

Generation of biogas from coffee-pulp and cow-dung co-digestion: Infrared studies of postcombustion emissions



Grisel Corro*, Laura Paniagua, Umapada Pal¹, Fortino Bañuelos, Minerva Rosas²

Instituto de Ciencias, Benemerita Universidad Autonoma de Puebla, 4 sur 104, 72000 Puebla, Mexico

ARTICLE INFO

Article history:

Received 20 February 2013

Accepted 13 July 2013

Available online 9 August 2013

Keywords:

Biogas production
Coffee-pulp
Cow-dung
Co-digestion
FTIR spectroscopy

ABSTRACT

Biogas could be produced by the co-digestion of coffee-pulp and cow-dung mixture under solar radiation. Gas chromatography and FTIR spectroscopy were used to analyze the chemical compositions of the generated biogas and its postcombustion emissions. From the first month of co-digestion at mesophylic conditions, methane content in the biogas attains 50% of the yield. This content increased up to 60% and remained almost constant for at least 8 months of further digestion. The FTIR gas spectroscopy analysis revealed the presence of over 70 chemical compounds in the biogas generated after 4 months of co-digestion along with several compounds hazardous to environment and animal health like isocyanic acid, and bromomethane. Combustion emission of the biogas contained several components like CH₄, C₃H₈, CO, SO₂, HI, and probably Br₂ which are strongly harmful to human and animal health. Results presented in this work indicate that if the biogas is to be considered as a fuel, the conventional combustion technology has to be upgraded to prevent these hazardous emissions to the atmosphere.

© 2013 Elsevier Ltd. All rights reserved.

1. Introduction

Global depletion of fossil fuels has led to the search for alternative sources of energy. Biomass has the largest potential and can only be considered as the best option for meeting the demand and insurance of future energy (biofuel) supply in a sustainable manner.

The biofuel production from renewable resources refers particularly to the lignocellulosic biomass/materials, as this makes up the majority of the cheap and abundant non-food materials available from the plants. Therefore, lignocellulosic feedstock can offer the potential to provide novel biofuels of the second generation [1].

The production of hydrogen, natural gas, bio-oils, biogas, alcohols and biodiesel from renewable biomass have been a major research topic around the world with a prospect to supplement petroleum fuels and reduce environmental pollution.

Methane production from a variety of biological wastes through anaerobic digestion technology is growing worldwide and is considered ideal in many ways due to its economic and environmental benefits [2–8]. Methane fermentation is the most efficient technology for energy generation from biomass in terms of energy output/

input ratio (28.8 MJ/MJ) among all the technologies used for energy production through biological and thermochemical routes [9].

Use of agricultural biomass for biogas production has been increased in recent years. Agricultural biomass includes food based portion (oil and simple carbohydrates) of crops such as corn, sugarcane, and the non-food based portion of crops such as the leaves, stalks and coffee pulp and husk. Use of specific microorganisms for pretreatment of wastes further promises to increase the yield and stability of the biogas end products. In addition, the use of agro-industrial residues in bioprocesses helps to reduce environmental pollution [10,11].

Coffee is the second largest traded commodity in the world and generates large amounts of by-products and residues during processing. Industrial processing of coffee cherries is performed to separate coffee beans by removing shell and mucilaginous part. In wet industrial processes a large amount (about 29% dry-weight of the whole coffee berry) of coffee-pulp is produced as the first by-product. The organic components present in coffee-pulp include cellulose (63%), lignin (17%), proteins (11.5%), hemicelluloses (2.3%), tannins (1.80–8.56%), pectic substances (6.5%), reducing sugars (12.4%), non-reducing sugars (2.0%), caffeine (1.3%), chlorogenic acid (2.6%) and caffeic acid (1.6%) [12–14]. Coffee wastes and by-products produced during coffee berry processing constitute a source of severe contamination and pose serious environmental problems in coffee producing countries. Therefore, disposal of coffee pulp is becoming an emerging environmental problem worldwide due to its putrefaction. Due to anaerobic conditions of open pulp-storage or composting areas, an uncontrolled emission of

* Corresponding author. Tel./fax: +52 (222) 22955 00 7294.

E-mail addresses: griselda.corro@correo.buap.mx (G. Corro), upal@sirio.ifuap.buap.mx (U. Pal).

¹ Address: Instituto de Física, Benemerita Universidad Autonoma de Puebla, Apdo. Postal J-48, 72570 Puebla, Mexico. Tel.: +52 222 2295610.

² Address: Instituto Politecnico Nacional, 90700 Tepetitla de Lardizabal, Tlaxcala, Mexico.

methane (CH₄) and nitrous oxide (N₂O) from these places cannot be excluded [15–17]. Hence the utilization and management of coffee wastes in large-scale still remains a challenge worldwide due not only to the generation of earlier gases, but also for their high contents of caffeine, free phenols and tannins, which are known toxic agents for many biological processes [18].

Previous studies have confirmed that the content of toxic materials in coffee pulp can be minimized by microbial degradation [19,20]. To that effect, generation of bioproducts such as biogas has been established at small scale. On the other hand, anaerobic digestion of animal manure has been investigated extensively [21–23]. The use of cow-dung for biogas generation is well established [24]. However, the costs of cow-dung digesters are not favorable due to their relatively low biogas yield in comparison with several other types of organic wastes such as food wastes [22,23].

One of the approaches for improving cost-benefit of cow-dung digesters is to increase their biogas production rate by co-digestion with more biodegradable wastes as long as such wastes are available in the vicinity of dairy farms and the farm land can use the nutrients and salts of the wastes. Co-digestion of different materials may enhance the anaerobic digestion process due to better carbon and nutrient balance [25,26]. According to Mata-Alvarez et al. [27], digestion of more than one substrate in the same digester can generate positive synergism and added nutrients can support microbial growth. During mesophilic anaerobic co-digestion of cow-dung and fruit or vegetable wastes in a continuous stirred tank reactor (CSTR) in mesophylic conditions (35 °C), Callaghan et al. [28] have found that increasing the percentage of fruits and vegetable wastes from 20% to 50%, the methane yield raised from 230 L to 450 L per kilogram of added volatile-solids. Misi and Forster [29] have found that batch co-digestion of cow dung with molasses (50% on dry weight basis) at 35 °C increases the biogas yield from 60 L to 230 L per kilogram of added volatile-solids.

Cow-dung contains a considerable amount of bacteria but low amounts of cellulose, lignocellulose, lignin and other organic components which are essential for bacterial growth and for biogas production. On the other hand, though coffee pulp contains bacteria nutrients (cellulose, hemicellulose, proteins) in large amount, it needs high concentration of bacteria to first degrade the toxic components (such as tannins and phenols), and then to produce biogas. These facts suggest that the mixture of coffee-pulp/cow-dung would result in a synergetic effect leading to a high biogas production.

Therefore, the first objective of this investigation was to evaluate the feasibility of using coffee-pulp from Mexican coffee harvest for biomethanation and the possibility of improving biogas yield by co-digestion of coffee-pulp with cow-dung in mesophylic conditions (35–40 °C).

The content and purity of methane (CH₄) in produced biogas are of great importance. Purity is highly affected by the presence of contaminants in trace or higher quantities, whose nature depends on the source of production. The most common contaminants are hydrogen sulfide (H₂S) and other malodorous sulfur containing compounds (i.e., mercaptans, such as CH₃SH) coming from the anaerobic fermentation of proteins and other sulfur bearing organic molecules. Depending on the composition of fermented organic material, the content of H₂S in biogas can vary from 10 to 10⁴ ppmV. H₂S, besides its bad smell, is non-desirable in energy recovery process as it gets converted to highly corrosive and environmentally hazardous sulfur dioxide (SO₂) and sulfuric acid (H₂SO₄). Therefore, H₂S must be removed for any eventual utilization of biogas.

Ammonia (NH₃) is another common contaminant coming from the anaerobic digestion of nitrogen-bearing organic molecules, which is not only corrosive but also presents a health risk.

However, its combustion only slightly increases the emission of nitrogen oxides (NO_x). On the other hand, siloxanes are a group of silicon (Si) bearing molecules found in landfill biogases. These compounds are considered to be the third most important contaminant. During combustion, siloxanes form glassy microcrystalline silica. The other reported components in biogas (O₂, N₂, CO₂, H₂O, Ar) are considered to be harmless.

The information on the complete biogas chemical composition is indispensable for determining the quality and quantities of combustible and hazardous components before using it as a fuel. However, to the best of our knowledge, a complete analysis of biogas composition using FTIR spectroscopy has not been reported in the literature. Thus, the second objective of this research was to perform a complete FTIR analysis of the biogas composition generated from coffee-pulp and cow-dung co-digestion in order to determine the presence of volatile compounds, which might have a potential corrosive or harmful effect on human or animal health.

On the other hand, combustion and emissions characteristics of produced biogases are scantily reported in the literature. In this article we report the results of a preliminary study on the composition of emissions from the combustion of biogas obtained from coffee-pulp/cow-dung co-digestion. This study was performed using a laboratory combustor combined with a FTIR gas spectrometer.

2. Material and methods

2.1. Collection and preparation of substrates

Cow-dung was collected from a dairy farm. The samples were scraped off the feed lanes and collected in a bucket. The samples were transported immediately to our laboratory and placed in the digesters. Coffee-pulp (comprising the skin and mesocarp of the coffee berry) was obtained directly from the pulping machine during the processing of coffee berries by wet process from Huitzilán de Serdan, a volcanic, semi-tropical region of Puebla, Mexico and transported to our laboratory in cotton sacks same day. The coffee pulp was dried for about 5 h (from 11:00 to 16:00) under solar radiation of about 1000 ± 50 W/m² for 5 days to reduce its moisture content before the digestion. A coffee-pulp weight loss of 50% (±1%) was measured after this direct solar drying.

2.2. Anaerobic digestion tests

2.2.1. Preliminary experimental performances

To optimize the coffee-pulp/cow-dung ratio in the digesters, we performed some simple tests in small vessels with different weight ratios of coffee-pulp and cow-dung. The volume of the test vessels was 1 L, with a working volume of about 0.5 L. 400 g of biomass with cow-dung/coffee-pulp ratios 1/0, 1/0.5, 1/1, 1/2 and 0/1 incorporated into the test vessels along with 0.1 L of water. The test digesters were equipped with a tap connected to an external pipe which enabled the sampling of the exhausted biogas. These digesters were placed in an oven operating at ~35 °C and were shaken manually twice a day.

The produced biogas was characterized for its CH₄ content (vol.%) through gas chromatography every day for one month (see Supporting Information, Fig. 1S). The results of such analysis revealed that the methanation capacity is best in the mixture containing 40 wt% coffee-pulp, 40 wt% cow-dung and 20 wt% water.

2.2.2. Experimental design and reaction system

The three batch digesters (Fig. 1) were therefore designed and built as follows. Stainless steel cylindrical vessels were equipped for the digestion process with an air-tight lid. The vessels had a

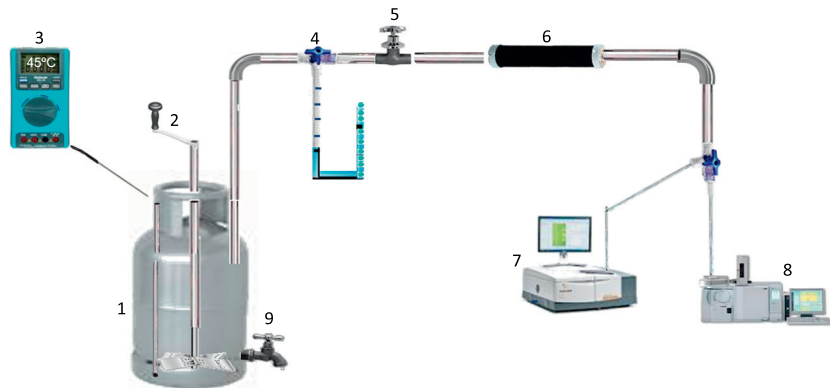


Fig. 1. Schematic layout of the equipment. (1): Digester; (2): mixing crank handle; (3): thermometer; (4): liquid column; (5) biogas flow; (6): activated carbon; (7): FTIR spectrometer; (8): gas chromatograph; (9): sampling valve.

volume of 35 L, with 30 cm inner diameter and a height of 50 cm. The working volume of the digesters was 15 L. Two holes were drilled on the lid of the digesters; one was used to insert thermometer, and the second one was used to place a release tap. Produced biogas could be sampled for chromatographic and infrared analysis purposes through the release tap, and also allowed to determine its volume by the water displacement method, which led the measure of the corresponding cumulative biogas for 8 months, as shown in Fig. 1(4).

The digesters were provided with a side sampling faucet which enabled the determination of the total solids (TS), volatile solids (VS) and pH variations. The feedstock was mixed manually (twice a day for 2 min) using a crank handle.

In order to determine the effect of coffee-pulp/cow-dung co-digestion, two reference digesters were loaded with only cow-dung and only coffee-pulp respectively as indicated below:

- Digester 1: 80 wt% cow-dung and 20 wt% water.
- Digester 2: 80% wt coffee-pulp and 20 wt% water.

Based on the results obtained, using the test digesters for determining the coffee-pulp/cow-dung composition for the optimum methane production, digester 3 was loaded as follows:

- Digester 3: 40 wt% coffee-pulp, 40 wt% cow-dung and 20 wt% water.

In order to obtain necessary heat for the mesophilic digestion conditions, the digesters were left outdoor under direct solar radiation. The digesters were not pretreated with any methanogenic inoculums. Maximum temperatures in between 35 and 45 °C were recorded inside the digesters under a 1000 W m⁻² average solar radiation.

2.3. Analytical methods

The pH of the biomass mixture in the digesters was measured every fortnight drawing the samples from the side faucet, using a Sartorius pH Analyzer (accuracy 0.05). The following analyses were performed for coffee-pulp and cow-dung before using them in the digestion process:

- Total carbon (TC) was determined by the Shimadzu TOC-L analyzer (accuracy 0.5).
- Total Kjeldahl nitrogen (TKN) was measured after Kjeldahl nitrogen digestion using a digestion mixture of H₂SO₄ and CuSO₄.

- Ammonia content of the sample was subsequently detected by an electric conductivity cell, as proposed by R. M. Carlson [30]. Ammonium-nitrogen (NH₄⁺-N) was measured by flow injection analysis after steam distillation into dilute H₂SO₄ [31].
- Total solids (TS) and volatile solids (VS) were determined according to the Mexican Standard Method [32].

The evolution of the percentage of total solids (%TS) and the percentage of volatile solids (%VS) in the digesters were determined twice a month. %TS conversion as a function of digestion time was calculated according to Eq. (1).

$$\%TS \text{ conversion} = \frac{\%TS_{\text{initial}} - \%TS_{\text{time}}}{\%TS_{\text{initial}}} \times 100, \quad (1)$$

where %TS_{initial} is the initial percentage of the total solids and %TS_{time} is the percentage of the total solids after a given digestion time in the digesters. A similar relation (Eq. (2)) was used to determine the %VS conversion with digestion time:

$$\%VS \text{ conversion} = \frac{\%VS_{\text{initial}} - \%VS_{\text{time}}}{\%VS_{\text{initial}}} \times 100. \quad (2)$$

The produced biogas was analyzed by gas chromatography (Shimadzu GC-14B) provided with a thermo-conductivity detector (TCD). The chromatograph used a Chromosorb 2000 column which allowed determining the volume percentages of carbon monoxide (CO), carbon dioxide (CO₂), methane (CH₄), and water (H₂O) in the mixture as a function of digestion time. The temperature of the TCD, the oven and the injector port were 200 °C, 120 °C and 120 °C respectively. N₂ was used as carrier gas at a flow rate of 19 mL min⁻¹. The CH₄% and CO₂% gas volumes were calculated by interpolating the values from the calibration curve obtained with a standard gas consisting of 50 vol.% CH₄, 30 vol.% CO₂ and 20 vol.% He. Biogas samples were analyzed by releasing the gas through the chromatograph automatic injection valve (0.5 mL), as shown in Fig. 1(8). The measurements were performed in duplicate twice a month.

After 4 months of co-digestion, the continuously produced biogas was conducted directly to a 136 mL gas cell (A-136/2-R suitable for qualitative and quantitative infrared absorption measurements of gaseous compounds) attached to a Bruker (Vertex 70) FTIR gas spectrometer. The analysis of biogas composition was performed using the QAssoft-quantitative analysis software (provided by Infrared Analysis Inc.) which allowed determining the quality and quantity of the emitted gases from the digesters. This software contains a spectral library of 270 standard compounds with 1 cm⁻¹ spectral resolution. The spectra permit the computation of concentrations from a sample spectrum without

the need for any calibration. The calibration is inherent in these reference spectra. The program allowed us to detect the presence or the absence of the 270 compounds in the biogas sample one by one.

As required by the QAsoft quantitative analysis method, all the measurements were performed in triplicate and the average values were considered. The volume of each compound given by the analysis software was used to calculate the relative volume of corresponding compound contained in the gas cell (136 mL) using Eq. (3):

$$\% \text{ vol of compound} = \frac{\text{Volume of compound}}{136 \text{ mL}} \times 100. \quad (3)$$

Combustion emissions of the biogas produced from coffee-pulp/cow-dung co-digestion in digester 3 were studied by burning it in a laboratory glass fuel burner (Fig. 2) provided with an external controlled gas flow recirculation system. This process was performed in following steps:

- Biogas flow generated in digester 3 was conducted to the laboratory glass fuel burner (5) at a flow rate of $50 (\pm 1) \text{ mL min}^{-1}$, controlled by valve (3).
- At the same time, a gas feed flow provided by a compression pump (6), consisting of 450 mL min^{-1} of O_2 and 50 mL min^{-1} of N_2 was conducted to the fuel burner (5) at the flow rate of $500 (\pm 1) \text{ mL min}^{-1}$, controlled by valve (4).
- The combustion air-to-fuel ratio (AFR) was calculated considering the mass of the major biogas constituents identified through FTIR analysis (CO_2 , CH_4 , and C_3H_8), following the relation (Eq. (4)) [33]:

$$\text{AFR} = \frac{\text{air mass}}{\text{biogas mass}} = \frac{\text{mass O}_2 + \text{mass N}_2}{\text{mass CO}_2 + \text{mass CH}_4 + \text{mass C}_3\text{H}_8}. \quad (4)$$

The mass of each gas in Eq. (4) was calculated according to Eq. (5) (e.g. for O_2):

$$\text{mass O}_2 = \frac{(\text{O}_2 \text{ flow rate})(\text{O}_2 \text{ molecular mass})}{22,400 \text{ mL min}^{-1}}. \quad (5)$$

The mixture of the biogas and feeding gas was supplied to the fuel burner through an ignition tube and burned. After 10 min of combustion of the gas mixture, the emissions were collected from the fuel burner exhaust and analyzed in a gas cell using Bruker FTIR (Vertex 70) gas spectrometer. The QAsoft-quantitative analysis

software provided with the spectrometer allowed us to detect the presence or the absence of 270 compounds in the biogas sample one by one.

3. Results and discussion

3.1. Estimation of digestion temperature

Table 1 reports the maximum average temperatures measured each month inside the three digesters and the average solar radiation received. Results presented in this table indicate that during the whole digestion period, on average, the reactors received a fixed amount of solar radiation and hence similar amounts of heat. This observation is supported by the maximum temperature values measured inside the digesters which remained rather constant.

Average solar radiation and the temperature attained in the digester 3 in between 8 am and 5 pm during the 4th month of digestion are shown in Fig. 3. The average solar radiance varied in between 0.0 and $\sim 1.3 \text{ kW/m}^2$ every day, and the maximum temperature attained inside the digester was about 48°C (at around mid-noon). Fluctuations in average solar radiance and average temperature (Fig. 3) are due to cloudy weathers at the time of measurements. The daily maximum temperature measured inside digester 3 during the 4th month of digestion is shown in Fig. S2.

3.2. Coffee pulp and cow-dung characteristics

The % C, % N and C/N ratio values estimated for the coffee-pulp and cow-dung are list in Table 2. In this table, it can be observed that the C/N ratio of cow-dung is 5.3, which is too low to meet the nutrients balance requirement of anaerobic microorganisms, however, coffee-pulp showed a higher C/N ratio. Now, it has been shown that the optimum C/N range ratio for anaerobic digestion is in between 25 and 35 [34]. These results suggest that the mixture of coffee-pulp/cow-dung could provide a more appropriate C/N ratio and more balanced nutrients for microorganisms' growth during co-digestion process, thus the mixture coffee-pulp/cow-dung co-digestion might increase the biogas production.

3.3. Estimation of pH, total solids (TS), volatile solids (VS), and CH_4 in biogas

It is well known that biogas generation is a complex biological process, which can be divided in four phases of biomass degradation

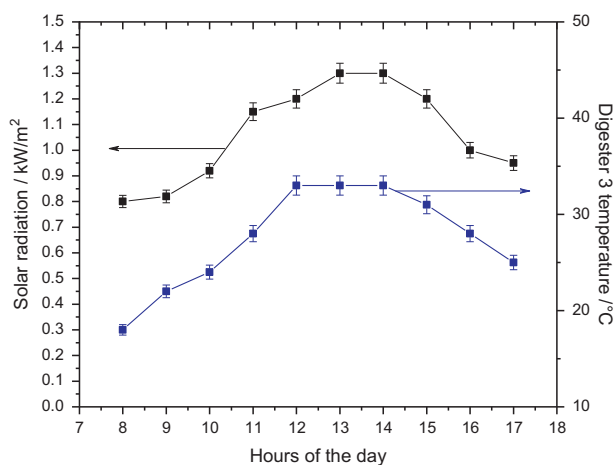


Fig. 2. Schematic layout of the biogas combustion equipment. (1) Digester; (2) thermometer; (3) biogas flow valve; (4) air flow valve; (5) biogas combustor; (6) gas compressor; (7) FTIR spectrometer.

Table 1

Average solar radiation and maximum average temperature measured inside the three digesters.

Digestion time (months)	Average radiation (kW/m ²)	Maximum temperature of the digesters (°C)		
		Coffee-pulp	Cow-dung	Mixture
0	1.022	31	30	35
1	1.026	39	41	40
2	1.031	37	39	37
3	1.033	46	45	44
4	1.022	35	35	33
5	1.005	29	29	28
6	1.000	30	30	29
7	0.996	27	29	29
8	1.020	31	31	35

**Fig. 3.** Variation of average solar radiance and digester (digester 3) temperature in between 8 am and 5 pm during the 4th month of digestion.**Table 2**

Characteristics of coffee-pulp and cow-dung used for digestion and codigestion.

Characteristic	Coffee-pulp	Cow-dung
TS (g/kg)	555.6	89.4
VS (g/kg)	910.9	603.6
wt% C dry basis	45.2	28
wt% N, % dry basis	0.8	5.2
C/N	57.2	5.3
NH ₄ ⁺ -N (g/kg TS)	1.6	12.7

and conversion, namely hydrolysis, acidogenesis, acetogenesis and methanation. The individual phases are carried out by different groups of micro-organisms (bacteria), which partly stand in syntrophic interrelation and place different requirements of the environment [35]. In biogas generation process, polymers in the

biomass are first hydrolyzed and converted into acetic acid and hydrogen. Chanakya et al. [36] have reported that sugars, pectin and hemicelluloses are rapidly hydrolyzed and converted to methanogenic intermediates mainly as volatile fatty acids. Intermediates from acidogenesis are converted to biogas by methanogens through methanogenesis [37].

In Table 3, the initial and final values of pH, %TS, and, %VS estimated in the three digesters are reported. Fig. 4 presents the evolution of pH measured in the mixtures of the three digesters as a function of digestion time. It is interesting to note that despite of different initial pH values, all the three reaction mixtures attained a final pH ~7, suggesting neutral digestion conditions achievement in all the digesters.

The evolution of TS and VS as a function of digestion time determined in the three digesters are presented in Figs. 5 and 6, respectively while the temporal evolution of vol.% methane (CH₄) generated in the biogas of the digesters has been presented in Fig. 7. A chromatogram used for the determination of % methane is shown in Fig. S3.

From Figs. 5–7, the following facts can be observed:

- In digester 1 (containing only cow-dung and water), we can observe high TS and VS conversion rates during the first month of digestion. Consequently, higher vol.% of generated CH₄ was detected in the biogas during this month (Fig. 5). However, during the subsequent months of digestion, the %TS and %VS conversion rates were very slow. These results suggest that cow-dung digestion rate for biogas production is limited by the low bacterial nutrients, which might have been rapidly consumed and finished by an initial high concentration of bacteria during the first month of digestion. As a result of bacterial nutrients depletion, during the subsequent digestion months, the amount of generated methane decreased drastically.
- In digester 2 (containing only coffee-pulp and water) the TS and VS conversion rates were seen to be low during eight months of digestion, suggesting that despite the high initial concentration of nutrients in coffee-pulp, the conditions for bacterial growth in the digester were not adequate. This result suggests that coffee-pulp digestion rate for biogas production is limited by bacterial growth. This assumption is supported by the fact that coffee-pulp contains caffeine, free phenols and tannins, which might be toxic to bacteria [18]. However, it is interesting to note that despite the presence of toxic compounds in coffee-pulp, conversion of TS and VS continue, though with slower rate. Thus a small fraction of the TS and VS might have been degraded by the low quantity of microorganisms probably due to their resistance to these aggressive digestion conditions. As a consequence, the CH₄ evolution with digestion time measured in the biogas emitted from digester 2 (containing coffee-pulp and water) shows a very slow CH₄ production during eight months of digestion. Only 20 vol.% of CH₄ was detected in biogas generated from this digester. After four months of digestion, only a slight increase in CH₄ production was observed, probably due to a slight increase of bacterial growth.

Table 3

Initial and final values (after 8 months of digestion) of pH, TS, and VS determined for coffee-pulp, cow-dung, and the mixture of coffee-pulp/cow-dung digesters.

Contents of the digester	pH		Total solids (TS) (wt%)		Volatile solids (VS) (wt%)	
	Initial	Final	TS _{initial}	TS _{final}	VS _{initial}	VS _{final}
1. Coffee-pulp-water	4.5	7.2	55.56	45.52	91.09	85.26
2. Cow-dung-water	6.5	7.0	8.94	4.55	60.36	42.31
3. Mixture-water	5.4	7.2	35.27	5.45	78.91	8.31

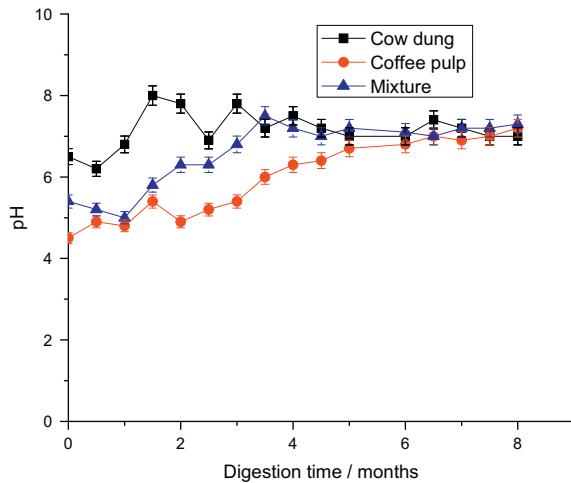


Fig. 4. pH evolution in the three digesters as a function of digestion time.

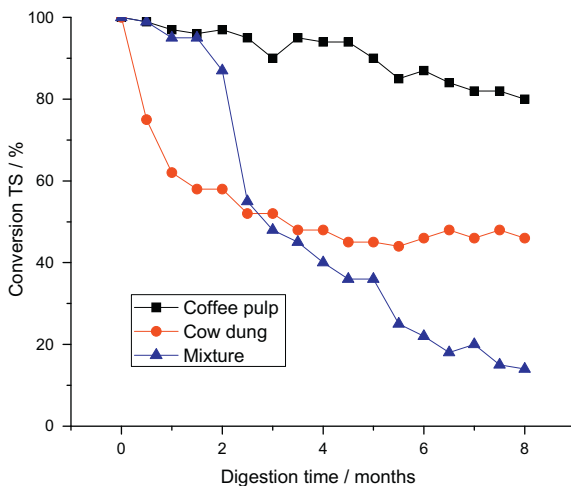


Fig. 5. Evolution of CH_4 (vol.%) in the biogas yield from cattle manure, coffee-pulp-waste and coffee-pulp-waste/cattle manure mixtures as a function of digestion time.

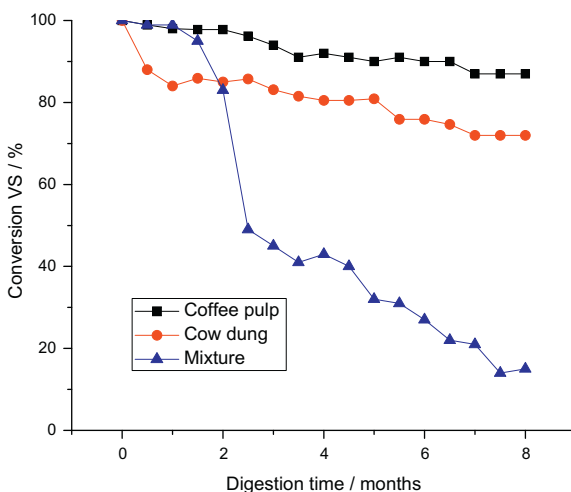


Fig. 6. Evolution of volatile solids conversion (vol.%) as a function of the digestion time for the three digesters.

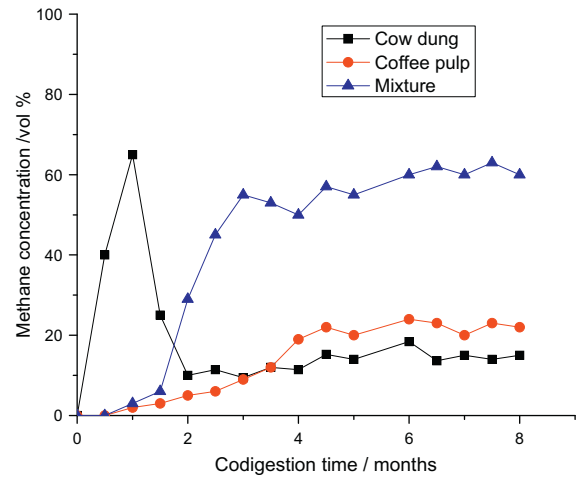


Fig. 7. Evolution of CH_4 (vol.%) in the biogas yield from cattle manure, coffee-pulp-waste and coffee-pulp-waste/cattle manure mixtures as a function of digestion time.

- In digester 3 (containing the coffee-pulp/cow-dung mixture and water), TS and VS conversion rates were low during the first month of digestion, suggesting a delay in bacterial growth in which bacteria present in cow-dung might have adapted to the stressful new conditions originated by the toxic caffeine, free phenols and tannins present in coffee-pulp. Under these stressful conditions, bacterial genetic adaptation might have taken place, resulting probably in a stationary mutation phase which might have led to a strong increase in bacterial population. Accordingly, during this first digestion month, no CH_4 was detected in the biogas emitted from the digester 3.
- However, after this time, the conversion rates of TS and VS increased substantially, probably due to a rapid bacterial growth, resulting in a rapid degradation of the nutrients, and therefore, CH_4 was generated at increased rate. After eight months of digestion, a slight slowdown in the TS and VS conversion rates was observed, suggesting a limiting bacterial growth due to nutrients depletion, resulting in the generation of CH_4 at constant rate.

The results presented above indicate that the co-digestion process was faster than the digestion of coffee-pulp-waste or cow-dung alone. The results are supported further from the results presented in Fig. 8, which shows that the biogas yield from digester 3 is higher in comparison to the same from the digesters 1 or 2. Previous investigations revealed a higher and more sustained biogas production from cow-dung and wastes co-digestion than the biogas produced from cow-dung or wastes alone [38,39]. However, these investigations report a decrease in biogas production after 5 months of co-digestion. It is worth noting that the results presented in this study, showed that coffee-pulp/cow-dung co-digestion generates high amounts of biogas, even after 8 months of co-digestion.

3.4. Biogas composition

The results obtained from the quantitative and qualitative analysis performed by FTIR spectroscopy of the biogas produced after 4 months of digestion in digesters 1–3, are summarized in Tables 4–9. A raw FTIR spectrum used for qualitative and quantitative analysis of the biogas is shown in Fig. S4.

The vol.% of the major components in the biogas yield has been reported in Figs. 9–14 the %volume of major components in the gas

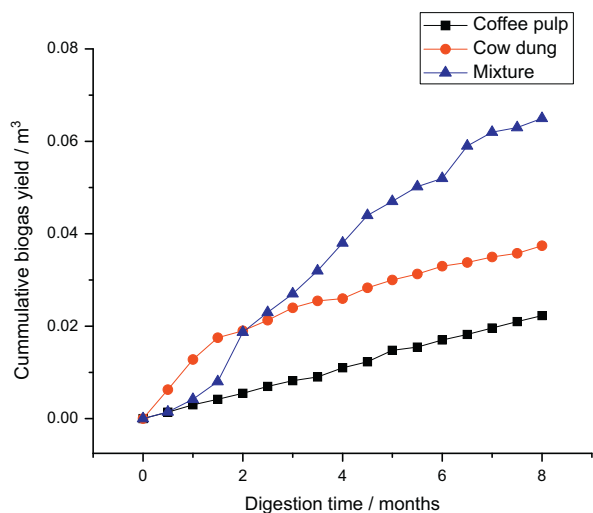


Fig. 8. Cumulative biogas yield from the three digesters during 8 months of digestion.

Table 4

Hydrocarbons contents in biogases generated in Digester 1 (cow dung and water), digester 2 (coffee pulp and water), digester 3 (coffee-pulp/cow-dung and water), and the emissions of biogas combustion from the digester 3.

Hydrocarbons C ₁ through C ₈	Contents (vol.%)			
	Digester 1 (cow-dung)	Digester 2 (coffee-pulp)	Digester 3 (mixture)	Digester 3 (biogas combustion)
Butane	0.71	0	0.09	0
1-Butene	0.31	0.29	0.02	0
Cis-2-Butene	1.01	1.03	0.09	0
Cyclopropane	1.49	0	0.17	0
Ethane	0.13	0.9	0	0
Isobutane	0.54	0	0.05	0
Methane	11.27	22.16	52.48	1.8
Propane	4.51	8.86	19.54	1.7
Propylene	0	0	0	0
3-Methyl-1-Butene	2.33	0.3	0.19	0.1
n-Pentane	0.16	0.14	0	0
2-Pentene	0.92	0	0.15	0
Cyclohexane	0.06	0.01	0	0
Cyclohexene	0.01	0.03	0	0
Dodecane	0.27	0.05	0.02	0
n-Hexane	0.18	0	0.02	0
1-Hexene	1.91	0.25	0.16	0
2-Methyl pentane	0.19	0.1	0	0
3-Methyl pentane	0.91	0.15	0.07	0
n-Octane	0.23	0.05	0.01	0
Ethyl benzene	0	0	0	0

yield has been represented. The results presented in these tables indicate that the rate of production of some of the compounds produced during the digestion of either coffee-pulp or cow-dung vary drastically (increase, decrease or does not emit at all) during the co-digestion of coffee-pulp/cow-dung mixture. In Table 4, the quality of hydrocarbons C₁–C₈ in the biogas generated in the three digesters along with the combustion products of the biogas generated in the digester 3 are presented. From the table, and from Fig. 9, it is clear that besides methane, a high amount of propane is generated in the coffee-pulp/cow-dung digester (digester 3). It is worth noting that lower amounts of these same gases are also generated in digester 1 (containing cow-dung and water) and digester 2 (containing coffee-pulp and water). Presence of propane in the

Table 5

Contents of hydrides, oxides, and peroxides in the biogases generated in Digester 1 (cow-dung and water), Digester 2 (coffee-pulp and water), Digester 3 (coffee-pulp/cow-dung and water) and emissions of biogas combustion from Digester 3.

Hydrides, oxides, peroxides	Contents (vol.%)			
	Digester 1 (cow-dung)	Digester 2 (coffee-pulp)	Digester 3 (mixture)	Digester 3 (biogas combustion)
Arsine	0	0	0	0
Hydrazine	0.01	0.01	0.01	0
Hydrogen chloride	0.02	0.01	0.02	0
Hydrogen iodide	4.45	1.89	6.16	4.23
Pentaborane	0.11	0.09	0	0
Phosphine	0	0	0.01	0
Carbon dioxide	53.28	51.26	7.00	74.56
Carbon Monoxide	1.50	1.54	1.04	7.77
Chlorine dioxide	0	0	0	0
Ethylene oxide	0.18	0	0.15	0
Tetrahydrofuran	0	0	0	0

Table 6

Contents of Ketones, alcohols, aldehydes, and esters in the biogases generated in digester 1 (cow-dung and water), digester 2 (coffee-pulp and water), digester 3 (coffee-pulp/cow-dung and water) and emissions of biogas combustion from the digester 3.

Ketones, alcohols, aldehydes and esters	Contents (vol.%)			
	Digester 1 (cow-dung)	Digester 2 (coffee-pulp)	Digester 3 (mixture)	Digester 3 (biogas combustion)
Acetophenone	0.08	0	0.08	0
2-Butanone	0.02	0.02	0	0
Cyclohexanone	0.58	0.5	0.13	0
Methyl vinyl ketone	0.17	0.15	0.04	0
Allyl alcohol	0.34	0.34	0	0
Diacetone alcohol	0.87	0.74	0.13	0
Isobutanol	0.11	0.11	0	0
Isopropanol	0.08	0.07	0	0
Acrolein	0.035	0.03	0	0
Benzaldehyde	0	0.08	0	0
Crotonaldehyde	0.06	0.06	0	0
n-Butyl acetate	0.02	0	0.04	0
2-Ethoxy ethyl acetate	0.01	0	0.03	0
Ethyl acrylate	0.01	0	0.18	0
Ethyl butyrate	0.11	0.09	0.02	0
Ethyl propionate	0	0	0.01	0
Hexyl Acetate	0.01	0	0.02	0
Isobutyl acetate	0.08	0	0.08	0
Methyl acetate	0.02	0.02	0	0
Vinyl acetate	0.58	0.5	0.13	0

generated biogas should contribute greatly to the total combustion heat due to its individual high combustion heat value [40].

The contents of hydrides, oxides and peroxides detected in the biogas are reported in Table 5, and Fig. 10. The high amounts of hydrogen iodide present in the three digesters can be attributed to the high amounts of this compound present naturally in the soil of the fields [41]. As the coffee-pulp and cow-dung studied in this investigation were collected from a region located at about 100 km from the Gulf of Mexico, iodine might have been transferred from the ocean to the atmosphere and adsorbed by the soils where coffee plants and forage crops (used for cattle feeding) are cultivated [42]. These plants might have integrated iodide ions into their cells naturally as it has been proposed by Shininaga et al. [43] to explain the transfer of iodine from soil to cereal grains.

Table 7

Nitrogen compounds contents in the biogases generated in digester 1 (cow-dung and water), digester 2 (coffee-pulp and water), digester 3 (coffee-pulp/cow-dung and water) and emissions of biogas combustion from the digester 3.

Nitrogenous compounds	Contents (vol.%)			
	Digester 1 (cow-dung)	Digester 2 (coffee-pulp)	Digester 3 (mixture)	Digester 3 (biogas combustion)
Ammonia	1.45	0.98	1.20	0
Dinitrogen Pentoxide	0.02	0	0.01	0
Isoocyanic acid	1.26	0.44	0.84	0.50
Nitric acid	0	0	0.01	0
Nitrogen dioxide	0	0	0	2.03
Nitrous acid	0.01	0	0.01	0
Diethyl amine	0	0.06	0.06	0.03
N,N-Dimethyl acetamide	0.01	0.15	0.16	0
Dimethyl amine	0	0.56	0.55	0
N,N-Dimethyl formamide	0	0	0	0
Methyl isocyanate	0.09	0	0.06	0
Nitroethane	0.025	0.13	0.15	0

Table 6 and Fig. 11 show the contents of ketones, alcohols, aldehydes, and esters generated in different digesters. Presence of some ketones, very low amounts of alcohols and volatile esters in the digesters 1 and 2 could be observed.

The contents of nitrogen containing compounds in the biogases generated in the three digesters are presented in Table 7 and Fig. 12. We can see that isocyanic acid and methyl isocyanate are present in the biogas generated in all three digesters. Other nitrogen compounds such as nitrous acid and dinitrogen pentoxide were also found in very low amounts. It is well known that in animals, isocyanic acid is the part of a chemical pathway associated

with cataracts and inflammation that can lead to cardiovascular disease and rheumatoid arthritis [44].

Sulfur containing compounds detected in the biogas yields from the three digesters are reported in Table 8 and Fig. 13. From these results, it can be observed that 3 vol.% of hydrogen sulfide (H₂S) is present in the biogas yields of the Digester 1 (cow-dung and water) and Digester 3 (coffee-pulp/cow-dung and water). Other sulfur containing compounds such as sulfur monochloride were also detected. The presence of H₂S in the atmosphere may cause serious eye effects [45]. In a study of the effects of repeated H₂S exposure on learning and memory in the adult rat by Partlo et al. [46] showed that H₂S may impair learning by increasing the animals' susceptibility to interference from irrelevant stimuli. Moreover, these authors established that the prefrontal cortex could be a potential target site of H₂S.

It is worth noting that sulfur dioxide (SO₂) was not detected in the biogas yields probably due to the anaerobic digestion conditions (absence of oxygen in the digester). The H₂S produced during digestion could not produce SO₂ as would be expected in aerobic condition following the equation:



The halogenated compounds detected in the biogas yields of the three digesters are reported in Table 9 and in Fig. 14. As can be seen, high amounts of bromomethane are present in the biogases generated in all three digesters. Presence of such compound in the generated biogases is not surprising considering that fumigants used during the growth of coffee beans and forage crops contain high amounts of this compound and other halogenated compounds [47–51]. The dangerous nature of bromomethane has been demonstrated in numerous literature reports, highlighting its fatal poisoning effects [50]. Reuzel et al. [51] have reported that the exposure to 90 ppm bromomethane induces lesions in heart (thrombi, myocardial degeneration), hyperkeratosis in the oesophagus, and fore stomach. Moreover, it has been shown that the emission of methyl bromide is environmentally detrimental because of its reaction with stratospheric ozone [52].

Table 8

Estimation of sulfur containing compounds in the biogases generated in the digester 1 (cow-dung and water), digester 2 (coffee-pulp and water), digester 3 (coffee-pulp/cow-dung and water) and emissions of biogas combustion from the digester 3.

Sulfur-containing compounds	Contents (vol.%)			
	Digester 1 (cow-dung)	Digester 2 (coffee-pulp)	Digester 3 (mixture)	Digester 3 (biogas combustion)
Diethyl sulfate	0	0.03	0.03	0
Hydrogen sulfide	3.01	0	2.12	0.1
Sulfur monochloride	0.24	0	0.23	0
Tetrahydrothiophene	0.06	0.02	0.09	0
Thionyl chloride	0.02	0	0.028	0
Sulfur dioxide	0	0	0	3.05

Table 9

Contents of halogenated compounds in the biogases generated in digester 1 (cow-dung and water), digester 2 (coffee-pulp and water), digester 3 (coffee-pulp/cow-dung and water) and emissions of biogas combustion from the digester 3.

Halogenated compounds	Contents (vol.%)			
	Digester 1 (cow dung)	Digester 2 (Coffee pulp)	Digester 3 (mixture)	Digester 3 (biogas combustion)
Bromochloromethane	0.02	0.01	0.01	0
Bromomethane	4.27	5.2	5.5	3.0
Dibromomethane	0.01	0	0	0
Bromoethane	0.1	0	0.13	0
Chloroethane	0.06	0.05	0	0
1,1 Dichloroethane	0	0	0.01	0
1,2-Dichlorotetrafluoroethane	0	0.05	0.01	0
Trans-1,2 Dichloroethylene	0.02	0.02	0	0
Perfluorobutane	0	0	0	0
Perfluoropentane	0	0	0	0
Vinyl bromide	0.01	0	0	3.0

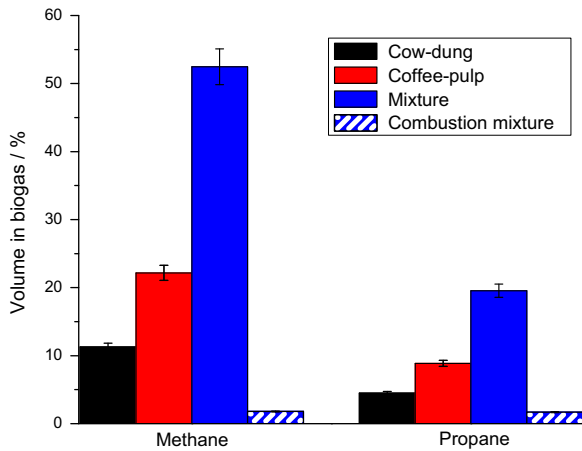


Fig. 9. Contents of methane and propane detected in the biogas yield by FTIR spectroscopy after 4 months of digestion in the three digesters and in the combustion emissions of biogas generated from the digester 3.

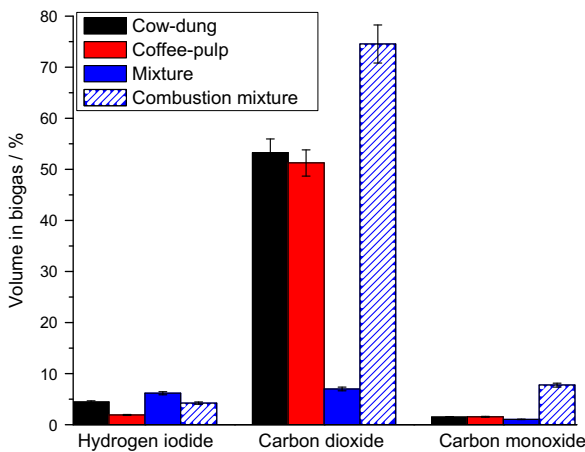


Fig. 10. Contents of hydrides, oxides and peroxides detected in the biogas yield by FTIR spectroscopy, after 4 months of digestion in the three digesters and in the combustion emissions of biogas generated from the digester 3.

3.5. Biogas combustion emissions

While the combustion of biogas, like natural gas, produces carbon dioxide (CO_2), a greenhouse gas, the carbon in biogas comes from plant that fixed this carbon from atmospheric CO_2 . Thus, biogas production is carbon-neutral and does not add to greenhouse gas emissions. Further, any consumption of fossil fuels replaced by biogas will lower CO_2 , carbon monoxide (CO), hydrocarbons (HC), nitrogen oxides (NO_x) and particulate matter (PM) emissions [53]. However, as far as our knowledge goes, the complete analysis of biogas combustion emissions has not been reported.

The results presented in Tables 4–9 showed that co-digestion of coffee-pulp/cow-dung mixture generate biogas containing valuable combustible gases (methane, propane). However, hazardous compounds such as isocyanic acid, methyl bromide and H_2S are also generated. These gases are harmful to human and animal health, thus their emission into the atmosphere must be prevented.

It is obvious that if biogas is to be produced from programmed digesters, it can be used as a fuel for feeding internal combustion engines or combustors-superheaters/boilers. Thus, its direct emission into the atmosphere is improbable. Therefore, it is absolutely compulsory to analyze the emissions from the biogas combustion, which may be different from the initial biogas components.

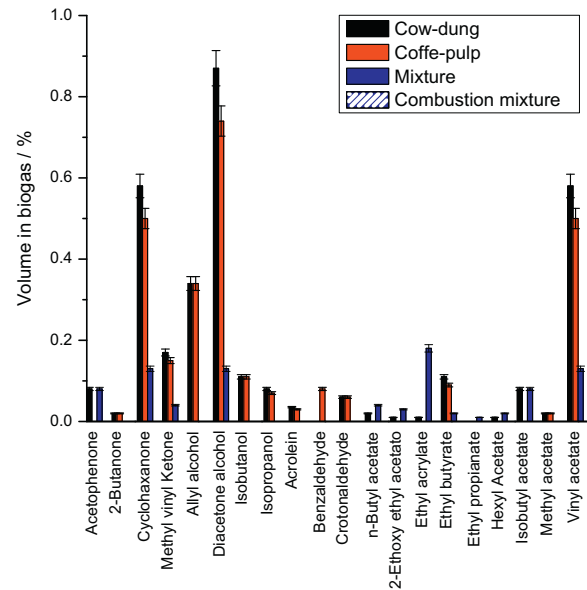


Fig. 11. Contents of ketones, alcohols, aldehydes and esters detected in the biogas yield by FTIR spectroscopy after 4 months of digestion in the three digesters and in the combustion emissions of biogas generated from the digester 3.

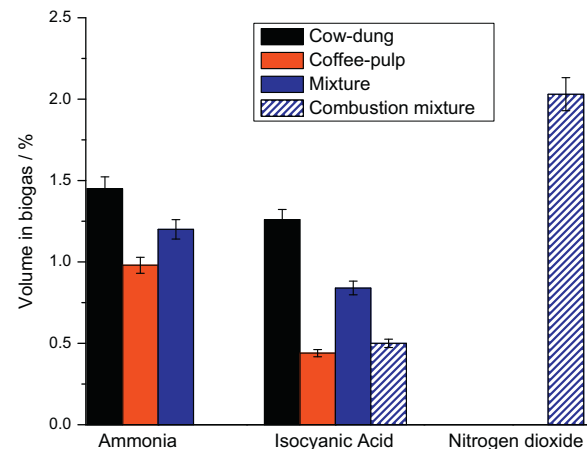


Fig. 12. Contents of nitrogen containing compounds detected in the biogas yield by FTIR spectroscopy, after 4 months of digestion in the three digesters and in the combustion emissions of biogas generated from the digester 3.

In order to determine the emissions generated from biogas combustion, the biogas produced from digester 3 (coffee-pulp/cow-dung and water) was burned in air in the gas combustor described in Fig. 2. A value of 19.55 of the AFR of our air/biogas mixture indicates that combustion took place in lean conditions [33]. This ratio was calculated according to Eq. (5) using the mass values of the different gases reported in Table 10.

Combustion emissions were analyzed by FTIR spectroscopy, and the results are presented in Tables 4–9 and in Figs. 9–14. From these results, the following facts can be observed:

- A strong decrease in hydrocarbon contents was observed during biogas combustion (Table 4 and Fig. 9). However, CH_4 was still detected in the exhaust. According to the IPCC 2001, the global warming potential of methane over the 100 years in comparison to carbon dioxide is 23 times higher [54].
- Hazardous hydrogen iodide and carbon monoxide were still detected in the biogas combustion emissions (Table 5 and Fig. 10).

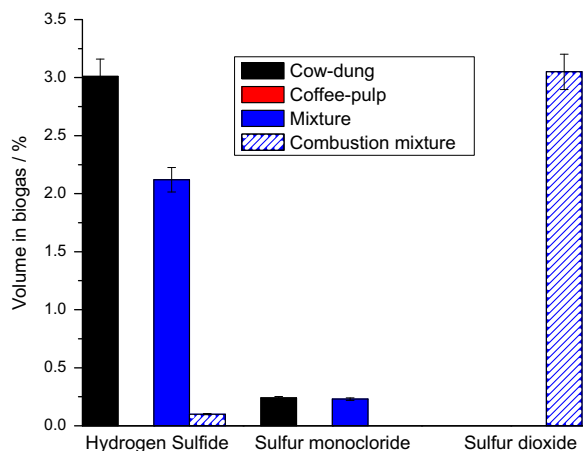


Fig. 13. Contents of sulfur containing compounds detected in the biogas yield by FTIR spectroscopy, after 4 months of digestion in the three digesters and in the combustion emissions of biogas generated from the digester 3.

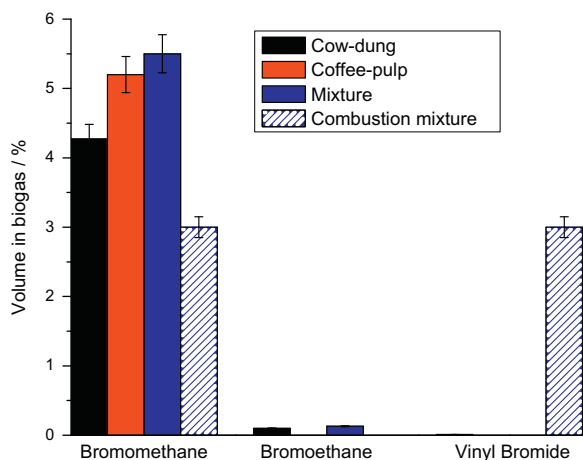


Fig. 14. Contents of halogenated compounds detected in the biogas yield by FTIR spectroscopy, after 4 months of digestion in the three digesters and in the combustion emissions of biogas generated from the digester 3.

Table 10

Mass of the different gases in 1 L of air/biogas mixture used for combustion and calculating air to fuel ratio (AFR).

Gas	Mass of the gas (g/L)
O ₂	1.167
N ₂	0.112
CH ₄	0.020
C ₃ H ₈	0.034
CO ₂	0.010

- No traces of ketones, alcohols, aldehydes and esters were detected after biogas combustion (Table 6 and Fig. 11).
- Methyl isocyanate was not detected (Table 7 and Fig. 12) due to its complete oxidation biogas combustion. However, traces of nitrogen dioxide and isocyanic acid were detected after biogas combustion.
- H₂S was eliminated almost completely by the biogas combustion process. However, sulfur dioxide was produced due to H₂S oxidation during biogas lean combustion (Table 8 and Fig. 13).

- Bromomethane was partially oxidized during biogas combustion (Table 9 and Fig. 14), probably generating Br₂.

Results presented revealed that biogas combustion emissions contain: CH₄, C₃H₈, CO, SO₂, HI, and probably also Br₂ which are strongly harmful to human and animal health, and to our natural environment. According to the IPCC 2001, to avoid global warming, if biogas is to be used as a fuel in engines, convenient catalytic converters must be developed to put at their exhausts to prevent the emission of these molecules to the atmosphere.

4. Conclusions

Co-digestion of coffee-pulp/cow-dung generates biogas with high content of methane at least for 8 months. It has been demonstrated that collected coffee-pulp mixed with cow-dung in appropriate proportion can act as a valuable biomass for the production of biogas containing high amounts of valuable combustion gases such as methane and propane.

The results of gas chromatography and FTIR analysis of the biogas generated by the co-digestion of coffee-pulp/cow-dung mixture under solar radiation revealed the presence of compounds such as isocyanic acid and bromomethane which are hazardous for the environment and animal health. However, some of these hazardous components get dissociated during the combustion of biogas. Presence of CH₄, C₃H₈, CO, and SO₂ in the emission of biogas combustion indicates that the combustion-postcombustion technology should be upgraded to prevent these emissions if the biogas produced by coffee-pulp/cow-dung co-digestion is to be used as fuel.

Acknowledgements

The authors acknowledge the financial supports extended by, VIEP-BUAP (Grants # Nat 36/2012, # Nat 38/2013, Mega Energy & VIEP/EXC/137/2012).

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.enconman.2013.07.017>.

References

- [1] Simpson-Holley M, Higson A, Evans G. Bring on the biorefinery. *J Chem Eng* 2007;163:46–59.
- [2] Fantozzi F, Buratti C. Biogas production from different substrates in an experimental Continuously Stirred Tank Reactor anaerobic digester. *Bioresour Technol* 2009;100:5783–9.
- [3] Tekin A, Coskun R, Dalgic A. Biogas production from olive pomace. *Resour Conserv Recycl* 2000;30:301–13.
- [4] Fantozzi F, Buratti C. Anaerobic digestion of mechanically treated OFMSW: experimental data on biogas/methane production and residues characterization. *Bioresour Technol* 2011;102:8885–92.
- [5] Bouallagui H, Touhami Y, Cheikh RB, Hamdi M. Bioreactor performance in anaerobic digestion of fruit and vegetables waste. *Process Biochem* 2005;40:989–95.
- [6] Gallert C, Henning A, Winter J. Scale-up of anaerobic digestion of the biowaste fraction from domestic wastes. *Water Res* 2003;37:1433–41.
- [7] Hamdi M. Anaerobic digestion of olive mill wastewater. *Process Biochem* 1996;31:105–10.
- [8] Lopes WS, Leite VD, Prasad S. Influence of inoculum on performance of anaerobic reactors for treating municipal solid waste. *Bioresour Technol* 2004;94:261–6.
- [9] Deublein D, Steinhauser A. Biogas from waste and renewable sources: an introduction. Weinheim: WILEY-VCH Verlag GmbH & Co. KGaA; 2008.
- [10] Brand D, Pandey A, Roussos S, Socol CR. Biological detoxification of coffee husk by filamentous fungi using a solid state fermentation system. *Enzyme Microb Technol* 2000;26:127–30.

- [11] Pandey A, Soccol CR, Nigam P, Brand D, Mohan R, Roussos S. Biotechnological potential of coffee pulp and coffee husk for bioprocesses. *J Biochem Eng* 2000;6:153–8.
- [12] Mussatto SI, Ercilia SEM, Martins S, Jose AT. Production, composition, and application of coffee and its industrial residues. *Food Bioprocess Technol* 2011;4:661–72.
- [13] Franca AS, Oliviera IS, Ferreira ME. Kinetics and equilibrium studies of methylene blue adsorption by spent coffee grounds. *Desalination* 2009;249:267–72.
- [14] Madahava Naidu M, Vijayanada P, Usha Devi A, Vijayalakshmi MR, Ramalakshmi K. Utilization of coffee by-products in food industry, preparation of jam using coffee pulp as raw material, Placrosym XIV. Plantation crops research and development in the new millennium; 2004. p. 201–203.
- [15] Adams MR, Dougan J. Biological management of coffee processing wastes. *Trop Sci* 1981;23:177.
- [16] Boopathy R, Mariappan M. Coffee pulp: a potential source of energy. *J Coffee Res* 1984;14:108–10.
- [17] Boopathy R, Mariappan M, Sunderasan BB. The carbon to nitrogen ratio and methane production of coffee pulp. *J Coffee Res* 1986;16:47–50.
- [18] Fan L, Soccol AT, Pandey A, Soccol CR. Cultivation of pleurotus mushroom on Brazilian coffee husk and its effect on caffeine and tannic acid. *Micol Aplicada Int* 2003;15:15–21.
- [19] Gaime-Perraud I, Roussos S, Martínez-Carrera D. Natural microorganisms from coffee pulp. *Micol Neotrop Apl* 1993;6:95–103.
- [20] Jayachandra C, Venugopal KA, Appaiah A. Utilization of phototoxic agro waste. Coffee husk through pretreatment by ascomycetes fungi *Mycotypha* for biomethanation. *Energy Sustain Develop* 2011;15:104–8.
- [21] Husted S. Seasonal-variation in methane emission from stored slurry and solid manures. *J Environ Quality* 1994;23:585–92.
- [22] Moller HB, Sommer SG, Ahring BK. Biological degradation and greenhouse gas emissions during pre-storage of liquid animal manure. *J Environ Quality* 2004;33:27–36.
- [23] Moller HB, Sommer SG, Ahring BK. Methane productivity of manure, straw and solid fractions of manure. *Biomass Bioenergy* 2004;26:485–95.
- [24] Chanakya HN, Venkatasubramanyan R, Modak J. Fermentation and methanogenic characteristics of leaf biomass formation, Bangalore, India: Technical reports, ASTRA. Indian Institute of Science; 1997. p. 1–19.
- [25] Mshandete A, Kivaisi A, Rubindamayugi M, Mattiasson B. Anaerobic batch co-digestion of sisal pulp and fish wastes. *Biores Technol* 2004;95:19–24.
- [26] Parawira W, Murto M, Zvauya R, Mattiasson B. Anaerobic batch digestion of solid potato waste alone and in combination with sugar beet leaves. *Renew Energy* 2004;29:1811–23.
- [27] Mata-Alvarez J, Mace S, Llabres P. Anaerobic digestion of organic solid wastes: an overview of research achievements and perspectives. *Biores Technol* 2000;74:3–16.
- [28] Callaghan FJ, Wase DAJ, Thayanithy K, Forster CF. Continuous co-digestion of cattle slurry with fruit and vegetable wastes and chicken manure. *Biomass Bioenergy* 2002;27:71–7.
- [29] Misi SN, Forster CF. Batch co-digestion of multi-component agro-wastes. *Bioresour Technol* 2001;80:19–28.
- [30] Carlson RM. Automated separation and conductimetric determination of ammonia and dissolved carbon dioxide. *Anal Chem* 1978;50:1528–31.
- [31] Switala K. Determination of ammonia by flow injection analysis. *Quik Chem Method* 10-107-06-1-A. Lachat instruments, Milwaukee, WI, USA; 1999.
- [32] Mexican Official Standard: NOM-AA-34-1976, ISO 14000; 1976.
- [33] Yunus C, Michael B. Thermodynamics: an engineering approach. 5th ed., McGraw Hill; 2006.
- [34] Zhang R, Zhang Z. Biogasification of rice straw with an anaerobic-phased solids digester system. *Bioresour Technol* 1999;8:235–45.
- [35] Deublein D, Steinhauser A. Biogas from waste and renewable sources: an introduction. Weinheim: WILEY-VCH Verlag GmbH and Co. KGaA; 2008.
- [36] Chanakya HN, Ganguli NK, Anand V, Jagadish KS. Performance and characteristics of a phase biogas fermenter. *J Energy Sustain Develop* 1995;1:43–6.
- [37] Vishwanath P, Devi SS, Nand K. Anaerobic digestion of fruit processing waste for biogas production. *Bioresour Technol* 1992;40:43–8.
- [38] Hartmann H, Ahring BK. Anaerobic digestion of the organic fraction of municipal solid waste: influence of co-digestion with manure. *Water Res* 2005;39:1543–52.
- [39] Macias-Corral M, Samani Z, Hanson A. Anaerobic digestion of municipal solid waste and agricultural waste and the effect of co-digestion with dairy cow manure. *Bioresour Technol* 2008;99:8288–93.
- [40] Perry RH, Gree DW. Perry's chemical engineers' handbook. 7th ed. Mc Graw Hill; 1997.
- [41] Muramadsu Y, Yoshida S, Uchida S, Hasebe A. Iodine desorption from rice paddy soil. *Water, Air Soil Pollut* 1994;86:359–71.
- [42] Dai JL, Zhang M, Hu QH, Huang YZ, Wang RQ, Zhu YG. Adsorption and desorption of iodine by various Chinese soils: II. Iodide and iodate. *Geoderma* 2009;153:130–5.
- [43] Shinonaga T, Gerzabek MH, Strobi F, Muramatzu Y. Transfer of iodine from soil to cereal grains in agricultural areas of Austria. *Sci Total Environ* 2001;267:33–40.
- [44] Chen K, Mackie JC, Kennedy EM. Toxic pollutants emitted from thermal decomposition of phthalimide compounds. *J Hazard Mater* 2011;187:407–12.
- [45] Stanek J, Gift J, Woodall G. Hydrogen sulfide: integrative analysis of acute toxicity data for estimating human health risk. *Encyclop Environ Health*, p. 124–139; 2011.
- [46] Partlo LA, Sainsbury RS, Roth SH. Effects of repeated hydrogen sulphide exposure on learning and memory in the adult rat. *NeuroToxicol* 2001;22:177–89.
- [47] Thompson RH. A review of the properties and usage of methyl bromide as a fumigant. *J Stored Prod Res* 1966;1:353–76.
- [48] Samtani JB, Aiwa HA, Webwe JB, Browne GT, Klose S, Hunzie J, et al. Evaluation of non-fumigant alternatives to methyl bromide for weed control and crop yield in California strawberries (*Fragaria ananassa* L.). *Crop Protect* 2011;30:45–51.
- [49] Banks HJ, Pinkerton A. Bromine containing residues resulting from fumigation of grain with methyl bromide-carbon dioxide mixtures. *J Stored Prod Res* 1987;23:105–13.
- [50] Von Oettingen WF. The halogenated aliphatic, olefinic, cyclic, aromatic and aliphatic-aromatic hydrocarbons, including the halogenated insecticides, their toxicity and potential dangers. *Publ Hlth Serv Publs, Wash* 1955;414: 1–430.
- [51] Reuzel PGJ, Dreef-van der Meulen HC, Hollanders VMH, Kuper CF, Feron VJ. Chronic inhalation toxicity and carcinogenicity study of methyl bromide in wistar rats. *Food Ahem Toxicol* 1991;29:31–9.
- [52] Gan J, Megonnell NE, Yates SR. Adsorption and catalytic decomposition of methyl bromide and methyl iodide on activated carbons. *Atmosph Environ* 2001;35:941–7.
- [53] Biogas as vehicle fuel: a European overview. Trendsetter report no. 2003:3. Stockholm; October 2003.
- [54] Demirbas A, Ozturk T, Demirbas MF. Recovery of energy and chemicals from carbonaceous materials. *J Energy Sourc A* 2006;28:1473–82.