

Experimental characterization of influential parameters of cow dung substrates in biogas production

Abstract

The present work on the production of biogas from cow dung substrates was carried out at the Laboratory of Renewable Thermal Energy (L.E.T.RE) of the Joseph KI-ZERBO University in collaboration with the National Program of Biodigester of Burkina Faso (PNB-BF). We focus in this work on the determination of the physicochemical characteristics of the substrates allowing the follow-up of the biogas production. We experimented with anaerobic digestion for 100 days each at mesophilic temperature, i.e. a hermetic enclosure included between 27 and 38°C. The average volume of biogas produced is $2.5m^3.d^{-1}$. The following physicochemical characteristics were observed for cow dung: dry matter 11.85%, volatile matter 58.83%, hydrogen potential 7.01, density $695 kg.m^{-3}$, carbon content 32%, nitrogen content 1.46%, nitrogen-carbon ratio 24.70, acids are around $0.18 kgCOD.m^{-3}$, and the average chemical oxygen demand $30 kgCOD.m^{-3}$. This characterization was performed on a $4 m^3$ pilot bioreactor with daily substrate loading ranging from 20 to 30 kg. These results are in agreement with the literature on anaerobic digestion.

Keywords: anaerobic digestion, characterization, cow substrates, biogas,

ABBREVIATIONS (The table needs to adjust the format. The name of the table must be modified. I suggest adding it as an appendix at the end of the article)

AGV:	Volatile fatty acid	$kgCOD.m^{-3}$
BMP:	Biomethanogenic potential	$m^3.d^{-1}$
C/N:	Carbon to nitrogen ratio	-
CT:	Total carbon	%
D :	Dilution rate	d^{-1}
COD:	Chemical Oxygen Demand	$kg.m^{-3}$
MS:	Dry matter	kg
MESSRS:	Mineral matter	kg

m_s :	Mass of the sample	kg
MV	Volatile matter	kg
ρ :	Density of the waste,	$kg.m^{-3}$
pH :	Hydrogen potential	-
Q :	Biogas flow rate	$m^3.d^{-1}$
Q_{in} :	Flow rate of the influent in the reactor	$m^3.d^{-1}$
T :	Digester temperature	$^{\circ}C$

INTRODUCTION

Burkina Faso, a landlocked Sahelian country with a total area of $274,000 km^2$, is implicitly characterized by an energy situation that depends mainly on imported fossil fuels[1]. According to the fifth general population and housing census of Burkina Faso published in 2022, the total population is 20,505,155 with 3 488,258 households. This census shows that 76.4% of households use firewood and coal [2]. To meet energy needs and preserve the environment, it is necessary to explore and develop new energy sources such as biogas. Anaerobic digestion of organic substrates is receiving increasing attention as a way to produce renewable energy, biogas, and fertilizer (digestate) while eliminating waste and by-products[3]. The monitoring of physical-chemical parameters can improve the technical performance of the digester process and make it more attractive especially in rural areas. The applications of these characterization results will concern the modelling of small on-farm anaerobic digestion units as well as larger installations treating residues of agro-industrial origin. The application of a mathematical model to anaerobic digestion is used to optimize the process, control the operation of the digesters, to formulate and validate hypotheses to better understand the methanization reaction. This model will allow us to have a knowledge of the influential factors and to bring a correction if necessary[4]. This model will be built from the specific parameters of the substrate by determining the BMP and the degradation kinetics. The main objective of the work whose first results are presented in this publication was to determine the different components of cow substrates for future use in a model for the simulation of the operation of a reactor in continuous mode. The article is organized by presenting the materials and methods used for waste characterization as well as biogas production in the first section. The second section is devoted to the presentation of the results and their discussion by comparing them with those of the literature. The article ends with remarks and concluding words on future work.

1. MATERIALS AND METHODS

1.1. Biodigester and biogas measurement

To carry out the continuous tests a pilot reactor of half-cylindrical shape is built in cement brick, a material resistant to temperature and pressure. Its height is $h = 1.5$ m and its inner radius $R = 1.5$ m. The resulting total volume is $v = 4 m^3$ with a maximum useful volume of 2,800 liters and a minimum of 1,600 liters. The cement shell allows to control the temperature in the reactor at around $35^{\circ}C$ and makes it hermetic to control the anaerobic conditions. On the upper part of the reactor is the biogas storage dome.

Also, the biodigester has an inlet basin and compost pits. The connection system allows the recovery of the biogas accumulated in the digester when the internal pressure becomes important compared to the atmospheric pressure.

The volume flow rate (Q) of the gas is obtained using the *smart-biogas* device which is a sensor using Arduino for online data acquisition. The Arduino is a microcontroller board based on the ATmega328 allowing the detection of the biogas flow (Flash-BMP method), temperature, and pressure and storing them directly in the memory of a computer. The biodigester model and the biogas bit measuring device are shown in Figure 1.



Figure 1 : Biodigester model (left) and the smartbioagas system (right)

1.2. Cow dung

The reactor was seeded with an initial load $S_{in} = 2.4m^3$ of cow dung from a farm in Kadiago province, Burkina Faso. To determine the kinetic parameters of the substrate that will be used to model the reactor continuously, daily feedings were performed with the addition of a dilution rate of 0.095 to $0.30d^{-1}$. The substrate loading is between 20 and 30 kg and supplemented with water at a ratio of $substrat/eau = 1$. The monitoring of the reactor operation was performed by measuring the concentration of volatile fatty acids (VFA) using the Perkin Elmer Clarus 580 type GC equipped with RFID detectors at $250\text{ }^{\circ}\text{C}$ and FID heated to $280\text{ }^{\circ}\text{C}$, and the soluble COD with NOVA 60 spectroquant photometer. Also, pH, total alkalinity, the volume of biogas produced, and its methane composition are determined.

1.3 Measurement protocol of physicochemical parameters

1.3.1 Organic matter

The contents of dry and volatile matter were determined according to the standardized methods implemented in the analysis of soils and organic waste (AFNOR, 1985)[5]. The dry matter (DM) content is deduced by the difference in weight after passing the sample in an oven for 24 hours maintained at a temperature of $105\text{ }^{\circ}\text{C}$. The dry matter is calculated by equation 1.

$$DM = \frac{m_{150^{\circ}C} - m_0}{m_s} \quad (1)$$

In this equation, m_0 = the mass of the empty crucible (mention the unit please), $m_{150^{\circ}C}$ = the mass of the crucible with the sample after drying (g) and m_s = the mass of the sample with the crucible (g).

The mineral content (MM) is obtained by calcining the sample from 150°C in a muffle furnace at 550°C for four hours. The volatile matter content is deduced by the difference between the dry matter content (DM) and the mineral matter content (MM). The mineral matter is calculated by equation 2.

$$MM = \frac{m_{150^{\circ}C} - m_{550^{\circ}C}}{m_{150^{\circ}C}} \quad (2)$$

(Attention to the no. of equations)

Finally, the mass of volatile matter (MV) is deduced by the difference between the dry matter (DM) and mineral matter (MM) rates. It is calculated by equation 3.

$$MV = DM - MM \quad (\text{please check the equation}) \quad (3)$$

(Mention the units of MM, MD and MV, please.)

1. 3. 2. Density

A quantity of 1 to 10 g of the dry substrate is placed in a volumetric flask of suitable volume (50 to 250 ml) previously tared. Water is added to the mixture to the mark. The total volume of water added is determined by weighing with a Pioneer precision PX4201/E-Ohaus, allowing the determination of the volume of the sample. The density used to calculate the initial concentration of the substrate (Q_{in}) is calculated according to equation 4.

$$\rho = \frac{m}{V} \quad (4)$$

With : ρ = the density ($kg.m^{-3}$), m = the mass obtained (kg) and V = the volume of the container (m^3).

1. 3. 3 Determination of organic carbon and total nitrogen

The binder thermostat type furnace DIN 12880 and the Nabertherm type incinerator series L 1/12-LT 40/12 allow the calculation of the carbon content. This method of determining the total carbon content is the standard ISO 10694 (1995) [6]. The total carbon is calculated by equation 4.

$$CT = \frac{MV}{2} \quad (5)$$

In this equation, CT = total carbon and MV = volatile matter.

The technique used for the determination of nitrogen is the Kjeldahl method developed in 1965 [5]. The sample collected is mineralized, consisting of the conversion of protein nitrogen from organic waste to ammonia nitrogen by oxidation of the organic matter in concentrated sulfuric acid at high temperature in the presence of 5 grams of Kjeldahl catalyst $CuSO_4$ and a salt. The nitrogen content of the sample is calculated by equation 5.

$$N_{NTK} = \frac{0,0014 \times 0,1 \times (V_2 - V_1)}{m_s} \times 10 \quad (6)$$

With m_s = the mass of the test sample; V_2 = the volume of sulfuric acid added from the indicator turns from green to pink and V_1 = the volume of sulfuric acid used for the blank determination. The titer of the solution is 0.1 and the molar mass of the nitrogen is $M_N = 0.0014 \text{ kg} \cdot \text{m}^{-3}$.

1. 3. 4. Dilution rate charges made

The digester is fed with the substrate at an inlet flow rate obtained in the experiment noted D. The dilution is defined as the ratio between the flow rate of the influent (Q_{in}) and the volume of liquid (V_{Liq}) in the digester [7]. Two phenomena can occur; a low dilution can lead to a crusting of the substrate but a high dilution can also lead to a leaching of the reactor. The dilution rate is obtained by equation 6.

$$D = \frac{Q_{in}}{V_{Liq}} \quad (7)$$

In this equation, Q_{in} = the concentration of the substrate to be vented (in $\text{kg} \cdot \text{m}^{-3}$); V_{Liq} = the volume of liquid (in m^3), and D = dilution rate (in d^{-1}).

2. RESULTS AND DISCUSSIONS

2.1 Evolution of the physicochemical parameters of the reactor

A characterization (MV, MS, COD, VFA, and biogas flow rate) on the capacity of the bacteria in the removal of substrate overloads and their persistence over time within the reactor is conducted at the beginning and during the digestion period. Table 1 shows the composition of the substrate. The pH of the reaction medium remained around neutrality i.e. 7.2 which is to the advantage of using cow dung. Studies in the literature have shown that the pH of the substrate of farmers is neutral (7.03 ± 0.23) ranging between 5 and 9 for solid waste[8]. The dry matter (DM) content is part of the criteria for the classification of substrates according to their ability to be more or less degradable in biochemical ways. This substrate with a dry matter content of $11.38\% \pm 0.6$ is suitable for anaerobic digestion by the "wet method", which is adapted to the treatment of waste with a dry matter content of between 5 and 20% (DM). The COD values at the outlet are approximately equal to those at the inlet. It is the same for the acids.

These remarks are because the daily loading increases the levels of these acids and the COD in the reactor, which the bacteria are unable to eliminate. It is possible to deduce that, to obtain a high COD abatement, a significant digestion time must be considered. In this study, the ratio of carbon to nitrogen is 24.70 and therefore in the order of the optimal values which are around 30. Density, volatile matter, and COD are necessary for the determination of input parameters such as (Q_{in}) di reactor. The nitrogen content of 1.35% is still below the toxicity threshold of this compound for digestion ranging from 1.5 to 3 $kgN.m^{-3}$ [9].

Table 1. Physicochemical characterization of cow substrates

Features	MS	MV	ρ	MV	C	N	DCO	AGV	pH	C/N
Units	%	$kg.m^{-3}$	$kg.m^{-3}$	%	%	%	$kg.m^{-3}$	$kg.m^{-3}$	-	-
Values	11.38	895.23	731	58.3	33.32	1.35	30.895	0.17	7.016	24.7

2.2 Dilution of the substrates applied in the reactor

The profile of the results of the temporal evolution of the dilution rate D in the 4000 liters' reactor is given in Figure 2. The horizontal areas correspond to the time interval dates when the same loads were performed. The inlet flow rate was chosen with a constant evolution in pieces between $D = 0,095d^{-1}$ and $D = 0,228d^{-1}$ to observe its influence on the dynamic behavior of the chemical species. The first loading gives a dilution of 0.11 per day and after we observed a fall between the 10th day and the 20th and a gradual rise in load whose average is around $D = 0,15d^{-1}$. In order to improve the productivity capacity of the biogas, we carried out heavy loading of the substrate after the twentieth day.

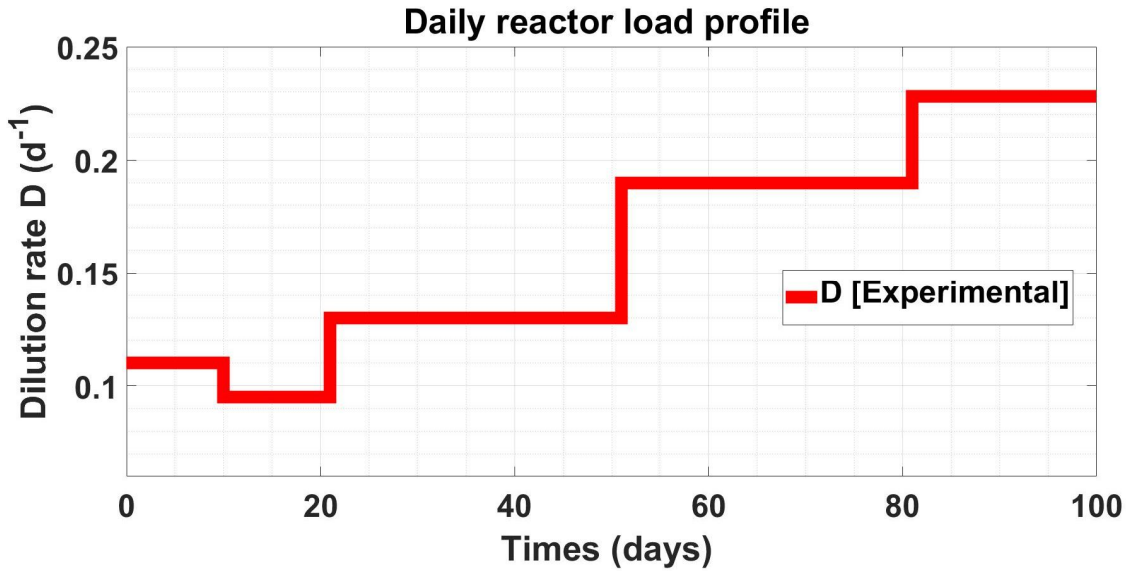


Figure 2. Loads of substrate dilution rates applied to the reactor

2.3 Biogas and methane production in the reactor

Figure 3 shows the biogas and methane flow rates as a function of time. The production increases to reach $3m^3.d^{-1}$ on day 70 before stabilizing around $3.4m^3.d^{-1}$ between 70 and 100 days. From 0 to 5 days, the production remains low around $0.1m^3.d^{-1}$. This result is because the reactor was not yet stabilized in the absorption of the daily substrate overloads. After the 5 days, the production increases to reach $1.5m^3.d^{-1}$ before stabilizing in this value until the time of 20 days. This is because the substrate dilution rate remained low around $D = 0.095.d^{-1}$ as in the literature[10].

For methane production, the time between 0 and 10 days methane production is around $1.4m^3.d^{-1}$. This drop can be explained by the plateauing of production kinetics during the first seven days after the daily substrate overloads. Indeed, during this overload, there was a notable accumulation of VFA due to a delay in the development of methanogenic bacteria. Also, during this period, the hydrogen potential (pH) was period, the hydrogen potential (pH) rose very quickly from 7.5 to a value of 7, effectively showing acidification of the culture medium. This accumulation of acid led to a decrease in methane production around $1.3m^3.d^{-1}$ during the first few days. From 10 to 20 days, the production increases exponentially to reach $1.9m^3.d^{-1}$. After the 10th day, the production remains stable around $1.95m^3.d^{-1}$ per day for the rest of the time. This stability is due to the satisfactory rhythm taken by the microorganisms in the digester. The results obtained show that the increase in the load does not necessarily lead to the total net production of biogas and methane. Knowing the right recipe for biomass allows good optimization of anaerobic digestion.

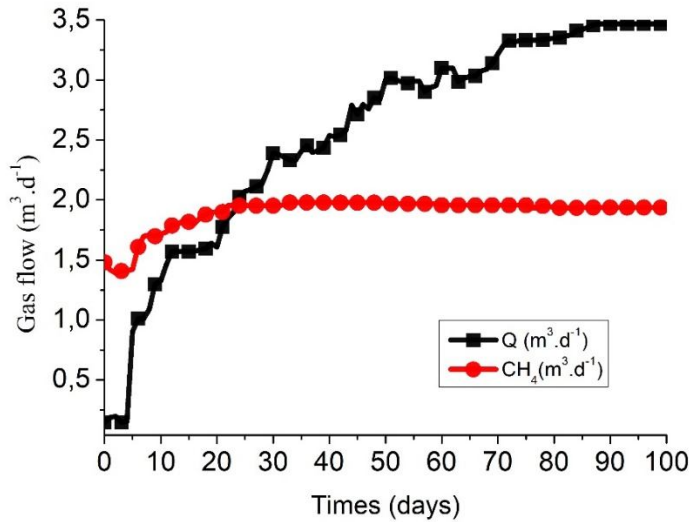


Figure 3. Evolution of biogas (Q) and experimental methane flow rates as a function of time

2.4 Influence of pH on biogas production and Temperature

Figure 4 shows the evolution of hydrogen potential and temperature within the bioreactor over time. The pH remained neutral during the 100 days of the study. During the first 10 days, we have a unit of pH = 7.4 and thereafter its value stabilizes at pH = 7.015. This is explained by the high reactivity of the methanogenic bacteria that consume the volatile fatty acids and avoids their strong fall. The temperature in the digester remained stable at around 35°C throughout the anaerobic digestion. This good result is due to the cement shell which allows to control the temperature in the reactor around 35°C and makes it hermetic to control the anaerobic conditions.

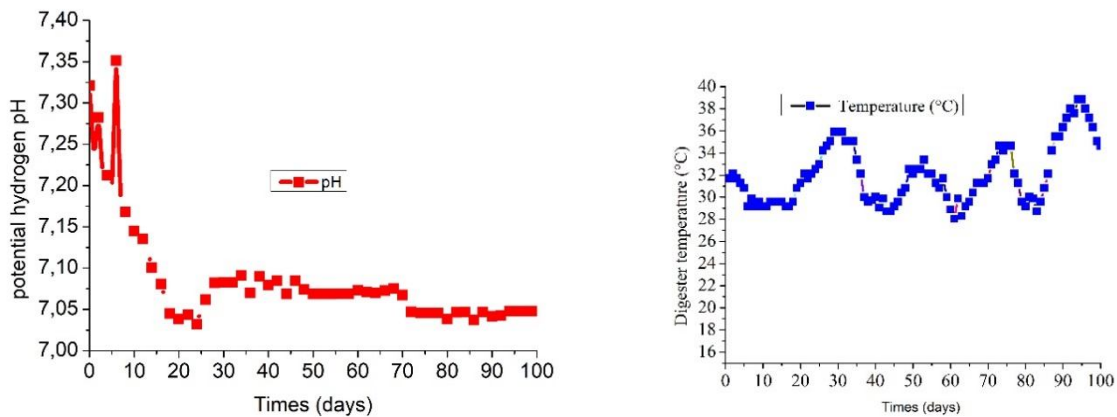


Figure 4 : Evolution of hydrogen potential and temperature as a function of time

2.5 Chemical Oxygen Demand and Acid Profile in the Reactor

The curves in Figure 5 show the changes in chemical demand and total VFA concentration in the reactor over the 100 days of the study. At the very beginning of the study, the COD production remained high. This increase in concentration is explained biochemically because during this period the microorganisms are not sufficient to degrade the effluent. Comparing the concentrations between the inlet and the outlet of the reactor we notice a great efficiency of the process to eliminate the organic matter, until stabilizing this demand.

Studies prove that a fluctuation in the concentration of volatile fatty acids in the digester admits a direct impact on the energy yield of anaerobic digestion[11]. Indeed, an imbalance between the acidogenesis and methanogenesis phases can be caused by an accumulation of acids. This concentration increases weakly as a function of time and does not reach the critical value where VFAs inhibit anaerobic digestion which is around 1000mgCOD.l^{-1} according to the work of Kouas et al 2017[12]. The concentration obtained through this study is between 0.15 and 0.3gCOD.l^{-1} .

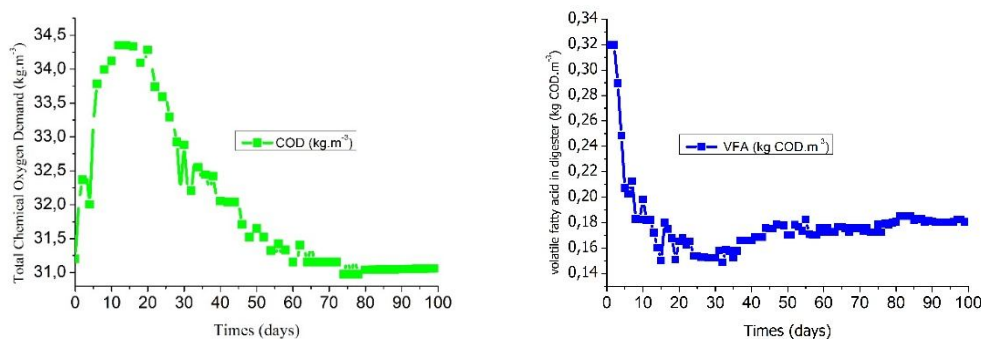


Figure 5 : Evolution of chemical oxygen demand and volatile fatty acids as a function of time

CONCLUSION

This study showed the importance of characterizing the physicochemical factors of the substrates within the bioreactor to improve their productivity in biogas. This study has also focused on the monitoring of the productions of the reaction medium in continuous mode of a pilot digester of 4 m^3 on. Thus, we observe that the average biogas flow rate (Q) is $2.5\text{ m}^3.\text{d}^{-1}$ and a methane flow rate of 1.9. Factors inhibiting biogas production are found to be 0.17kgCOD.m^{-3} for fatty acids and a hydrogen potential $pH = 7.015$ which remained below the literature threshold values. One of the objectives we have achieved was to provide decision-makers or operators of anaerobic digestion facilities with reliable information for the quantitative evaluation of the energy potential of organic waste in Burkina Faso. Future work will consist of the implementation of these different parameters of the experiment in a numerical model of anaerobic digestion.

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