Limiting factors for biogas production from cow manure: enero-environmental approach

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Abstract
The main innovation of the study is the use of a novel enero-environmental approach for investigation of biogas production, and analysis of the amount of methane and biogas produced in terms of energy production and global warming potential (GWP). Two types of reactors (laboratory-scale and semi-industrial reactors) were prepared for biogas production to perform a detailed study and for exact consideration of treatments in terms of production. Based on the results, the maximum methane production in the laboratory-scale set-up was related to a carbon/nitrogen (C/N) ratio of 30 at mesophilic temperature (35,967 ml/kg volatile solids). Accordingly, the C/N ratio in the semi-industrial reactor was considered to be 30; methane production was equal to 14,489 m³ at loading rates of 237.5, 2.580 and 234.92 kg for cow manure, wheat straw and water content, respectively. The maximum biogas production occurred on day 65, from the viewpoint of energetic analysis. The highest daily net electricity production occurred on day 12, with a positive energy balance. However, considering GWP effects in the production and use of biogas, it would be better to stop production on day 48, in which case methane production would be equal to 77% of the final limit of biogas production.

1. Introduction
Today, despite the ever-increasing environmental concerns over the dependency on non-renewable energy resources, the major global energy systems still depend on fossil fuels (Florio et al., 2019; Lim & Biswas, 2019; Nosratabadi et al., 2019; Sharma, Ansari, Pal, Singh, & Lalhriatpuia, 2019). However, because of environmental concerns, the world is shifting towards renewable energy resources (Afsharzade et al., 2016; Baena-Moreno et al., 2019; Eder & Mahlberg, 2018; Lyttimäki, 2018; Nethengwe, Uhunamure, & Tinawo, 2018; Rosa et al., 2018; Vochozka, Maroušková, & Šule, 2018). Consequently, we have also been witnessing major technological advances in renewable energy systems (Baranyai, Mosavi, Vajda, & Varkonyi-Koczy, 2017; Imani, Zalzar, Mosavi, & Shamshirband, 2018; Moeini, Ahmadpour, Mosavi, Alharbi, & Gorji, 2018; Mosavi, Rituraj, & Varkonyi-Koczy, 2017; Mosavi et al., 2019; Najafi, Ardabili, Mosavi, Shamshirband, & Rabczuk, 2018). There are numerous reasons to move towards renewable resources (Acosta-Silva et al., 2019; Bushur et al., 2019; Fathi, Mehрабipour, Mahmoudi, Mohd Zin, & Ramli, 2019; Fortier, Teron, Reames, Munardy, & Sullivan, 2019; Li et al., 2019; Razmjoo & Davarpanah, 2019; Samson, Babatunde, & Denwigwe, 2019; Yilmaz Balkan, Scott, Matopoulos, & Wright, 2019). On the one hand, fossil fuel resources are limited and, on the other hand, renewable energy resources such as putrescible liquid and solid wastes are abundant (Afazeli, Jafari, Rafiee, & Nosrati, 2014; Dalmo, Simao, Nebra, & Santana, 2019; Dlamini, Simatele, & Serge Kubanza, 2019; Fardad et al., 2018; Ghosh et al., 2019; Nam-Chol, Hye-Song, Yong-Chol, Yong-Hyok, & Yong-Nam, 2018; Oliveira, Kerkelund, Horta, Labrincha, & Dias-Ferreira, 2019; Sharma, Ganguly, & Gupta, 2019; Vaish et al., 2019). Therefore, there has been an emerging
motivation to move towards using various types of solid wastes for the purpose of energy production (Dabe et al., 2019; Lino & Ismail, 2018; Tiwary et al., 2019; Vuppaladadiyam et al., 2019a, 2019b).

Currently in Iran, the rate of promoting renewable energies is very slow, unlike in other countries (Ijadi Maghsoodi, Ijadi Maghsoodi, Mosavi, Rabczuk, & Zavadskas, 2018). There are several reasons for the significant lack of renewable energies, such as lack of public awareness about renewable energies, inexpensive fossil energy resources in Iran, a lack of a sense of environmental pollution threats and the high cost of renewable energies in Iran (Seyyed aram & Najafi, 2016). The literature includes a number of methods to address this issue (Dabe et al., 2019; Lino & Ismail, 2018; Tiwary et al., 2019; Vuppaladadiyam et al., 2019a, 2019b). One of the most efficient proposed methods is to switch to biogas production technology (BPT), which can provides a part of the energy needs as a clean energy resource. In Iran, despite the high potential of BPT, little attention has been directed to this important yet abandoned energy resource (Fardad, 2017). Anaerobic digestion refers to the biological degradation process of organic materials in the absence of oxygen (Sawatdeenarunat, Surendra, Takara, Oechsner, & Khanal, 2015). Biogas is a renewable energy source that can be obtained through the anaerobic digestion of organic wastes (Morero, Groppelli, & Campanella, 2015). Many of the studies on biogas production have pointed to limitations of fossil fuel resources and the environmental pollution crisis, and have highlighted that fossil fuels as energy resources have considerable greenhouse gas (GHG) emissions. Therefore, biogas has been introduced as an alternative fuel resource that is produced from organic wastes and is able to reduce GHG emissions (Beneragama, Lateef, Iwasaki, Yamashiro, & Umetsu, 2013; Hijazi, Munro, Zerhusen, & Effenberger, 2016; Insam, Gómez-Brandón, & Ascher, 2015; Khan & Martin, 2016; Moreda, 2016; Putra, Liu, & Lund, 2017; Zhang & Chen, 2016; Zhang, Tan, & Zhang, 2016).

Biogas fermentation, biogas technology and anaerobic digestion are involved in the BPT of organic substrates in the absence of oxygen (Deng et al., 2016; Uddin et al., 2016; Zhang, Hu, & Lee, 2016). This follows the removal of environmental pollutants (Fehrenbach et al., 2008; Verma, Singh, & Rai, 2007). The product of the fermentation process in the absence of oxygen is a mixture of methane (CH₄; 55–70%) and carbon dioxide (CO₂; 30–45%). Methane, which makes up the greatest portion of the gas produced in this process, has a high energy potential and can be used for heating and electricity production purposes (Beltram, Ranzan, Hinrichs, & Hitzmann, 2016). The quality of the produced gas mixture depends on the feedstock characteristics (Tada et al., 2005). One of the important benefits of biogas production is that it can reduce the consumption of natural gas and oil in industry and agricultural systems by using the biogas directly, which reduces the environmental air pollution (Karki, 2009). According to the thirteenth-century adventurer Marco Polo, covered sewage tanks were probably used in China 2000–3000 years ago (He, 2010). In addition, Sheikh Bahai, in the early sixteenth century, pioneered the use of biogas for water heating in the city of Isfahan in Iran. The first biogas production digester, with a volume of 5 m³, was reportedly built in 1975, in Niaabad village of Lorestan province in Iran, to use livestock waste to heat water and for household uses (Noorollahi, Kheirrouz, Asl, Yousefi, & Hajinezhad, 2015). There are two main types of digester for BPT, i.e. the Chinese and Indian types (Balanbramaniyam, Zisengwe, Meregi, & Buyssman, 2008). The major input of the Chinese type is manure, and the main characteristics of this type are that there is no need to cover the digester and the gas pressure is high (about 1000 mmHg). The main product of the Indian type is biogas. It has floating caps which measure the volume of gas through variation of its height, and it has a low pressure value (Fardad, 2017; Taleghani & Kia, 2005). Figure 1 illustrates the two types of digester (Gunnerson & Stuckey, 1986; Surendra, Takara, Hashimoto, & Khanal, 2014): Figure 1(a) refers to the Chinese system and Figure 1(b) to the Indian system.

The biogas production process involves multiple related biochemical processes with microorganisms that work together to achieve the degradation of organic matter into methane and carbon dioxide (Moreda, 2016). The first stage is hydrolysis, in which the complicated components and molecules are converted into simpler molecules and components. In this state, generally, the complicated carbohydrates, lipids and proteins are transformed into simpler sugar molecules and/or amino acids, and further fatty acids. In the next stage, i.e. the acidogenesis stage, the resulting materials are transformed into volatile fatty acids, hydrogen and carbon dioxide. The volatile fatty acids continue to be converted to hydrogen, carbon dioxide and acetic acids in the acetogenesis stage, and finally the methanogenesis stage decomposes the hydrogen, carbon dioxide and acetic acid, and produces methane (Abatzoglou & Boivin, 2009; Demirbas & Balat, 2009; Kao et al., 2012; Ramaraj & Dussadee, 2015; Salmi nen & Rintala, 2002a). The main components of biogas are methane (50–75%) and carbon dioxide (25–50%) (Maghanaki, Ghobadian, Najafi, & Galogah, 2013). Various studies have been carried out on biogas production. Tasnim, Iqbal, and Chowdhury (2017) performed a comparative study of biogas production through anaerobic co-digestion utilizing cow manure,
Livestock waste, with its considerable potential to produce biogas, has been targeted as a source of biogas production in recent years (Adeoti, Ayelegun, & Osho, 2014; Calise, Cremonezi, di Vastogirardi, & d’Accadia, 2015; He, Zhang, Zeng, & Zhang, 2016; Xueqing, Lijuan, & Dongxing, 2011). There are approximately 72 million livestock in Iran, producing 74,946 t of waste annually, with a potential for biogas production of 8668 million m$^3$ (Maghanaki et al., 2013).

Because of the volume of waste produced and the feasibility of biogas production, and because it supplies its own energy requirements, there is a need for exact environmental and energetic studies on this subject. The main innovation of the present study is the introduction of a novel energo-environmental approach, which employs both energetic and environmental perspectives for analyzing the biogas and methane production, and

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**Figure 1.** Types of biogas production digester: (a) Chinese system; (b) Indian system.

**Table 1.** Review of methane yield for different types of substrate.

| Biomass material                  | Content                        | References               |
|-----------------------------------|--------------------------------|--------------------------|
| Water hyacinth using additives    | Water hyacinth using additives | Raja and Lee (2012)      |
| Cattle excreta                    | 179                            | Goberna, Schoen, Sperl, Wett, and Insam (2010) |
| Cattle manure                     | 620                            | Cavinato, Fatone, Bolzonella, and Pavan (2010) |
| Fruit and vegetable waste         | 611                            | Bouallagui, Lahdheb, Ben Romdan, Rachdi, and Hamdi (2009) |
| Cow manure                        | 329                            | Satyanarayan and Murkute (2008) |
| Food wastes                       | 297–489                        | Sathianathan (1975)      |
| Potato waste                      | 382                            | Cho, Park, and Chang (1995) |
| Sewage sludge                     | 210–345                        | Zhang et al. (2007)      |
| Slaughterhouses                   | 540                            | Heo, Park, and Kang (2004) |
| Grease trap sludge of poultry     | 278                            | Budiyono, Seno, and Sunarso (2009) |
| Slaughter waste of poultry        | 550                            | Parawira, Murto, Zvauya, and Mattiasson (2004) |
| Slaughterhouses                   | 500                            | Wang, Yang, Feng, Ren, and Han (2012) |
| Fish waste                        | 390                            | Moreda (2016)            |
| Biological oil                    | 340                            | Long, Aziz, Francis, and Ducoste (2012) |

Sewage sludge, kitchen waste and water hyacinths. Experiments were conducted under mesophilic conditions (37°C) with 1.5 wt% of NaOH to obtain the desired pH. Cruz-Salomón et al. (2017) produced biogas from a native beverage vinasse; owing to the high value of organic materials and high degradable index, this can be a potential nutrient source for biogas production by anaerobic digestion. Bayrakdar, Molaey, Sürmeli, Sahinkaya, and Çalli (2017) investigated the use of poultry manure in a mesophilic anaerobic digester. Deepanraj, Sivasubramanian, and Jaryaj (2017) studied the influence of independent variables of biogas production, volatile solid degradation and chemical oxygen demand degradation during the anaerobic digestion of food waste. They used Taguchi-based gray relational analysis to determine the optimum conditions for anaerobic digestion. Table 1 indicates the resources for biogas production around the world.
obtains the limiting factors for biogas production from cow manure.

2. Material and methodology

2.1. Biogas production on the laboratory scale

In the present study, a set of reactors for biogas production was designed and constructed. The reactors were Chinese and batch-type 3 liter plastic bottles. The volume of biogas produced was measured by the water displacement method. Figure 2 illustrates the laboratory-scale biogas production set-up.

The largest portion of biogas contains methane and carbon dioxide. Only the methane has heat value. Therefore, to determine the portion of methane in the produced biogas, 0.5 M NaOH solution was used. In this way, the alkaline solution is employed for remaining the pure methane by absorbing the carbon dioxide in the biogas.

The volume of methane was measured by the water displacement method. Figure 3 shows a schematic of the methane measuring system.

In the following, the cow manure was collected from a dairy farm in Ardabil province, Iran. Wheat straw was prepared to control the carbon/nitrogen (C/N) ratio of the substrate. The organic carbon and Kjeldahl nitrogen were measured according to the American Public Health Association (APHA) standard. To measure the total solids (TS) (mg/L), the sample was placed in an oven at 105°C; to measure the volatile solids (VS), the sample was placed in a furnace at 550°C for 3 h. These values indicate the initial properties of the substrate. Table 2 presents the initial properties of cow manure and wheat straw.

Four samples were prepared with C/N ratios of 27, 30, 33 and 36 by mixing the cow manure and wheat straw. To set the TS value to 10, water was added to the prepared samples. Table 3 presents the values of water, wheat straw and cow manure for each sample.

An anaerobic digestion process requires microorganisms; therefore, in this study 50 g of inoculum was added for each reactor. To prepare the inoculum, 1 kg of the contents of the cow rumen was mixed with 1 kg of water and placed in the oven at 37°C for 1 week (Wijtes, McClure, Zwietering, & Roberts, 1993). NaHCO3 was used to set the pH values within the neutral range. All reactors were placed in a water bath with a temperature of 35 ± 2°C (mesophilic temperature).

2.2. Design and construction of a biogas production reactor on a semi-industrial scale

A biogas production reactor on a semi-industrial scale (with a volume of 500 l) was designed and manufactured by considering the results of the laboratory-scale production in the previous step. The results of the laboratory-scale production were used to obtain the maximum biogas production conditions.

A plastic tank (with a diameter of 70 cm and height of 130 cm) was used as the reservoir of the reactor. A heating system with water was used to provide the thermal needs of the reactor. Therefore, a system with heating and water-circulating capabilities was required. For this reason, a galvanized cylinder (diameter 45 cm and height 75 cm) equipped with a 50 W power thermal element was used. A 0.37 W pump was used for circulating the heated water inside the spiral tubes embedded in the reactor. To control the temperature of circulating water and the temperature inside the reactor, two digital temperature controllers (SUN15-T1) equipped with PT100 sensors were used (accuracy 1°C). The temperature of circulating water was set to 60°C and the temperature of the inside of the reactor was set to 35°C.
To ensure uniform conditions and to eliminate the hard layer created above the solution inside the reactor, a manual mechanical stirrer (with eight vertical vertices) was used (Thi, Kumar, & Lin, 2015). The biogas was stored in a float tank in the water. Thus, two tanks with diameters of 40 and 45 cm were inversely placed inside each other. The space between the two tanks was filled with water to hold the biogas inside the smaller tank. The volume of biogas was measured by the displacement of the small tank. It should be noted that the displacement of the smaller tank and the volume inside it were initially calibrated. To purify the produced biogas, it was passed through a reservoir containing 0.5 M NaOH solution to obtain pure methane.

In the semi-industrial-scale reactor, 237.5 kg of cow manure was mixed with 2.580 kg of wheat straw and 234.92 kg of water. This condition produced a C/N ratio of 30 and TS value of 10%, in accordance with the results of the laboratory-scale production. This condition is related to the maximum biogas production. Data recording continued for 90 days. Figure 3 shows a schematic of the semi-industrial-scale biogas production system.

2.3. Electricity consumption in the semi-industrial-scale reactor

In the semi-industrial-scale reactor, the electricity consumption was related to the heating and water-circulating systems. To calculate the electricity consumption of the heating element (50 W) and the water-circulating pump (0.37 W), their operating times were measured. Equation (1) obtains the total electricity consumption:

\[ Q_{\text{con}} = 50 \Delta t_H + 0.37 \Delta t_P \]  

where \( Q \) is the total electricity consumption (J), \( \Delta t_H \) is the operating time of the heating element (s) and \( \Delta t_P \) is the operating time of the circulating pump (s). The average operating time of the heating element and the water-circulating pump in the semi-industrial reactor was 6 h per day. Therefore, according to Equation (1), the amount of power consumed was approximately 1.0879 MJ/day.

2.4. Modeling methane production in the semi-industrial reactor

In the present study, the volume of biogas produced was modeled based on the growth of the bacterial population through anaerobic digestion. For this purpose, a modified logistic model was used to estimate methane production as a function of the production time (Equation 2):

\[ Y = \frac{A}{1 + \exp \left( \frac{4 \mu}{X} (\lambda - t) + 2 \right)} \]  

where \( Y \) is the cumulative methane production (ml), \( A \) is the potential of the cumulative biogas production (ml), \( \mu \) is the maximum rate of cumulative biogas production (ml/day) and \( \lambda \) is the delay time for the start of biogas production.

2.5. Potential of electricity production from the produced biogas

The produced biogas was passed through the 0.5 M NaOH solution and pure methane was obtained. A single-cylinder spark-ignition RME 1000 engine experimentally consumed the produced methane. The engine was 98 cc capacity with a maximum power of 800 W. Table 4 presents the engine specifications.

The engine was a gasoline-fueled engine, which required some modifications for the consumption of the produced methane. To enable the use of methane gas
in the 1000 RME generator engine, the engine was converted into a dual-fueled mode by fitting a separate duct behind the carburetor to import the methane gas into the engine. To control the entrance of air, another separate valve was inserted into the inlet duct (Figure 4).

A variable resistor, type TDGC2–5 kVA, and a 1 kW heater were used for loading the engine. By calculating the engine brake power using measuring currency and voltage. [The ampere–voltage (DC) product represents the value of power.] The QRO-401 pollutant measuring system (QROTECH Co.) was used to measure the amount of exhaust emissions from the engine.

During the engine test, initially, the engine was started with gasoline; after 5 min, when the engine had warmed up, the gasoline flow was closed and the methane gas flow was opened, simultaneously. In this state, the amount of biogas and inlet air was adjusted so that the working conditions of the engine would be stable. Once stability was achieved, data on power generation and emissions of carbon monoxide (CO), CO₂ and unburned hydrocarbons (UHCs) were measured and recorded.

3. Results

3.1. Biogas production in the laboratory-scale reactors

The results for the biogas generated in the laboratory-scale reactors are shown in Figure 5. As can be seen, the highest volume of daily biogas production in the sample occurred at C/N = 30. In all four samples, the volume of the biogas produced daily on days 2–5 has a jump state, which may be due to the activity of the microorganisms enriched in the inoculum (Ye et al., 2013).

The second biogas production peak occurred on days 15–18, owing to the activity of digestible bacteria. The highest amounts of daily production in the first and second peaks were 2652/64 and 2345/985 ml/kg.VS, which occurred on days 4 and 8, respectively.

Figure 6 shows the cumulative production of biogas, methane and carbon dioxide. VS = volatile solids.

Figure 4. Methane and air inlets to the engine.

Figure 5. Daily biogas production in four laboratory-scale reactors. C/N = carbon/nitrogen ratio; VS = volatile solids.

Figure 6. Cumulative production of biogas, methane and carbon dioxide. VS = volatile solids.

3.2. Methane production in the semi-industrial reactor

Methane production in the semi-industrial reactor under the optimal condition (C/N = 30) was modeled using

Table 4. Engine specifications.

| Engine type       | Single cylinder, four stroke |
|-------------------|-----------------------------|
| Engine power      | 800 W                       |
| Fuel type         | Gasoline                    |
| Volume            | 98 cc                       |
| Starting system   | Recoil system               |
Table 5. ANOVA table.

| Source          | Sum of squares | df | Mean squares |
|-----------------|----------------|----|--------------|
| Regression      | 9494.982       | 3  | 3164.994     |
| Residual        | 15.679         | 87 | 0.180        |
| Uncorrected total | 9510.661     | 90 |              |
| Corrected total | 2371.080       | 89 |              |

Dependent variable: CH4

Note: \( R^2 = 1 - \frac{\text{Residual sum of squares}}{\text{Corrected sum of squares}} \) = 0.993.

Figure 7. Experimental and predicted data by the logistic model.

The logistic model in SPSS software. \( A, \mu \) and \( \lambda \) were calculated as 14.484, 0.326 m³/day and 12.099 days, respectively. According to the table of analysis of variance of the model (Table 5), the determination coefficient of the model (\( R^2 \)) is equal to 0.993, which indicates the high accuracy of the logistic model in predicting the methane gas production.

Figure 7 presents the experimental data and the predicted data using the logistic model. The vertical axis shows the cumulative methane production and the horizontal axis the retention time. Points are taken from the experimental results and the line indicates the predicted values from the logistic model. This demonstrates the accuracy of the developed model as there is clearly there is a good correlation between the two sets of values.

3.3. Energetic comparison of the production and consumption of biogas

The experiments indicated that the daily amount of power consumed was approximately 1.0879 MJ and the net produced value of energy (MJ) was calculated using Equation (3):

\[ \Delta E = 0.25 \times 57 \times Y_{\text{day}} - 1.0879 \]  

where 57 is the heating value of methane (MJ/m³), 0.25 is the efficiency of the generator and \( Y_{\text{day}} \) is the daily amount of methane production (m³).

The loading rate of the semi-industrial reactor is equal to 237.5 kg of cow manure, 2.580 kg of wheat straw and 234.92 kg of water, in this state, the C/N ratio according to the optimal conditions is 30, and TS is equal to 10%. Figure 8 shows the production and energy balance of biogas. It is clear that from day 1 to 10, as well as from day 65 to 90, the energy balance is negative. This is because, during this period, energy is consumed for heating the system, but biogas production is lower. However, from day 10 to 65, the energy balance is positive. During this period, the produced biogas not only provides the needed energy for heating the system, but also significantly increases the amount of electricity generated. The best time to complete the production of biogas was on the 65th day. The highest net daily electricity production, of 5.43 MJ, occurred on day 12.

3.4. Environmental comparison of the production and consumption of biogas

Table 6 shows the effect of methane produced from biogas purification, as an alternative fuel to gasoline, on CO, CO₂ and UHC pollutants. As can be seen, using methane gas derived from anaerobic fermentation of animal residues, the amount of CO, CO₂ and CH₄ emission of pollutants is reduced by 46%, 88.27% and 34.94%, respectively, compared to gasoline. This is because the amount of carbon in methane gas is far less than that in gasoline. As a result, the use of refined biogas in the generator engine reduces the emission of GHGs compared to using gasoline.
Table 6. Effect of methane produced from biogas and gasoline treatment on engine pollution.

|                       | CO₂ (vol. %) | UHC (ppm) | CO (vol. %) |
|-----------------------|--------------|-----------|-------------|
| Biogas-fueled engine  | 0.8883       | 119,732   | 0.1773      |
| Petroleum-fueled engine| 1.6454       | 184,043   | 1.5125      |
| Variation of methane compared to petroleum | -46% | -34.94% | 88.27% |

Note: UHC = unburned hydrocarbons.

3.5. Effect of methane production from anaerobic fermentation of cow manure on global warming potential (GWP)

The greenhouse effect refers to the process of reflection of sunlight towards the Earth's surface by the atmosphere (Hosseinzadeh-Bandbafha, Nabavi-Peleharaei, Khanali, Ghahtderijani, & Chau, 2018). Water vapor, carbon dioxide, methane and ozone are the most effective GHGs. The greenhouse effect causes global warming. The type of GHG and its longevity affect the GWP (Nabavi-Pelsharaei, Khanali, Fuglestvedt, Hailemariam, & Stuber, 2005).

It seems that the combustion of methane from anaerobic fermentation of cow waste and its conversion into carbon dioxide can have less impact on global warming. Therefore, two different scenarios are examined.

In the first scenario, cow manure is dumped in an open space on a dairy farm, and the methane gas and carbon dioxide derived from fermentation are thus introduced into the atmosphere. The global warming potential in non-combustion mode (GWP₀) is calculated as follows:

\[
GWP₀ = GWP_{CO₂} + GWP_{CH₄}
\]  

where \( GWP_{CO₂} \) is the global carbon dioxide potential of carbon dioxide, which in this study was calculated as a coefficient of 1 for the emission of 1 m³ of carbon dioxide into the atmosphere; and \( GWP_{CH₄} \) is the global methane gas heating potential. In this study, the rate for emission of 1 m³ of methane to the atmosphere was 28. As a result, Equation (4) can be written as follows:

\[
GWP₀ = 1 \times V_{CO₂} + 28 \times V_{CH₄}
\]  

where \( V_{CO₂} \) and \( V_{CH₄} \) are, respectively, the cumulative volume of carbon dioxide and methane produced in the anaerobic fermentation process in terms of 1 m³.

In the second scenario, the cow manure inside the reactor is fermented anaerobically and carbon monoxide from the fermentation is released into the atmosphere. The methane gas from fermentation is flushed into an internal combustion engine and converted to carbon dioxide. The combustion of methane gas with air is expressed in terms of Equation (6) under stoichiometric conditions. The combustion of 1 mole of methane gas produces 1 mole of carbon dioxide gas, based on Equation (6):

\[
CH₄ + 2(O₂ + 3.76N₂) \rightarrow CO₂ + 2H₂O + 2 \times 3.76N₂
\]  

The anaerobic fermentation process, along with methane gas production, also produces carbon dioxide gas. Therefore, the total amount of carbon dioxide entering the atmosphere is equal to the sum of carbon dioxide produced in the process of methane production and consumption. In this case, the \( GWP₁ \) value is calculated as:

\[
GWP₁ = 1 \times V_{CO₂-p} + 1 \times V_{CO₂-c}
\]

where \( V_{CO₂-p} \) is the cumulative volume of carbon dioxide produced in the methane production stage and \( V_{CO₂-c} \) is the cumulative volume of carbon dioxide produced in the methane combustion stage by 1 m³.

Figure 9 shows the effect of methane combustion resulting from the anaerobic fermentation of cow manure and its transformation into carbon dioxide. As can be seen, from day 1 to 48, the \( GWP₀ \) value is bigger than \( GWP₁ \). This means that the first scenario (the release of waste in nature and the release of methane and carbon dioxide from fermentation) increases the GWP; hence, combustion of methane produced in the engine has less environmental damage. However, from day 48 onwards, \( GWP₁ \) is greater than \( GWP₀ \), and the second scenario increases the GWP. This is because after 48 days the amount of methane produced is lower than that of carbon dioxide, and the use of a small amount of methane produced in the engine and its transformation into carbon dioxide does not have a significant effect on the GWP. Therefore, if the GWP is considered in the production and the use of biogas, it would be better to stop production on day 48, in which case the methane production would be equal to 77% of the final limit of biogas production (Figure 8).

3.6. Determination of the optimal conditions for biogas production

Given the methane gas production model (Equation 1), if the time goes to infinity \( (t \rightarrow \infty) \), the maximum amount of methane produced \( (Y_{max}) \) will be 14.489 m³. Methane production follows an exponential function, and given that the best time to stop the production of biogas is 65 days, at this time, the ratio of cumulative production of biogas to final biogas \( (14.448 \text{ m}^³) \) is 92%. In other words,
4. Conclusion

The main innovation of the present study is the use of a novel enero-environmental approach for studying biogas production from cow manure, which discusses the methane and biogas production in two terms of energy production and GWP. Two types of reactors (laboratory-scale and semi-industrial reactors) were prepared for biogas production in order to perform a detailed study and enable exact consideration of treatments in terms of production. Based on experiments, the maximum production of methane in the laboratory-scale set-up was related to the C/N ratio of 30 at mesophilic temperature (35,967 ml/kg.VS). Therefore, a C/N ratio of 30 was considered in the semi-industrial reactor. The energetic comparison of the consumed and produced biogas indicated that from day 1 to 10, as well as from day 65 to 90, the energy balance was negative, but from day 10 to 65, the energy balance was positive. On the 65th day, it could reach 92% of the total methane production potential. Based on environmental comparisons of the consumed and produced biogas, from day 1 to 48, the GWP0 value was bigger than GWP1. This means that the first scenario (the release of waste in nature and the release of methane and carbon dioxide from fermentation) increased the GWP, and hence combustion of methane produced in the engine caused less environmental damage. However, from day 48 onwards, GWP1 was greater than GWP0, and the second scenario increased the GWP. On day 48, it could reach 77% of the total methane production potential. In general, there are two limitations stopping the biogas production process from cow manure, namely energetic and environmental limitations, and the maximum retention times based on these limitations are 65 and 48 days, respectively. By considering an enero-environmental approach, the retention time has to be 48 days to reach the maximum net energy as well as the minimum GWP.

Disclosure statement

No potential conflict of interest was reported by the authors.

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