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Characterization of the anaerobic digestion of cashew apple pulp from of the casamance

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Anaerobic digestion is considered a good method for processing organic waste. The end result is an almost complete conversion of biodegradable organic matter into finished products like methane, carbon dioxide, hydrogen sulphide, etc. The relative proportions of these gases depend on the nature of the fermented substrates and the fermentation conditions. Moreover, these substrates exist in Senegal with potential not yet fully exploited; as an example, Senegal remains the 15th largest exporter of cashew nuts with an annual production of around 18,000 tons. Kolda, Ziguinchor, Sédhiou and Fatick are the main producers of cashew apples. Thus, each year, after the cashew nut campaign, more than 342,000 tons of cashew apples, pressed or not, are rejected without being valued, and therefore doomed to rot. This work aims to characterize the anaerobic digestion of cashew apples in the presence of inoculum, with a prior pretreatment of the apple. The physico-chemical characterization shows that the cashew apple essentially contains 98.81% organic matter with a C/N ratio equal to 23.27%. The carbon content was determined by an empirical method and that of nitrogen by the Kjeldahl method. The biogas produced is composed of 63.60% methane and 32.71% carbon dioxide.

Key words: Anaerobic digestion, cashew apple pulp, inoculum, biogas.

INTRODUCTION

Climate change is arguably the most imminent environmental threat facing the world today. The rise in global temperature will have some major effects on ecosystems, wildlife, food chains and ultimately human life. There is a general consensus that global warming is due to the large-scale anthropogenic emission of greenhouse gases, which are mainly caused by heat and electricity production. Indeed, much of the world's energy demand is still met through the use of fossil fuels. According to the International Energy Agency (IEA), fossil fuels accounted for up to 81% of the world's primary energy supply in 2007 (Appels et al., 2011), while

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renewable energy sources only contributed 13%. Although much attention is paid to the technical and economic development of the implementation of renewable energy sources, fossil fuels remain the most dominant source of energy in the world, estimated at 77% for the period 2007 to 2030 (International Energy Agency, 2004). This small drop in supply will be more than offset by the 2.5% annual increase in energy demand until 2030. Most of the increase will be achieved by higher consumption of coal, followed by gas and oil (Appels et al., 2011).

It is clear that renewable resources will play a crucial role in current CO_2 mitigation policy. In this respect, energy from biomass is seen as one of the most important renewable energy sources in the future. In addition, solid waste with a high organic content is frequently treated by composting or by anaerobic digestion. Anaerobic digestion is a natural biological process of degradation of organic matter in the absence of oxygen. Degraded organic matter is found mainly in the form of biogas (Fabien Bova et al., 2012). Biogas is an alternative and renewable energy source produced during the anaerobic (oxygen-free) digestion of organic matter. Organic matter is converted into a combustible biogas rich in methane (CH_4) and a liquid effluent called digestate (Jactone et al., 2009). Indeed, at present, there are a large number of biogas plants that process different types of organic waste such as solid waste, the organic fraction separated by solid waste sources, mainly food waste and gardening, manure, sewage sludge and various industrial organic wastes (Ponsá et al., 2011). Applied anaerobic digestion can help reduce the use of fossil fuels and reduce greenhouse gas emissions that can contribute to climate change. Additionally, methane is considered a potent greenhouse gas that can stay in the atmosphere for up to 15 years, and is about 20 times more effective at trapping heat in the Earth's atmosphere than carbon dioxide (Scott and Campbell, 2012; Solomon 2007).

In addition, agricultural residues such as wheat chaff, rice husk and corn stalks are produced in large quantities all over the world every year. Since agricultural waste is an abundant source of organic matter, it can be used as a valuable alternative feedstock for biogas production. Moreover, in Senegal, cashew cultivation, initiated well before independence (1946-1947) by the Water and Forests Service for reforestation and soil conservation purposes, remains today an industrial crop which interests many countries (China and India). It has played three main functions during its development, namely, (i) an environmental management function centered on the protection and conservation of natural resources, (ii) an economic function of creating wealth and jobs, (iii) a function medicinal (treatment of colic, diarrhea, skin infections, bronchitis, diabetes, etc.) (Dieng et al., 2019). Currently, Senegal is the 15th largest exporter of cashew nuts with a production of more than 18,000 tons per year, in 2018, according to the PADEC study (Support Program for the Development of Casamance). Four regions (Kolda, Ziguinchor, Sédhiou and Fatick) are the main producers of cashew apples. In Casamance (Kolda, Ziguinchor, Sédhiou), each year after the cashew nut season, more than 342,000 tons of cashew apples, pressed or not, are rejected without being valued, and therefore doomed to rot (Faye et al., 2020). The purpose of this study is to characterize the production of cashew apple pulp (Photo 1), which is very acidic with a pH that is between (4.2 and 5) which can inhibit the process of anaerobic digestion.

MATERIALS AND METHODS

Preparation of the substrate

In this study, we used cashew apple pulp (Figure 1) from an apple fruit juice processing unit, located near Assane Seck University in Ziguinchor.

The cashew apple, very acidic characteristic with a pH between 4.2 and 5, very fibrous; after collection, has been pretreated to reduce the effects of these two characteristics which are inhibiting factors during its anaerobic digestion (Photo 2). To do this, the cashew apples were ground using a manual grinder, to an average particle size of less than 2 mm. After grinding, the pH of the pulps was adjusted with lime to around neutrality, which is important for a substrate to be methanized, because most methanogens have an optimal pH of between 7 and 8, whereas acid-forming bacteria often have a lower optimum (Angelidaki and Ahring, 1994). If the pH of the waste to be tested is outside the optimal range, and there is not enough buffering capacity, the anaerobic process may be inhibited (Angelidaki, 2004).

After this pretreatment step, the substrate was mixed with inoculum (digested cow dung) before being methanized. Figure 2 describes the cashew apple pulp pretreatment process.

Experimental procedure

The cashew apple pulps and the inoculum were placed in 750 mL capacity bottles for the determination of the production kinetics or the quantitative production of the substrate. A 5 L reactor was used to analyze the composition of the biogas produced under mesophilic conditions at 37°C (Manyi-loh et al., 2013), following a substrate/inoculum ratio of 1/1. The mesophilic inoculum used in this study is taken from a 10 m^3 reactor fed by cow dung and installed on the bioenergy platform of the Assane Seck University of Ziguinchor. The mixtures were prepared homogeneously. During the production of biomethane, there were no added nutrients, including enzymes and chemicals; this in order to assess the quantity and quality of the biogas produced by the apple pulp thus used. To do this, the liquid displacement method (Figure 1) and that of the biogas stock produced (Figure 2) were used. A hat-trick was achieved for the try. The value obtained, expressed as the volume (in mL) of biogas produced per gram of organic matter (OM) added (mLbiogas/g OM), and is the average of the triplet.

Analytical methods

For determination of percentage dry matter (%DM) and moisture

Photo 1. Pile of cashew apple pulp substrate.

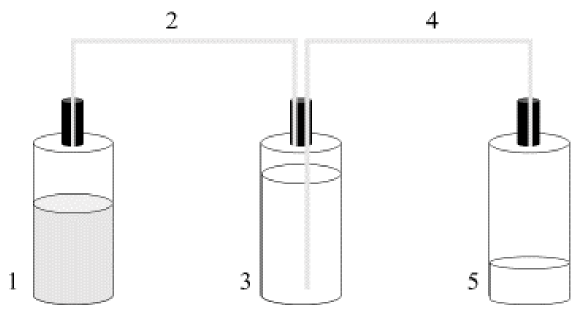

Figure 1. Liquid displacement method. 1: Reactor; 2: Biogas transport pipe; 3: Bottle filled with water; 4: Water transport pipe coming out of the bottle; 5: Graduated bottle for measuring collected water.

content (%H), the substrates were dried in a ventilated oven at 105°C for 24 h (Cheng et al., 2014; Park et al., 2014).

For measuring the organic matter content (% OM) and the percentage of mineral matter (% MM), the substrate sample was dried, then ground and finally calcined at 550°C for 4 h in a muffle furnace (Nikiema et al., 2015; Park et al., 2014).

The percentage of total carbon (%C) is determined by the empirical method (Afilal et al., 2014) using the formula of Equation 1 opposite.

$$\%C = \frac{\%MO}{1,724} \quad (1)$$

Nitrogen was assayed by the Kjeldahl method carried out following mineralization with concentrated sulfuric acid and in the presence of a mineralization catalyst (K_2SO_4 and $CuSO_4$), the nitrogenous compounds are mineralized into ammonium sulphate. The ammonia displaced by the soda is entrained by the vapor of the solution and trapped in a boric acid solution to then be dosed with a hydrochloric acid solution (Labconco, 2015; Nikiema et al., 2015). This method gives the percentage of nitrogen (%N) of the sample by calculation from Equation 2.

$$\%N = \frac{V \times T \times M_N}{m \times 1000} \times 100 \quad (2)$$

where V: volume of HCl, T: titration of the HCl solution, M_N : molar mass of nitrogen, and m= mass of the sample.

The composition of the biogas produced will also be evaluated using a biogas analyzer, model Optma7 Biogas.

RESULTS AND DISCUSSION

Physico-chemical characterization of substrates

The study aimed to assess the production of biogas from cashew apple pulp in the presence of inoculum. The process of anaerobic digestion was carried out in the regular state where the temperature of the process takes place in a mesophilic medium (temperature set at 37°C by a water bath) (Manyi-loh et al., 2013; Scully et al., 2005). The physico-chemical characteristics of the cashew apple pulp and the inoculum are shown in Table 1.

Table 1 shows that cashew apple pulps mainly contain organic matter (%OM>98%) with a low content of mineral matter (%MM<2%). This is therefore an interesting result because organic matter (OM) is considered to be the part of the substrate that is likely to transform into biogas, including methane (Cheng et al., 2014).

Furthermore, the volumetric yield of methane can be significantly improved for high organic matter content of

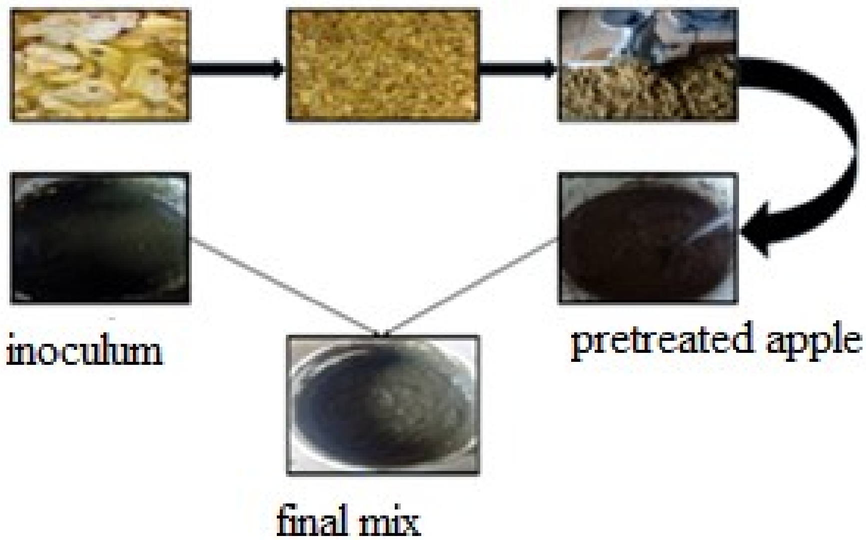

Photo 2. Method of preparation and mixing of the substrate with the inoculum.

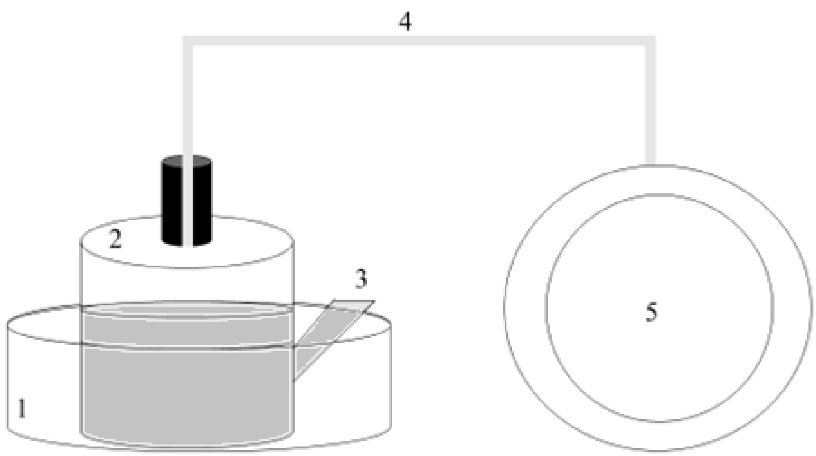

Figure 2. Experimental biogas production device. 1: Water bath at 37°C; 2: 5 L reactor; 3: Sampling nozzle; 4: Pipe for transporting biogas to the air chamber; 5: Air chamber for collecting the gas produced.

Table 1. Physico-chemical characterization of the studied substrates.

Settings	Substrates	
	Cashew apple	Inoculum
% Dry matter (DM)	14.56	7.51
% Humidity (H)	85.44	92.49
% Organic matter (OM)	98.81	48.30
% Mineral matter (MM)	1.19	51.71
% Volatile matter (VM)	56.78	27.76
% N	2.44	1.46
C/N	23.27	19.05

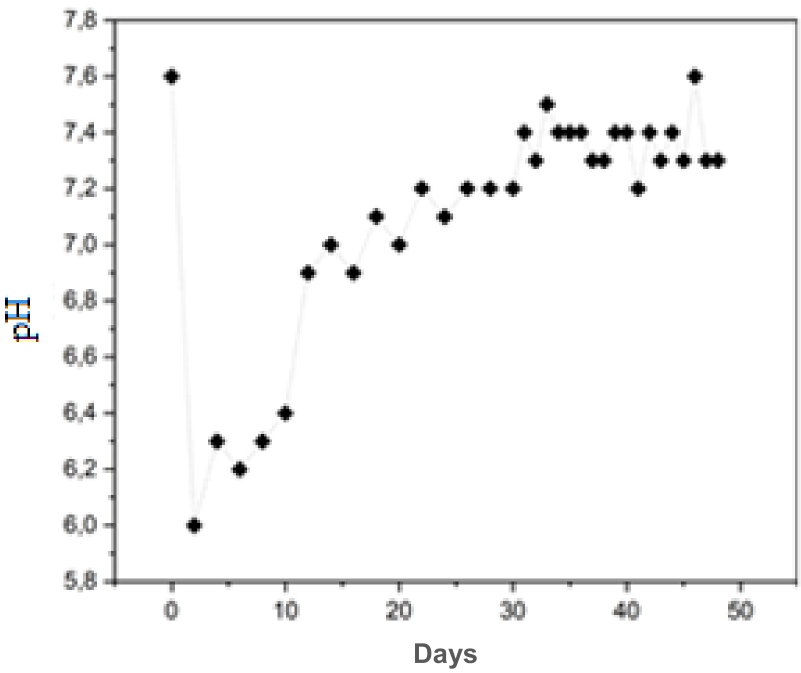

Figure 3. Evolution of pH during digestion of cashew apple pulp with inoculum.

loaded substrates (Asam et al., 2011). It was also found that the carbon content of apple pulp is quite high (56.78%). The nitrogen content is 2.44%. A C/N ratio equal to 23.27 was obtained, ideal for anaerobic digestion with an optimal C/N ratio of between 20 and 30 (Zhang et al., 2008).

The inoculum used, with an OM content of less than 50%, does not in any way increase the yield of the biogas or that of the methane, but it does allow a certain stability of the anaerobic digestion process. In the literature, experimental data have demonstrated that the ultimate methane yield as well as the methane production rates are substrate and inoculum specific (Eskicioglu and Maryam, 2011). Large inoculation volumes ensure microbial activity, low risk of overload and low risk of inhibition (Angelidaki and Wendy, 2004; Cabbai et al., 2013). A study found that inocula applied to the anaerobic digestion process can significantly improve the performance of the process. It is also mentioned that the better performance of digesters with inoculated substrates can be associated with the accelerated reproduction of microorganisms that contribute to the fermentation of organic matter in the digesters (Lopes et al., 2004). Also, another study mentioned that inoculum has an important role in starting the anaerobic digestion process as it is able to balance the populations of certain bacteria which include syntrophobacter which is responsible for the degradation of propionate as well as butyrate and methanogens (Pandey et al., 2011).

Evolution of pH during anaerobic digestion

pH plays a major role in anaerobic digestion. It influences the activity of enzymatic hydrolysis and active micro-organisms. The anaerobic digestion process occurs in the pH interval located from 6.0 to 8.3 and 6.5 to 7.5 (Djaafri et al., 2014). Most methanogens have an optimum pH between 7 and 8. If the pH of the waste to be tested is outside the optimum range, and the memory buffering capacity is not sufficiently present, the anaerobic process may be inhibited (Angelidaki, 2004).

Adjusting the pH can minimize the inhibitory effects of acid build up and accelerate the rate of waste degradation (Vavilin et al., 2003). Anaerobic digestion processes are strongly influenced by pH. In Figure 3, it can be seen that the pH varies during the anaerobic digestion. The pH evolution curve can be divided into three stages described opposite.

The first stage is the hydrolysis and acidogenesis stage which led to a rapid drop in pH from a value of 7.6 to 6 from the first two days. This decrease in pH value is due to the breakdown of substrate polymers into monomers and the production of volatile fatty acids (VFAs), such as acetate, butyrate, propionate or lactate, into other organic acids (lactate) and alcohols using acidogenic microorganisms (Amani et al., 2010).

The second stage begins from the third day until the tenth day, where there is a fluctuation of the pH value between 6 and 6.5. This is the stage of acetogenesis; it is

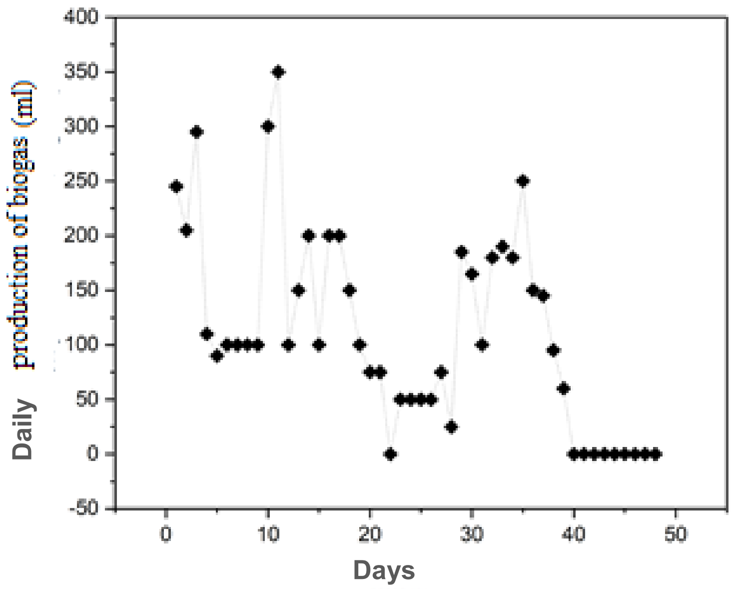

Figure 4. Daily production of biogas from inoculated cashew apple pulp.

due to the formation of acetate from the products of hydrolysis and acidogenesis. This conversion can take place according to two metabolic pathways, thanks to bacteria consuming either VFAs or CO_2 and hydrogen (Batstone et al., 2002). One of the pathways is the second metabolic pathway of acetogenesis, called homoacetogens, the other is hydrogenoclastic methanogenesis. There is therefore an obligatory association between the species producing hydrogen and those which consume it; this is called a syntrophic relationship (Delgenes et al., 2003; Nie et al., 2008; Schink, 1997).

The third stage is methanogenesis, which starts on the eleventh day until the end of the experiment, on the 48th day; signaled by the depletion of organic matter following an inflation of the inner tube. During this step, acetate, H_2 and CO_2 are transformed into CH_4 and CO_2. This reaction is carried out by archaea of several types:

(1) Methanogenic acetoclastic archaea which use acetate as a substrate. This metabolic pathway produces 70% of total CH_4 in anaerobic digestion (Pavlostathis, 2009) and involves different microorganisms such as *Methanosaeta concilii* or *Methanosarcina acetivorans* (Amani et al., 2010).

(2) Hydrogenotrophic methanogenic archaea that produce CH_4 from CO_2 and H_2. This pathway corresponds to 30% of the production of total CH_4 in anaerobic digestion even if this reaction is more energetically efficient (Hattori et al., 2000) and can be carried out by *Methanobacterium bryantii, Methanobrevibacter arboriphilus* (Amani et al., 2010; Faye et al., 2020; Moletta, 2003).

Figure 4 shows the evolution of the daily production of biogas during the anaerobic digestion of inoculated cashew apple pulp.

The daily biogas production kinetics of the pulps lasted 48 days until the production of biogas was no longer observed. Biogas production started immediately from day one and daily biogas production peaks were observed after day one. The highest biogas production rate was obtained on day 11 with a maximum biogas production rate of 350 mL. From the 12th day, the production continued, but the values fluctuated between about 75 and 200 mL. On the 22nd day, the production of biogas from the pulp was zero (0 mL).

This may be due to the formation of crusts on the production surface, which can prevent contact between bacteria and create a production disruption. From the 23rd day, a second phase of production was observed. This production phase extends until reaching a maximum production of 250 mL on the 35th day. And then, a drop in production is observed from the 36th day to the 39th day. Between the 40 and 48th days, no biogas production was observed.

Figure 5 illustrates the cumulative biogas production kinetics of inoculated cashew apple pulps.

The volume of biogas produced is an important parameter for controlling and monitoring the anaerobic digestion process, it also tells us about the production potential of our substrate to ferment. Furthermore, a substantial production of biogas reflects both the stability and the proper functioning of the digester (Zerrouki et al., 2017). Figure 5 shows the cumulative production of

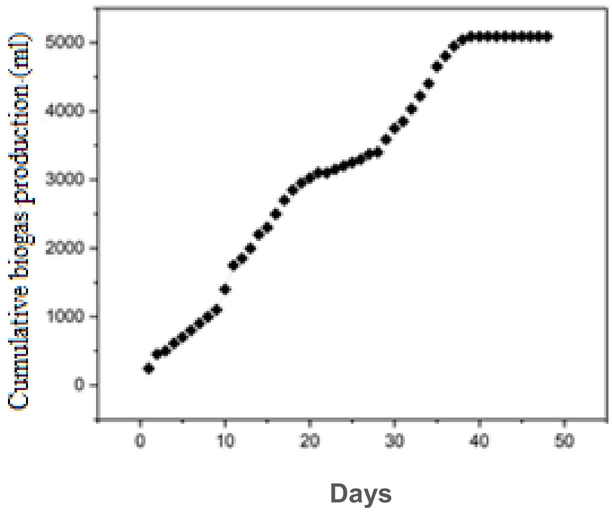

Figure 5. Cumulative production of biogas from inoculated cashew apple pulp.

Table 2. Composition of biogas produced from cashew apple pulp.

Symbol	Unit	Settings
CH_4	%	63.60
H_2S	ppm	6
CO_2	%	32.71
LHV	Kcal/kg	5148
HHV	Kcal/m^3	6582

biogas during the duration of the experiment, which is 48 days. The volume of biogas recovered is 5089 mL and stabilizes after 41 days of anaerobic digestion. The quantity of biogas produced is interesting compared to the organic load introduced into the digester, which is 333 g/L. It was noted that the kinetics of biogas production is subdivided into three main phases.

(1) Slowdown phase: This phase corresponds to the adaptation phase of the free microorganisms contained in the substrate to their environment. The duration of this phase is 10 days. And this is the phase that records the lowest production. This period corresponds to the liquefaction phase during which hydrolysis, acidogenesis and acetogenesis take place.

(2) Exponential phase: During this phase, the multiplication of micro-organisms is maximum, which results in a favorable living environment for bacteria, for good biogas production. This leads to optimal biogas production on the 41st day of fermentation, with biogas production reaching 5089 mL.

(3) Stabilization phase: During this phase, from the 41st day, the production of biogas is stabilized due to the exhaustion of organic matter in the digester. Table 2 gives us the composition of the biogas and the calorific values of the cashew apple pulps studied.

The quality of the biogas produced is essentially assessed by the percentage of methane (CH_4) it contains. A biogas is all the better as its percentage of methane is high (Sadak et al., 2011). According to the results in Table 2, from a qualitative point of view, the cashew apple pulps show good results with a methane percentage of 63.60%. At the exit of the digester, the biogas obtained is difficult to recover in its raw composition. In addition to CH_4 and CO_2, it contains volatile matter, and is saturated with water vapour. Thus, the use of biogas for cooking (combustion) requires a control of the flammability limit of the CH_4 produced. During combustion, the mixture of CH_4 and O_2 burns to give CO_2, H_2O and heat (energy) (Equation 3).

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O + Energy \quad (3)$$

The biogas-air mixing index for complete combustion for our sample is composed of 63.6% methane and that the air contains 21% oxygen and 79% nitrogen (only O_2 participates in the combustion reaction) is expressed by:

(1) $\alpha = \frac{1}{0.636} = 1.57233$, volume of CH_4 required for complete combustion

(2) $\beta = \frac{2}{0,21} = 9.52381$, volume of O_2, necessary for complete combustion

(3) also we noted, $\delta = \frac{\beta}{\alpha} = \frac{9.52381}{1.57233} = 7.057132$ reagent volume,

(4) reagent mixing index $\eta = \frac{1}{1+\delta} = \frac{1}{1+7.057132} = 0.1417$ in % η = 14.17% of biogas in the air (stoichiometric air requirement).

Biogas burns in a narrow range of mixtures from 9 to 17% biogas in the air. So the CH_4 obtained from our sample has complete combustion, because η obtained is included in the 9 to 17% range.

However, in the energy field, the lower heating value (LHV) and higher heating value (HHV) are used as an indicator. The LHV is of paramount importance for the thermal recovery of substrates. It represents the amount of heat released by the complete combustion of the substrate with the formation of water vapor (Moletta and

Cansell, 2003). The results of this study also show us that the biogas from apple production contains a lower calorific value greater than that of cow dung which is equal to 4.330 kcal/kg (Faye et al., 2020). The value of the higher calorific value of the biogas produced by the pulps of the cashew apple is included in the range given by Sadak and Abenm (2014). According to these authors, the calorific value of biogas is proportional to its CH_4 content and it varies between 5000 and 8500 kcal/m³.

Conclusion

This study shows that the adjustment of the pH before the start of the anaerobic digestion process with cashew apples which have a very acidic pH is essential for the optimization of the bio-methanization process.

The results of the study show that:

(1) apples have a high content of volatile organic matter with a value of 98.81%;
(2) a ratio (C/N) favorable to anaerobic digestion, equal to 23.27%;
(3) the anaerobic digestion of apples gives very interesting concentrations of bio-methane, with a composition of 63.60% methane and 32.71% carbon dioxide;
(4) very high caloric values, 5148 kcal/kg for lower heating value and 6582 kcal/m^3 for higher heating value (HHV), which are higher than those of cow dung produced at the bioenergy platform, which are 4330 kcal/kg for the LHV and 6172 kcal/m^3 for the HHV.

This work thus allows us to conclude that cashew apples are favorable for the start-up of new digesters of different types, for the rural population.

CONFLICT OF INTERESTS

The authors have not declared any conflict of interests.

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