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# A biochemical methane potential of pig slurry

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**Abstract**

This study assesses the methane production potential for the Anaerobic Digestion of Pig Slurry, using two different Substrate to Inoculum Ratios, 0.65, and 1, and its comparison with the theoretical prediction. The Specific Biogas Production, the Specific Methane Production, and the average methane content were determined for both experiments and adjusted to Standard Temperature (273.15 K) and Pressure (1 atm). The results reached in this study show that the experience conducted with a SIR of 1 produced more volume of biogas, with higher methane content than the one with the lower SIR. With a SIR of 1.0, it was achieved a SMP of 0.568 NL $CH_4$/g VS with an average methane content of 83%. The Technical Digestion Time was found to be 12 days. By comparing the experimental BMP with the estimated value of 0.623 NL $CH_4$/g VS, it was possible to conclude that the estimated value presented a deviation of just 2.96 % during the assay with a SIR of 1.


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*Keywords:* Anaerobic digestion; Biochemical methane potential; Circular economy; Methane production; Pig slurry; Theoretical methane prediction

## 1. Introduction

Pig production has been increasing over the last few years in European Union due to the African Swine Fever (ASF) spread in China and other countries in south-eastern Asia [1]. The former contributes to increasing environmental issues on water, soil, and air due to the high organic load present in pig manure, producing bad smells and gases, and causing acidification and eutrophication of the soils. The manure from pig farming can be divided into (a) slurry, which is a mixture of feces, urine, and water, (b) solid manure, composed of feces, and litter remaining from scrapping with cleaning water. The amount of manure produced depends on the number of pigs and their growth state, as well as on the feed composition [2]. Due to its simplicity, reliability, and rentability, the

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Anaerobic Digestion (AD) is the most common wastewater treatment applied to manure management. AD converts organic matter into energy and reduces pollutant gas emissions. With this procedure, it is also possible to convert the agriculture and organic by-products into fertilizer, fuel, or electricity, finding a place in the circular economy and reducing the environmental impact [3].

Biochemical Methane Potential (BMP) measures the sample biodegradability. Therefore, these assays are employed to understand and analyze parameters such as pH, agitation, temperature, inoculum substrate ratio, among others, and the respective impact on the maximum methane production for a given substrate [4]. For the BMP tests, a substrate is mixed with an anaerobic bacteria culture, generally from an active digester. The mixture is incubated under mesophilic conditions and continuously mixed over consecutive days until the achieved methane production is lower than 1% [5]. During the incubation period, the volume of biogas produced is measured as well as the methane content. Theoretical methods for predicting the BMP are fast and straightforward to implement. For this, it is assumed that the substrate is completely degraded [6]. Additionally, it is necessary to address that the accuracy of this method relies on the biodegradable fraction of the substrate composition. The Specific Biogas Production (SBP) and the Specific Methane Production (SMP) are tools used to evaluate the BMP assay. The first is described as the volume of biogas produced per VS mass fed to the reactor and the second one is the volume of methane produced per VS mass fed to the reactor. When the SBP and the SMP have similar values, the biogas produced has a high methane concentration. The analysis of the SMP curve of any BMP essay should describe a similar behavior of other SMP curves for different substrates [7].

The primary purpose of this study is to determine the best operational conditions for the AD of Pig Manure (PM) at 8% concentration (on TS basis) to achieve maximum biogas production. As a final goal, the authors want to address the feasibility of reusing the pig slurry wastewater to produce energy while reducing the organic matter content. To evaluate the Biochemical Methane Potential (BMP) of the pig manure, the two selected Substrate Inoculum Ratio (SIR) for the batch operation were 0.65 and 1.

## 2. Materials and methods

### 2.1. Substrate and inoculum and experimental setup

The substrate used in this study was Pig Manure (PM), collected from a pig farm placed in the central region of Portugal. Anaerobic sludge from the anaerobic digester of a municipal wastewater treatment plant was used as inoculum. The experimental procedure was conducted in the AD Reactor located at Instituto Superior de Engenharia de Coimbra, Portugal. Fig. 1 presents a graphic representation of the AD Reactor used [8].

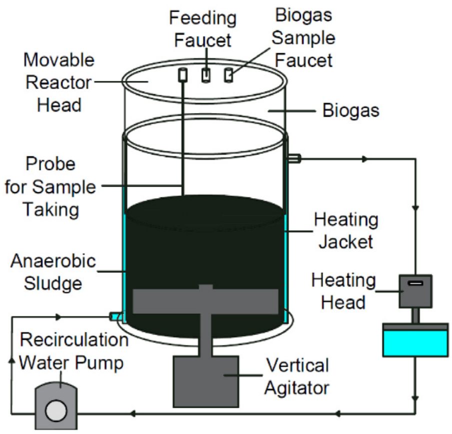


**Fig. 1.** Schematic representation of the laboratory-scale anaerobic digester.

It is constructed in transparent acrylic and has 24.0 cm of diameter and 40.5 cm of total height when the head that retains the biogas is down. The head of the AD reactor can move to accumulate the biogas produced. The head storage can retain a total of 13.6 $dm^3$. To assess if the inoculum had any methane production potential, before each essay, a blank test was performed, with the volume of the substrate to be used being replaced with distilled water.

### 2.2. Analytical methods

Chemical Oxygen Demand (COD) total ($COD_t$) and soluble ($COD_s$) was determined by the 5220 D method established in the Standard Methods (Closed Reflux). The Total Solids (TS), Volatile Solids (VS), Total Suspend Solids (TSS), and Volatile Suspend Solids (VSS) were calculated using the 2540 B, D, and E in the Standard Method [9]. The Methane content was evaluated using the Absorption of $CO_2$ in the alkaline liquid method proposed by Abdel-Hadi [10]. The measured biogas and methane volumes were adjusted to Standard Temperature (273.15 K) and Pressure (1 atm). The elementary molecular analysis was conducted on the equipment Fisons Instruments model EA1108 to determine the amount of Carbon (C), Oxygen (O), Hydrogen (H), Nitrogen (N), and Sulfur (S) that is present in the PM.

### 2.3. The Biochemical Methane Potential (BMP)

In this study, besides the experimental determination of the BMP, the Elementary Composition (EC), Chemical Composition, and Chemical Oxygen Demand of biomass were applied to estimate the theoretical BMP of the substrate.

#### 2.3.1. Elemental composition

The Buswell formula, Eq. (1), allows estimating theoretical BMP. With this equation, it is required to know the chemical composition of the substrate [6].

$$C_aH_bO_c + \left(a - \frac{b}{4} - \frac{c}{2}\right) H_2O \rightarrow \left(\frac{a}{2} + \frac{b}{8} - \frac{c}{4}\right) CH_4 + \left(\frac{a}{2} - \frac{b}{8} + \frac{c}{4}\right) CO_2 \tag{1}$$

Eq. (1) was modified by Boyle [11] to include the nitrogen and the sulfur, to obtain the amount of ammonia and hydrogen sulfide produced during the AD process, Eq. (2).

$$C_aH_bO_cN_dS_e + \left(a - \frac{b}{4} - \frac{c}{2} + \frac{3d}{4} + \frac{e}{2}\right) H_2O \rightarrow \left(\frac{a}{2} + \frac{b}{8} - \frac{c}{4} - \frac{3d}{8} - \frac{e}{4}\right) CH_4 + \left(\frac{a}{2} - \frac{b}{8} + \frac{c}{4} + \frac{3d}{8} + \frac{e}{4}\right) CO_2 + dNH_3 + eH_2 \tag{2}$$

Eq. (3) allows estimating the theoretical methane potential according to Achinas and Euverink [12].

$$BMP_{th\ EC}\,(\mathrm{NL\ CH_4}/VS) = \frac{22.4 \times \left(\frac{a}{2} + \frac{b}{8} - \frac{c}{4} - \frac{3d}{8} - \frac{e}{4}\right)}{12.017a + 1.0079b + 15.999c + 14.0067d + 32.065e} \tag{3}$$

#### 2.3.2. Chemical Oxygen Demand and substrate biodegradability

Nielfa et al. [5] proposed Eq. (4) that allows estimating the maximum methane potential using the mass of Volatile Solids ($VS_{added}$) and the COD concentration of substrate. The authors assumed that the integral oxidation of the substrate $C_aH_bO_c$ consumes 64 g of oxygen per each mole of the estimated formed methane calculated from Eq. (1).

$$BMP_{th\ COD}\,(\mathrm{NL\ CH_4}/g\ VS) = \frac{n_{CH_4} \times R \times T}{P \times VS_{added}},\ where\ n_{CH_4} = \frac{COD}{64\ \left(\frac{g}{mol}\right)} \tag{4}$$

The substrate biodegradability can be calculated according to Eq. (5) [13]:

$$Biodegradability\,(\%) = \frac{Cumulative\ methane\ yield\ (l\ \mathrm{CH_4}/\ g\ VS)}{Theoretical\ methane\ yield\ (l\ \mathrm{CH_4}/\ g\ VS)} \times 100 \tag{5}$$

## 3. Results and discussion

The experimental BMP assay was performed with two different SIR, 0.65 and 1.0, BMP1 and BMP2, respectively. For both assays, the initial and final conditions of the reactor sludge, as well as the biogas production and methane content, were evaluated. The characterization of the inoculum and the substrate used in the BMP assay are presented in Table 1. Before each experiment, a blank assay was performed, and the biogas production associated with the sludge was removed.

**Table 1**. Characterization of the substrate and the inoculum used in the BMP assay in terms of CODt, CODs, TS, VS, TSS, VSS, TC, and TN.

| Parameter [g/L] | $COD_t$ | $COD_s$ | TS | VS | TSS | VSS | TC | TN |
|---|---|---|---|---|---|---|---|---|
| Inoculum | 40.62 | 2.278 | 29.48 | 17.32 | 23.08 | 11.77 | 1.195 | 0.725 |
| Substrate | 7.391 | 2.182 | 3.657 | 2.732 | 2.225 | 1.815 | 0.716 | 0.183 |

### 3.1. Experimental biochemical methane potential

For the first BMP assay (BMP1), the SIR was set at 0.65, for a working reactor volume of 8.6 L. In the second BMP assay (BMP2), a SIR of 1 and a working volume of 14.25 L were used. The temperature was maintained at 36 ± 1 °C and the stirring at 8 rpm. Fig. 2 shows the biogas production during the BMP tests for both assays. The biogas production and methane content were assessed every day, except weekends.

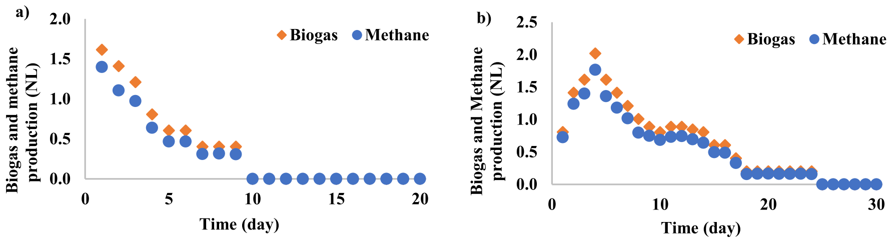


**Fig. 2.** Biogas and methane volume produced (NL) for (a) BMP1 and (b) BMP2.

On day one, BMP1 biogas production reached a maximum output of 1.60 NL representing 1.39 NL $CH_4$. From this point forward, the biogas production decreased until day 10, with biogas production ceasing with the experiment being stopped on day 20. Regarding the BMP2, the biogas production started slower than for BMP1, reaching the maximum biogas production on day 4 with 1.99 NL with a $CH_4$ of 1.75 NL. After day four, biogas production decreased until day 18, producing just about the same volume every day until day 24. On day 25, the biogas production stops, and the experiment was terminated on day 30. Fig. 3 represents the cumulative methane production during the BMP1 and BMP2.

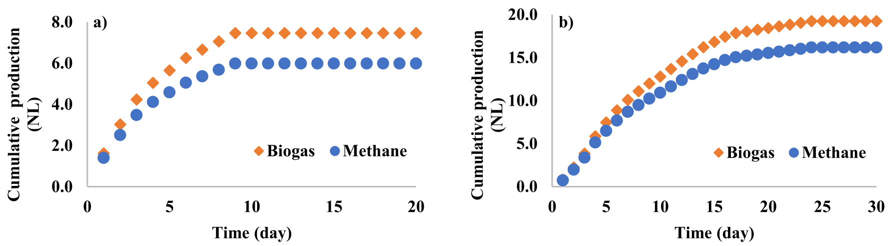


**Fig. 3.** Cumulative biogas and methane production (NL) for (a) BMP1 and (b) BMP2.

For BMP1, the cumulative biogas and methane production reached their maximum on day 9, with 7.39 NL and 5.93 NL, respectively. On the other hand, BMP2 reached the cumulative biogas and methane production at day 25, with 19.06 NL and 16.03 NL, respectively. It is possible to understand that the increment from BMP1 to BMP2 was considerable, 61.2% for the total biogas production and 63.0% for the total methane production.

Comparing the results of both tests, BMP2 produced better results than BMP1. For the first assay, the SBP was 0.410 NL/g VS and the SMP of 0.329 NL $CH_4$/g VS. The average methane content during the assay was 79.0 ± 3.2%. In BMP2, it was possible to achieve an SBP of 0.675 NL/g VS, and SMP of 0.568 NL $CH_4$/g VS.

The average methane content during this assay was 82.8 ± 3.2%. Therefore, the percentage of methane produced on BMP2 was, on average, 3.8% higher since the ratio of substrate to inoculum was higher than in BMP1. Another aspect worth mentioning is the technical digestion time (TDT), defined as the time required to reach 80%–90% of total biogas production [14]. This variable is crucial to make the scale-up of the anaerobic digesters because it can be assumed as the Hydraulic Retention Time (HRT) for the proposed conditions and under continuous operation. For the second experiment, the TDT was reached between days 12 and 16, when 77.9% and 91% of the total biogas production was achieved. In the first experiment, the TDT is between days 5 and 7, when 76.6% and 89.6% of the total biogas was produced.

Kafle et al. [15] used a SIR of 0.5 and a VS concentration of 2.5 g VS/L had achieved an SBP of 0.394 NL/g VS and an SMP of 0.325 NL $CH_4$/g VS. Using the same SIR and increasing the VS concentration to 3.5 g VS/L, Kafle and Chen [14], reached SBP of 0.495 NL/g VS and an SMP of 0.323 NL $CH_4$/g VS. When comparing the results obtained in both papers, it can be seen that the increase of the VS concentration improved the biogas production, but the methane content decreased from 82.6% to 63.5%. Sun et al. [16] executed a BMP assay in 500 ml flasks with a working volume of 400 mL, with a VS concentration of 10 g VS/Land a SIR of 0.5 at 36 °C. The substrate had a concentration of 5.1% on TS basis. An experimental methane yield of 0.308 NL $CH_4$/gVS and a predicted methane yield of 0.479 NL $CH_4$/gVS were achieved, which are lower than the ones obtained in this paper for both cases with SIR 0.65 and 1.

Zhang et al. [17] used a SIR of 1.5 and a substrate concentration of 40 gVS/L. The initial pH was adjusted to 7.0 ± 0.1, and the temperature inside the digesters was maintained at 37 ± 1 °C. The duration of the experiment was dependent on the biogas formation. In their experiments, they achieved 0.359 NL $CH_4$/gVS. The presented results indicate that a SI of 1 produces the best results when compared to SI of 0.5, 0.65, and 1.5. However, it is necessary to keep in mind that the type of reactor, sludge, inoculum, and other experimental conditions are different.

### 3.2. Theoretical biochemical methane potential

An elementary molecular analysis was conducted to determine the amount of Carbon (C), Oxygen (O), Hydrogen (H), Nitrogen (N), and Sulfur (S) that is present in the PM. The composition is presented in Table 2

**Table 2**. Composition of the substrate in % (m/m) of each element.

| Element | C | H | O | N | S |
|---|---|---|---|---|---|
| % (m/m) | 41.7 | 5.18 | 22.4 | 1.84 | 0.0100 |

The theoretical maximum methane potential was predicted by applying Eqs. (4) and (5), with the obtained values presented in Table 3, as well as the percentage of biodegradability of the substrate and the deviation between the theoretical and experimental BMP. Analyzing Table 3, it is possible to conclude that the BMP2 consumes higher amounts of substrate when compared with BMP1. This leads to a conclusion that using a SIR of 1 the AD's performance will be optimized, the maximum methane that it is possible to achieve from this substrate will be attained.

**Table 3**. Theoretical prediction of the BMP through the EC and COD, biodegradability, and deviation.

| Parameter | $BMP_{th\ EC}$ | $BMP_{th\ COD}$ | BMP1 | BMP2 |
|---|---|---|---|---|
| N L $CH_4$/g VS | 0.623 | 0.947 | 0.329 | 0.568 |
| | | Biodegradability (%) | 52.8 | 91.1 |
| | | Deviation to $BMP_{th\ EC}$ (%) | 67.5 | 2.96 |

## 4. Conclusions

The BMP is shown to be a very useful tool to select operational conditions to improve biogas production during the anaerobic digestion process. Comparing the results of both assays, the BMP2, in which a higher SIR was used (1.0), produced better results than BMP1 (SIR 0.65). It was registered an increase of 60.6% for the SBP, and the SMP improved by about 62.7% with the average methane content increasing from 79.0 to 82.8%.

The technical digestion time was found to be 5–7 days for the first assay and 12–16 days for the second one. These numbers can be a reference of HRT for future work with similar conditions. The results obtained in BMP2 were much closer to the theoretical predictions of BMP, indicating that with a SIR of 1.0 the amount of substrate added to the digester was enough to achieve a methane production closer to the theoretically attainable value.

## CRediT authorship contribution statement

**Andreia D. Santos:** Investigation, Data curation, Conceptualization, Formal analysis, Validation, Writing – original draft. **João R. Silva:** Data curation, Writing – review & editing. **Luis M. Castro:** Conceptualization, Supervision, Validation, Writing – review & editing. **Rosa M. Quinta-Ferreira:** Conceptualization, Supervision, Writing – review & editing, Project administration, Funding acquisition.

## 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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