestion of PS and Flax. This condition does not induce an inhibitory effect, either by acidification of the medium by excessive production of volatile fatty acid, due to an excess of carbon, or by activation of the nitrobacteria responsible for the accumulation of ammonia where there is an excess of nitrogen as discussed in the literature for this ratio, but with other substrates [33]. Note however that the C/N ratios only relate to the initial state, and since the system operates in batch mode, this parameter will change over time. Identification of the best C/N ratio therefore depends on the synergy of a set of parameters, that is, daily production, CMY, methane content and percentage of VS removal.

3.1.3. Estimate of stoichiometric methane (Bo) yield of substrates at different C/N ratios

The Buswell equation was used to estimate the theoretical maximum CH_4 production (as it assumes 100% organic biomass breakdown) and the related proportions of CH_4 and CO_2, as well as H_2S and NH_3 production.

Table 4 summarizes the experimental and theoretical methane conversion yield for each BMP reactor. The CH_4 calculated using the Buswell equation is always higher than can be obtained in the AD process, since a small amount of biomass is consumed in the anabolic metabolic pathways and therefore converted to microorganisms. This effect was observed in this work, the theoretical methane yield after correction with the biodegradability factor varying from 427.51 to 302.96 mL CH_4/g VS_{add}, depending on the composition of the reactor. The errors obtained in this work (Table 4) were between 44% and 141%. These values are greater than those observed in the literature for other substrates [19], due to there being a fraction of substrate not easily biodegradable. Simple substrates (e.g., starch, albumin, oleic acid) usually have biodegradation yields close to 100%. Nevertheless, certain complex polymeric structures (lignins, keratin, melanoidins, etc.) and dense organizational macrostructures of the organic matter (lignocellulosic matrices, microbial flocs from aerobic biological sludge, etc.) can induce negative effects on the biodegradation yields of the substrate, resulting in differences between the theoretical potential and the BMP measured. For this work, the biodegradable fraction was based on observation of the shape of the daily CMY curve, but it is also demonstrated through the kinetic study of anaerobic digestion (discussed below). Note that some of the organic material is used for the maintenance and development of microorganisms, and the proportion of this depends on the state of the inoculum and its level of activation. All these reasons may explain this difference between the theoretical and experimental BMP.

Note also that the smallest error between the experimental and theoretical BMP tests was observed at C/N = 20 (44%), relating to the case with the highest BMP test. Likewise, where a high BMP was observed, errors were less than 100% (C/N = 15 and 25). This clearly shows that the anaerobic digestion yield, compared to the optimal theoretical case, depends on the experimental conditions, especially the C/N ratio.

3.2. Co-digestion study of PS and flax based on headspace gas volume fraction (HSVF)

3.2.1. Daily yield and CMY from co-digestion of PS and flax at different HSVFs

The effect of the HSVF on daily methane production is given in Fig. 5. All experiments were carried out with the optimal C/N ratio of 20 identified in the first series of measurements. As with the C/N ratio effect, maximum daily production was observed between days 11 and 17, with optimum production observed with the HSVF at 2.33. This curve shape for daily production is usually observed in the BMP tests, starting with low biogas productivity followed by accelerated production, with a peak around day 15 and deceleration over the remaining days. This demonstrates that the HSVF parameter does not affect the biogas production kinetics, corresponding to destabilization of the physiological balance of the bacterial consortium present in the inoculum, but does enable the emergence of an inhibition phenomenon due to the change in experimental conditions.

The CMYs from co-digestion of PS and flax at different HSVFs are shown in Fig. 6. A one-way analysis of variance showed a significant difference between the mean cumulative methane yields between HSVF levels at the 95.0% confidence level. Where the HSVF was 1 (250/250 mL),

Table 4
Experimental and theoretical BMP

Reactor number		BD_{VS} (%)	BMP_{exp} (mL CH_4/g VS)	BMP_{th} (mL CH_4/g VS)	BMP_{thBD} (mL CH_4/g VS)	Error
D1	C/N = 10.0	64.1	172.5 ± 3.6	542.27	347.77	–1.02
D2	C/N = 15.0	68.4	247.6 ± 0.9	572.61	391.92	–0.58
D3	C/N = 20.0	72.8	297.3 ± 1.9	587.60	427.51	–0.44
D4	C/N = 25.0	71.3	229.3 ± 0.5	596.56	425.28	–0.85
D5	C/N = 30.0	69.5	194.3 ± 3.2	602.64	418.64	–1.15
D6	PS	63.2	125.5 ± 7.8	479.03	302.96	–1.41
D7	Flax	64.1	183.7 ± 1.1	621.78	398.77	–1.17

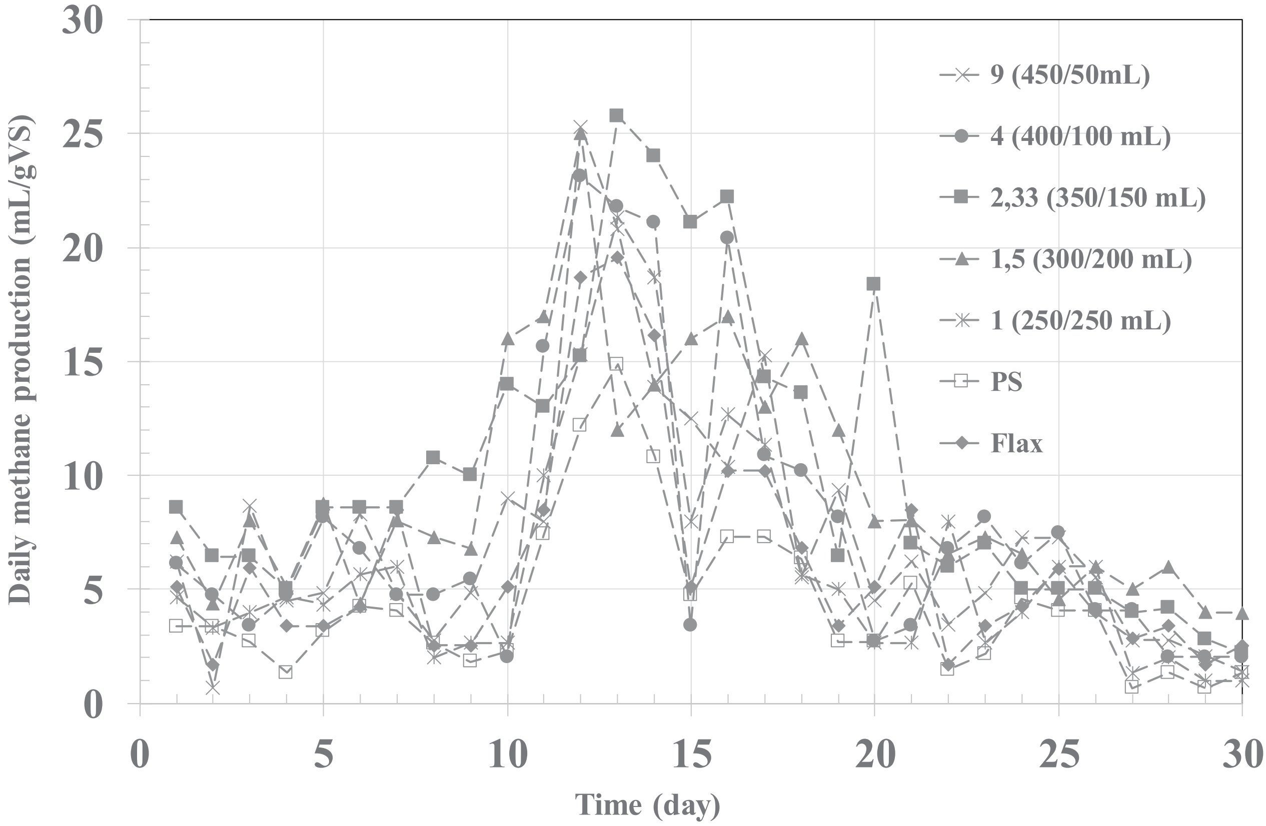

Fig. 5. Daily methane production for different HSVFs.

1.5 (300/200 mL), 2.33 (350/150 mL), 4 (400/100 mL) and 9 (450/50 mL), the CMYs recorded were 218, 229.3, 303.6, 278 and 182.2 mL/g VS_{add} respectively. The best value was conducted at the HSVF of 2.33 (350/150 mL) and the lowest at the HSVF of 1 (250/250 mL).

These results correspond to those described in the literature: a high HSVF causes an increase in headspace pressure and produces favorable conditions for some of the bacteria in the headspace responsible for the hydrolysis of organic matter (hydrolytic bacteria), and the production of volatile fatty acid (acidogenic bacteria) [13]. This was true with batch G3 (2.33), for which the best CMY was obtained. However, when the pressure continued to increase, the pH continued to decrease with greater activity by acidogenic bacteria [9]. These phenomena affect both biogas production and composition, which could explain the CMYs obtained with HSVF 4 and HSVF 9. Other authors have shown that increasing the pressure in the headspace has other effects too, depending on the nature of the gas present [11]. Where there are high concentrations of CO_2, the increase in pressure causes an acidification effect due to the increased solubilization of carbon dioxide in the medium with increased headspace pressure, potentially perturbing some microbial activity. Indeed, the increase in biogas production could be accompanied by a modification of the bacterial activity which produces more CO_2 or ammonia, depending on the composition of the medium, and therefore reduces the biomethane concentration, potentially altering the activity of the methanogens [12]. Similarly, Yan et al. [13] and Lyberatos and Skiadas [34] showed that higher H_2 pressure in the headspace could inhibit the acetogenic biomass growth rate; this observation was explained by the high concentration of H_2 inhibiting the generation of propionic and butyric acids.

3.2.2. CH4 content and VS removal from co-digestion of primary sludge (PS) and flax with different HSVFs

Fig. 7a shows the daily evolution of CH_4 content (a) from co-digestion of PS and flax with different HSVFs. Throughout the BMP test, the highest percentages of methane were obtained with an HSVF of 1.5, although this does not correspond with the best CMY result, which demonstrates the effect this factor has on biogas composition and confirms the findings presented above. Producing more biogas does not mean producing more methane, and the increase in headspace pressure has consequences on the physicochemical parameters of the mixture, in particular the pH, and subsequently on the activity of the bacteria present in the medium. It is therefore important to have an intermediate ratio of medium volume to headspace for optimal biogas productivity, as is the case with this study (HSVF between 1.5 and 2.33), and also a high methane concentration. This will avert the added costs of biogas treatment.

In terms of the VS removal efficiency (Fig. 7b), the highest values were obtained for the batches with HSVFs of 4, 2.33 and 1.5 (respectively 37.5%, 74.5% and 71.2%). This result is consistent with the results for CYM, with the

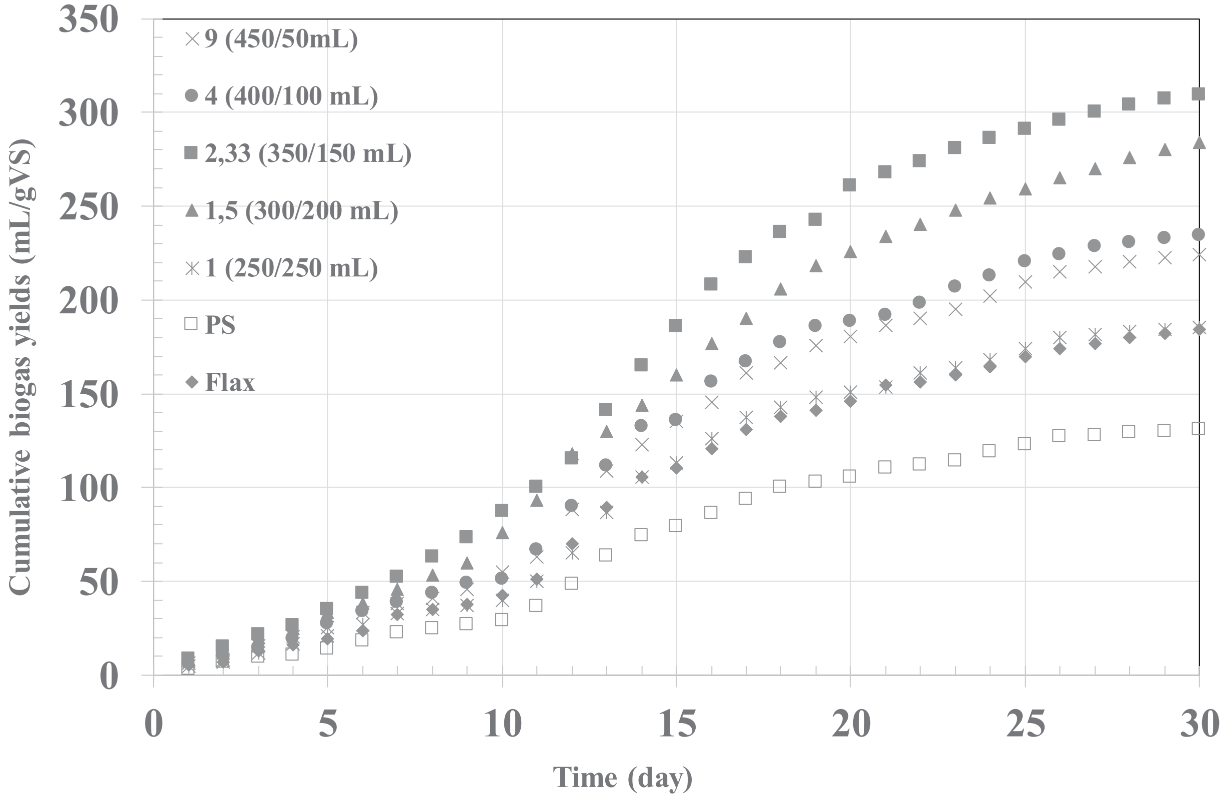

Fig. 6. CMY from co-digestion of PS and flax at different HSVFs.

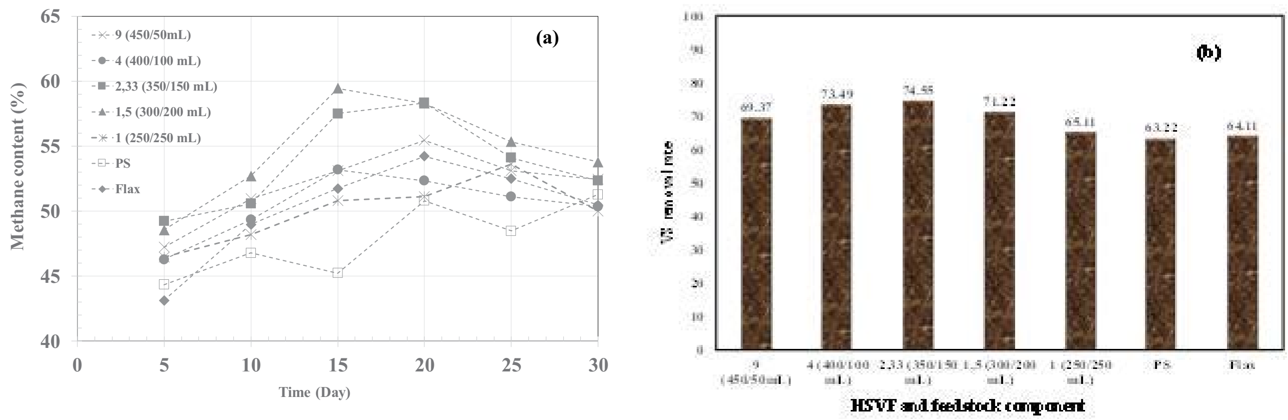

Fig. 7. Average CH_4 content (a) and VS removal efficiency (b) from co-digestion of PS and flax at different HSVFs.

highest rate obtained at HSVF = 2.33. The division between the low rate of VS removal (at HSVF of 1) and high rate (at HSVF of 2.33) of degradation indicating biodegradable and less-biodegradable components. This result shows also that the range of HSVF between 2.33 and 4 constitutes optimal conditions for the degradation of organic matter by microorganisms.

3.3. Kinetic analysis of cumulative biogas production

Fig. 8a and b show the experimental BMP results under different test conditions and the estimated curves with the kinetic model developed in this study. Given the shape of the CMY curves, a mixed model combining the first-order and modified Gompertz models was proposed. A BMP test of this mixture with inoculum and substrates (PS/flax) presented a particular appearance, with low biogas productivity in the early days due to the presence of organic matter in the monomer state, which can be converted directly into biogas following the activity of methanogens, and a more complex organic matter fraction which required a hydrolysis stage to commence biogas production, the extent of which is dependent on the nature of the substrate. This explains the proposed model, which has a dual rate of biogas production to identify the easily-biodegradable fraction and the lag-phase time, at the end of which the less-biodegradable substrate is hydrolyzed and ready to produce biogas.

The estimated curves were consistent with those determined experimentally for all C/N ratios and HSVFs. This is demonstrated by the RMSE parameter, which is less than 3 in most cases (Tables 5 and 6).

Analysis of Tables 5 and 6 shows that the various estimated $BMP^{G}_{t\to\infty}$ values are consistent with the BMP results determined experimentally, in terms of both C/N ratio and HSVF. In addition, with the C/N = 20 ratio, the $BMP^{1st}_{t\to\infty}$ and $BMP^{G}_{t\to\infty}$ is better than with the other conditions, which is consistent with the results obtained experimentally. Apart from where C/N = 10, all other cases showed an almost identical fraction of easily-biodegradable organic matter ($x_{eb} \approx 0.21$). This could be explained by the fact that this fraction comes from the inoculum, since the same amount was introduced in each batch. The few variations are due to the effect of C/N conditions on bacterial activity, as explained above. The lag-phase times, which are also almost identical, may confirm this finding. In terms of the constant rate (k) and maximum methane production rate (R_m), the highest values were obtained where C/N = 20.

For the kinetic parameters estimated by studying the different HSVFs, the condition 2.33 (350/150 mL) gave the highest $BMP^{G}_{t\to\infty}$, with a value consistent with that determined experimentally (306.35 mL CH_4/g VS). On the other hand, variations in the easily-biodegradable fraction (x_{eb}) were greater than those obtained when studying the C/N factor, due to the significant effect that the headspace fraction had on the bacterial balance in certain batches, where the increase in pressure modified the operating parameters

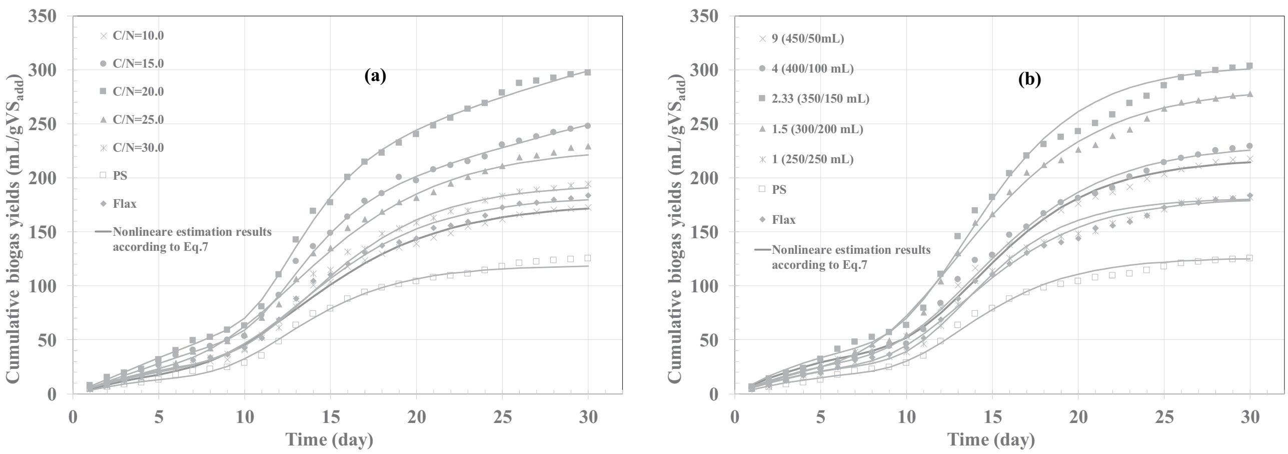

Fig. 8. Estimated and experimental CMYs from co-digestion of PS and flax at different C/N ratios (a) and HSVFs (b).

Table 5
Kinetic parameters of BMP tests at different C/N ratios calculated from non-linear regression of Eq. (7)

	$BMP^{1st}_{t\to\infty}$ (mL CH_4/g VS)	$BMP^{G}_{t\to\infty}$ (mL CH_4/g VS)	k (d^{-1})	R_m (mL/g VS d)	λ (d)	RMSE	x_{eb}
C/N = 10.0	33.13	176.40	0.147	10.85	8.35	1.93	0.188
C/N = 15.0	53.00	241.66	0.136	17.20	9.00	2.85	0.219
C/N = 20.0	64.01	304.63	0.134	19.00	8.90	3.54	0.210
C/N = 25.0	48.93	228.22	0.120	13.40	8.10	2.28	0.214
C/N = 30.0	40.00	194.35	0.154	13.51	9.58	2.24	0.206
PS	25.91	119.53	0.140	9.35	8.84	1.51	0.217
Flax	40.00	183.85	0.139	12.04	9.00	2.25	0.218

Table 6
Kinetic parameters of BMP tests at different HSVFs calculated from non-linear regression of Eq. (7)

HSVF	$BMP^{1st}_{t\to\infty}$ (mL CH_4/g VS)	$BMP^{G}_{t\to\infty}$ (mL CH_4/g VS)	k (d^{-1})	R_m (mL/g VS d)	λ (d)	RMSE	x_{eb}
9	53.00	218.10	0.159	15.039	10.10	2.66	0.243
4	46.00	231.05	0.157	15.253	9.50	2.81	0.199
2.33	62.00	306.35	0.145	21.80	9.40	4.22	0.203
1.5	54.50	284.78	0.116	18.141	8.30	3.22	0.191
1	40.34	181.90	0.142	15.549	10.10	2.85	0.222

(pH, solubility of gaseous CO_2, etc.). The lag-phase time and $BMP^{1st}_{t\to\infty}$ followed the same trend for the reasons explained above. Note the high maximum methane production rate (R_m = 21.80) with the HSVF condition 2.33 compared to the other cases, which explains the high value of BMP obtained experimentally and by estimation using Eq. (7).

4. Conclusion

BMP tests were carried out to identify the effect of C/N ratio and HSVF on biogas production, after co-digestion of PS and flax. The effect of each parameter is discussed using kinetic modeling, and the theoretical methane production is discussed using the Buswell equation.

The highest CMYs and maximum methane content were recorded at a C/N ratio of 20. This balance is very important for the anaerobic digestion process, particularly batch processing where all the parameters change over time. This explains the benefit of studying the kinetics of anaerobic digestion and determining the parameters for assessing the relevance of different operating methods.

Experiments with different HSVFs demonstrated how this factor affects production yield and biogas composition, and an optimal HSVF of 2.33 was identified for the production of biogas. However, the best methane content was obtained with an HSVF of 1.5. This demonstrates that an increase in pressure in the headspace has consequences on the physicochemical parameters of the mixture, in particular the pH.

In terms of the kinetics of biogas production, the proposed model adequately describes the dual-rate kinetics observed with the shape of the CMY curves, explained by the presence of an organic matter fraction easily convertible into biogas and another fraction less biodegradable, which required a lag-phase time to undergo a biological hydrolysis stage. This model also enables identification of the easily-biodegradable fraction and discussion of the effects that experimental conditions have on biogas productivity.

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