

ANAEROBIC DIGESTION OF WASTEWATER FROM COFFEE AND CHEMICAL ANALYSIS OF BIOGAS PRODUCED USING GAS CHROMATOGRAPHY: QUANTIFICATION OF METHANE, AND POTENTIAL ENERGY GAS EXCHANGER

DIGESTÃO ANAERÓBIA DA ÁGUA RESIDUÁRIA DO CAFÉ E ANÁLISE QUÍMICA DO BIOGÁS PRODUZIDO UTILIZANDO CROMATOGRAFIA GASOSA: QUANTIFICAÇÃO DO METANO, POTENCIAL ENERGÉTICO E PERMUTABILIDADE GASOSA

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ABSTRACT: Methane is the main constituent of biogas, being responsible for its calorific value. This work objective was to present the analysis of methane concentration in the biogas originated from anaerobic treatment system of wastewater of coffee wet processing (CWP) at laboratory scale, using coffee coconut. The methane concentration were performed by gas-solid chromatography (GSC) analyses. The system was composed of a column Restek RT-Q-PLOT, with the stage sets, the divinyl-benzene, nitrogen as mobile phase and a flame ionization detector (FID). The results of the concentration of methane in the biogas ranged from 48.60 to 68.14%. The upper and lower calorific values were 25,654 and 23,777 kJ.m⁻³, respectively. For interchangeability, obtained a Wobbe number of 7,851 kcal.m⁻³, resulting in their interchangeability with piped gas (city gas).

KEYWORDS: Bioenergy. Methane. Anaerobiosis calorific power. Renewable energy.

INTRODUCTION

Analyses of the chemical composition of the biogas by gas chromatography has several advantages over other methods and has high resolving power and good speed of separation, and allows continuous monitoring of the effluent in the column, the exact quantitative measurement and repeatability and reproducibility analysis with automation of the analytical procedure and data processing (Prado and Campos, 2008; Campos et al., 2010). Columns Rt-Q-PLOT are suitable for analysis of hydrocarbons such as methane and solvents such as alcohols, and showed good stability up to 310°C, excellent permeability, providing low pressure variations, suitable for ambient temperatures and allowing rapid analysis with peaks well defined (PRADO et al., 2010).

The calorific value of a fuel can be experimentally determined using a calorimeter, or may be estimated theoretically by means of stoichiometric calculations, using the Dulong hypothesis, based on the calorific values of the elementary components of a fuel. The substitutability of a combustible gas is defined when two gases are compared in terms of heat production,

at the same pressure, or when they have the same Wobbe number. By knowledge of the interchangeability of gases, makes up the replacement of one fuel by another in a given case. Since the proportion of methane in the biogas obtained from the treatment of CWP, its variation occurs according to the levels of biodegradable organic matter present in this liquid effluent and the type of treatment systems used. Dinsdale et al. (1997), treating wastewater from soluble coffee using UASB bench, obtained biogas with an average percentage of methane of 62.3%. Campos et al. (2010), in laboratory tests with wastewater from anaerobic digestion of coffee wastewater, found 56% to 63% methane in biogas. Clarke and Macrae (1987) report that it is possible to produce 0.067 m³ biogas.kg⁻¹ of coffee pulp, with approximate 70% of methane and 30% of carbon dioxide by anaerobic processes, with 90% efficiency in removal of organic matter.

Bruno and Oliveira (2008) used an anaerobic system of two separate phases for biogas production from coffee pulp juice and found a methane percentage ranging from 69 to 89% in the reactor 1 and from 52 to 73% in the reactor 2.

This study aimed at determining the concentration of methane in the biogas from the anaerobic treatment of wastewater from coffee wet process (CWP) using gas chromatography analysis. Biogas analysis was collected from a UASB reactor operated at mesophilic temperature. As already mentioned the quality of biogas varies depending on the physical-chemical characteristics of the effluent, and thus we evaluated the interference of these factors on the concentration of biogas. In this research were also performed theoretical calculations of the lower calorific value or net calorific value (NCV), and higher calorific value or Gross calorific value (GCV), also the interchangeability of biogas via the Wobbe number.

MATERIAL AND METHODS

Sampling of biogas

The biogas used for the analysis was assembled from an experiment in the Laboratory of Water Analysis of Engineering Department (DEG) at the Federal University of Lavras (UFLA), where the liquid effluent originated from wet coffee process, underwent anaerobic treatment.

The treatment system consisted of a acidification and equalization tank (AET), an upflow anaerobic sludge blanket (UASB), a facultative aerated pond (FAP), an equalization tank, a gas tank, two metering pumps and a heating system. The equalization tank had the function of

maintaining the level of biogas in the UASB. The gas produced by the three-phase separator (TPS), passed through the equalization tank and was subsequently sent to the gas tank, which had the task of accumulating the biogas. Silicone hoses were used to conduct the biogas, since they are flexible and allow a good seal. The biogas sampling was withdrawn in the output of the three-phase separator of the UASB reactor, using collection device and an apparatus consisting of two points and a vacuum tube. The apparatus of two nozzles was mounted with a hypodermic needle and an intravenous catheter 40/12 16, glued to the ends in opposite directions, with which it is pierced with one end in the silicone hose and with the other end to the vacuum tube. The vacuum tube was used brand BD Vacutainer®, siliconized glass, without additive, nominal volume of 10 mL. The collection of biogas was performed until the pressure inside the tube would stabilize the pressure in the reactor. The tube was weighed before and after collection, to certify the presence of biogas inside.

Characterization of gas chromatography

For the analysis of methane concentration in biogas was used gas-solid chromatography (GSC). Analyses were performed at the Central Analytical Chemistry and Exploration (CAPQ), Department of Chemistry (DC), Federal University of Lavras (UFLA). The flow chart of the system used can be seen in Figure 1.

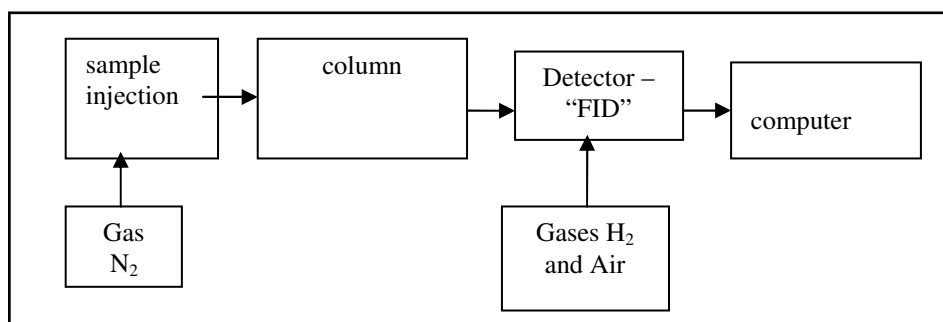


Figure 1. Flow chart of gas chromatography

A gas chromatograph Varian Chrompack PC-3800 coupled to a microcomputer was applied in this research. For carrier gas and make-up gas was used nitrogen. The column used was a column Restek Rt-Q-PLOT, 0.53 mm internal diameter (id) and 15 m long, built in fused silica, having as the solid phase-divinyl benzene (DVB), 20 µm film thickness (df). For sample injection, a gas-tight syringe type, brand SGE 1MR-GT, 1 mL, with divisions of 0.02 mL was used. The flame ionization

detector (FID) was used, powered by hydrogen and synthetic air. The software used was the Varian Star 4.5 # 1, Burger, (2004).

The nitrogen passed through filters to remove possible contamination by ambient air and humidity. The filters used were a Chrompack 17 971 and 17 970.

Calibration of the method of analysis

The chromatographic method of analysis used was calibrated using a standard methane having the following characteristics: methane 2.5 Cil G, 99.50% mol / mol of purity, of White Martins.

The sample of the pattern of methane gas was transferred from the cylinder to a reservoir sampler rubber, and was subsequently collected using a gas-tight syringe. A vacuum pump was used to expel completely the rubber tank before filling with methane, to ensure the absence of any contaminant. A calibration curve was performed for each day of analysis. Calibration curves utilized were linear equations of the of methane standard concentrations (mg L^{-1}) for the area obtained in the chromatogram, according to Equation 1.

$$Y = ax + b \quad \text{Equation (1)}$$

Where:

Y= methane concentration (mg L^{-1});

a = angular coefficient;

x = area;

b = interception point on the y-axis.

In determining the standard of methane concentration (Y) in each standard volume injected, the following calculations were used (ABBOTT; VAN NESS, 1992):

a) through Equation 2, known as the equation of ideal gas, the number of moles (n) for each test portion has been determined:

$$P.V = n. R. T \quad \text{Equation (2)}$$

Where:

Po = atmospheric pressure at STP (101,325.0 Pa);

M = average molar mass of air (0.02890 kg mol⁻¹);

g = gravitational constant (9.80665 m s⁻²);

z = altitude site (922.12 m);

R = universal gas constant (8.3144126 J K⁻¹mol⁻¹);

T = temperature (K).

The pressure has been corrected using the barometric formula, according to Equation

Where:

$$P = P_0 \cdot e^{\frac{-Mgz}{RT}} \quad \text{Equation (3)}$$

P = local conditions pressure(Pa);

P_o = atmospheric pressure at standard temperature and pressure (101325.0 Pa);

M_{ar}= average molar mass of air (0.02890 kg mol⁻¹);

g = gravitational constant (9,80665 m s⁻²);

z = local elevation (922,12 m);

R = universal gas constant (8,3144126 J K⁻¹mol⁻¹);
T = temperature (K).

The temperature was measured using a mercury thermometer, range -10 to 110°C, with divisions of 1°C, according to the method 2559 B (APHA, 2005). The local altitude of 922.12 m, was determined through March 3045U IBGE, located in front of the building UFLA (IBGE, 2005).

a) From Equation 4, the mass of methane in taking the test pattern was calculated:

$$M = n. M \quad \text{Equation (4)}$$

where,

m = mass of methane (g);

n = number of moles (moles);

M = molecular weight of methane (16.0430 g).

b) From Equation 5, the concentration of methane in taking the test pattern was calculated:

$$C = \frac{m}{V} \quad \text{Equation (5)}$$

where,

C = concentration of methane (mg L^{-1});

m = mass of methane (mg);

V = volume of test-taking pattern (mL).

Calculations of the concentration of methane in biogas

The concentration of methane in biogas was obtained by analysis of samples, in triplicate, intest-taking volume corresponding to 0.3 mL. It was used to calculate the concentration of methane, the following motion of calculations:

a) from the area in the chromatogram obtained, the concentration (C₁) of methane in mg L^{-1} through the linear equation of the calibration method (Equation 1) was calculated;

b) from C₁, was calculated the C₂ concentration by volume of methane per volume of biogas ($\text{L CH}_4 - \text{L biogas}^{-1}$), using Equation 2 (the ideal gas equation);

c) from C₂, the C₃ concentration in methane percentage in biogas was calculated, using Equation 6:

$$C_3 = C_2 \cdot 100 \quad \text{Equation (6)}$$

where,

C₃ = concentration of methane (%);

C₂ = concentration of methane ($\text{L CH}_4 - \text{L biogas}^{-1}$).

Theoretical calculations of the calorific values of biogas

The theoretical calculations of the lower calorific value or net calorific value (NCV), and higher calorific value or gross calorific value (GCV), were performed by means of the Dulong hypothesis, according to the following motion calculations:

- the elemental composition of methane (CH₄), defines the percentage of carbon (C) and hydrogen (H₂) in the formula;
- using the calorific values of elementary C and H₂, defined the lower and higher calorific values of methane;
- the result of the concentration of methane in the biogas, defined the lower and higher calorific values of biogas.

The gas calorific value is the amount of heat released in complete combustion of one unit mass of fuel. The lower or net calorific value (NCV) is the amount of heat released in combustion minus the amount lost to vaporization of water in the process (RUSSOMANO, 1987). The calculations of the calorific values of biogas, the following values were considered:

- Atomic weight: carbon, 12.01115 g; hydrogen, 1.00797 g;
- Methane molecular weight: 16.04303 g;

- Calorific elementary: carbon, 8133 kcal kg⁻¹, hydrogen, 34.500 kcal kg⁻¹;
- Loss of heat by the vaporization of water: 539.74 kcal kg⁻¹ water (RUSSOMANO, 1987).

Calculations of the interchangeability of biogas

The interchangeability of biogas was obtained in relation to natural gas, piped gas (city gas) and LPG (liquefied petroleum gas), using the number of Wobbe (W) according to Equation 7.

$$W = \frac{GCV}{\sqrt{\rho}} \quad \text{Equation (7)}$$

where:

W = number of Wobbe (kcal m⁻³);

GCV = gross calorific value (kcal m⁻³);

ρ = density of gas.

Physico-chemical analysis of coffee wastewater

The frequency and methodology used for the physical and chemical parameters analyzed in the coffee wastewater for correlation with the quality of biogas are presented in Table 1.

Table 1. Physico-chemical parameters, output frequency analysis and methodologies used for monitoring the quality of coffee wastewater

Physical-Chemical Parameters	Frequency	Referencies
pH	Daily	APHA, AWWA, WPCF (2005)
Total (TA), partial (PA) and intermediated alkalinity (IA)	3 x week	Ripley et al. (1986), Jenkins et. al (1983)
Chemical Oxygen Demand (COD)	3 x week	APHA, AWWA, WPCF (2005)
Biochemical Oxygen Demand (BOD ₅)	Weekly	APHA, AWWA, WPCF (2005). Wincley methodology
Total (TS), Fix (FS) and Volatile (VS) Solids	Weekly	APHA, AWWA, WPCF (2005)
Total Kjeldahl nitrogen (TKN)	2 x month	APHA, AWWA, WPCF (2005)
Total phosphorus (P)	2 x month	APHA, AWWA, WPCF (2005)
Total acidity (AVT)	3 x week	Potenciometric method (NaOH 0,02N)
Phenolic compounds	2 x month	Méthod 5550B- APHA, AWWA, WPCF (2005). Using extraction with methanol, standardized curve with tartaric acid and read in spectrophotometer.

The operational parameters applied and system performance studied are presented in the Prado and Campos (2008); Prado and Campos (2010) and Campos et al. (2010).

The theoretical metanogênica activity (TMA) presented in the results and discussion was

calculated using the concepts and methodology presented in Silva et al. (2011a) and Silva et al. (2011b).

Statistics

For calculations, the Sisvar software, version 4.6 (Build 63) and the software Excel for

Windows XP was used. The data entered in Excel files were converted into dBase IV and processed by Sisvar for statistical analysis:

- Measures of location: mean (x), maximum (max) min (minimum);
- Measures of variability: standard deviation (s) and coefficient of variation (cv);
- Measures of comparison and decision making: analysis of variance (ANOVA) and means were compared by the test of Student-Newman-Keuls (SNK).

RESULTS AND DISCUSSION

Results of the calibration method

Sampling for biogas analysis was performed during 86 days with intervals of two days. The total samples analysis performed was 41. The values obtained can be seen in Tables 1, 2 and 3. From the data in Table 3, was obtained the linear equation, $y = 0.0000089167x - 0.595738807$.

Table 1. Parameters of the chromatography

Chromatography Parameter	Value
Column temperature (°C)	50
Run time (min)	4
Injector temperature (°C)	220
Split rate in the injector	10
Detector temperature (°C)	250
Detector range (g sec ⁻¹)	1 x 10 ⁻¹²
Linear velocity of gases (cm.s ⁻¹)	51
Flow of N ₂ in the column (mL min ⁻¹)	6,2
Total flow in the column (mL min ⁻¹)	72,4
Total pression of N ₂ (psi)	85
Pressure of H ₂ (psi)	60
Pressure of synthetic air (psi)	85
Pressure in the column (psi)	1,2

Table 2. Environmental Parameters

Environmental Parameters	Value
Environmental temperature (K)	293.95
High (m)	922.12
Column pressure (atm.)	0.899

Table 3. Parameters of stander curve.

Stand volume (mL)	Parâmetros da curva padrão	
	Concentration (mg L ⁻¹)	Chromatogram area
0.060	3.5679247277	453,182
0.100	5.9465412128	723,841
0.140	8.3251576979	1,053,060
0.180	10.7037741830	1,271,816
0.220	13.0823906681	1,496,392
0.300	17.8396236383	2,071,600

The pressure values set to the N₂, H₂ and synthetic air were regulated to maintain the flow within specification: for N₂, flow rates from 0.5 to

Analysis results of methane

10 mL m⁻¹ column and 20-25 mL m⁻¹ as make-up gas, for the H₂ flow rate of 35 to 40 mL m⁻¹ and the synthetic air, flow rate 350-400 mL m⁻¹.

The analysis results in average concentrations of methane can be seen in Table 4.

The average concentration in percentage had a minimum value of 48.60%, a maximum value of 68.14% and an average of 57.19%. The standard deviation (s) was 4.41%, demonstrating a low variability around the mean.

The treatment process was divided into periods and sub-periods depending on the pH and alkalinity, the addition of NaOH in the CWP was

according to Table 5. A sampling of the biogas was also divided into periods and sub-periods, followed by the same criterion.

In Tables 6 and 7 are the analysis of variance and comparison of the average concentrations of methane by the test of Student-Newman-Keuls (SNK) for the periods and sub-periods.

Table 4. Average concentrations of methane

Sample	Average concentrations of methane		
	(mg L ⁻¹)	(LCH ₄ L ⁻¹ biogas)	(%)
1	384.17	0.645	64.47
2	372.00	0.624	62.43
3	382.67	0.650	65.04
4	349.65	0.594	59.43
5	351.56	0.598	59.61
6	312.19	0.531	53.35
7	319.23	0.541	54.09
8	343.01	0.581	58.12
9	345.32	0.587	58.69
10	330.32	0.560	55.97
11	330.73	0.562	56.21
12	338.59	0.575	57.55
13	331.66	0.562	56.20
14	335.38	0.568	56.83
15	308.01	0.514	51.41
16	310.57	0.518	51.84
17	376.42	0.628	62.83
18	369.86	0.617	61.73
19	367.96	0.614	61.42
20	408.25	0.681	68.14
21	339.25	0.571	57.14
22	361.79	0.609	60.94
23	309.70	0.522	52.16
24	343.21	0.578	57.81
25	316.55	0.528	52.84
26	352.04	0.588	58.76
27	333.40	0.556	55.65
28	335.53	0.563	56.35
29	346.96	0.583	58.26
30	372.72	0.626	62.59
31	347.42	0.583	58.34
32	353.38	0.594	59.43
33	337.83	0.566	56.56
34	344.86	0.579	57.91
35	337.14	0.564	56.44
36	290.32	0.486	48.60
37	290.40	0.486	48.62
38	314.47	0.526	52.65
39	299.66	0.502	50.17
40	332.63	0.557	55.69
41	314.29	0.526	52.62

Table 5. Division of periods and sub-periods of treatment of (CWP)

Period	Sub-period	Total of days	Addition of NaOH	NaOH (%)	Local of addition
IV	A	21	yes	10.0	AET
IV	B	27	no	-----	-----
V	A	14	no	-----	-----
V	B	18	yes	10.0	AET
VI	A	06	yes	10.0	AET
VI	B	15	yes	2.5	

UASB, with pump

Table 6. Analysis of variance of the concentration of methane during periods and sub-periods

FV	GL	SQ	QM	Fc
Periods and sub-periods	5	1,120.55	224.11	19.52*
Experimental error	117	1,343.16	11.48	
Total	122	2,463.71		

CV = 5.92%; FV: Varying sources examined in the analysis of variance; GL: degrees of freedom; SQ: Sum of squares; QM: Mean Square; Fc: calculated value for the test statistic F.

Table 7. Average concentrations of methane in the periods and sub-periods

Period and sub-period	Methane (%)
IV-A	63.98 a
IV-B	57.22 b
V-A	55.14 b
V-B	62.03 a
VI-A	55.39 b
VI-B	55.33 b

Means followed by the same letter do not differ by SNK test at 5% probability.

It can be observed the significant differences at 5% probability in methane concentration between periods. The highest values of average concentrations of methane were obtained in periods IV-A and VB, which are significantly different from the results of other periods. The low CV shows a good precision in the analysis.

One can compare the average concentrations of methane in the periods and sub-periods with the mean values of pollutant removal efficiencies and analysis obtained during the treatment of ARC, according to Tables 8, 9, 10, 11, 12 and 13.

The coefficient of simple correlation (r) was 0.399 for CH_4/COD ; to CH_4/BOD_5 was 0.163 and for CH_4/N , was -0.633, for CH_4/P was -0.386 and for $\text{CH}_4/\text{compounds phenolic}$ were - 0.321. The values obtained show a low correlation. The correlation CH_4/N showed the greatest value, however, still down 0.80 and its negative sign indicates that the variation of methane concentration is opposite to the variation of removal efficiency in the reactor.

The simple correlation coefficient (r) for CH_4/N , was 0.158 and for CH_4/P was -0.404 and for $\text{CH}_4/\text{phenolic compounds}$, was -0.549. The low

values obtained for correlations with N and P, show a low correlation between the concentration of methane with concentrations of N and P. For the correlation with the phenolic compounds, it appears that there is a negative correlation median, indicating that the methane concentration increases in the opposite direction to the concentration of phenolics.

The variation in concentration of phenolic compounds in the CWP caused negative interference in methane concentration, as these compounds are toxic to bacteria, interfering with the metabolism of them.

The removal efficiencies of COD, BOD_5 , N and P in all periods, showed no significant correlations in the variation of the concentration of methane in the biogas from the CWP.

Considering the I-UASB, the simple correlation coefficient (r) for CH_4/pH was 0.504 and for CH_4/temp , was 0.673, indicating the existence of a positive correlation median, where the concentration of methane is correlated with the increase of pH and temperature.

Whereas E-UASB, the simple correlation coefficient (r) for CH_4/pH was 0.355 and for

CH₄/temp, was 0.619, indicating the existence of a positive correlation with respect to the median temperature, which increased methane concentration is correlated with the increasing of temperature. For pH, the correlation was very low.

The simple correlation coefficient (r) was 0.317 for CH₄/PA; for CH₄/IA was -0.344, for CH₄/TA was -0.090, for CH₄/IA/PA was -0.623 and, for CH₄/AVT, was -0.743, indicating low correlation with respect to PA, IA and TA. There is

a negative median correlation coefficient of methane with the IA/PA and the acidity, which increases the concentration of methane, is related to the decrease of IA/PA and acidity.

The simple correlation coefficient (r) was -0.182 for CH₄/PA; to CH₄/IA was -0.313, for CH₄/TA was -0.253, for CH₄/IA/PA was -0.336 and for CH₄/acidity, was -0.433, indicating low correlations with the variables in E-UASB and methane concentration.

Table 8. Methane (%) and pollutants removal efficiency (%) in the UASB reactor

Period and sub-period	CH ₄	COD	BOD	N	P	Phenolic compounds
IV-A	63.98	76.09	75.50	-23.35	15.76	19.54
IV-B	57.22	82.17	86.63	32.51	-7.43	22.04
V-A	55.14	72.04	73.99	-0.79	37.16	-3.75
V-B	62.03	77.21	78.17	1.89	20.66	1.78
VI-A	55.39	70.54	71.95	---	27.38	---
VI-B	55.33	74.43	73.25	13.37	30.43	27.75

Table 9. Methane (%) and nitrogen, phosphorus and phenolic compounds (mg L⁻¹) in the influent (I-UASB)

Period e sub-period	CH ₄	N	P	Phenolic compounds
IV-A	63.98	19.27	186.17	84.55
IV-B	57.22	23.43	200.83	49.78
V-A	55.14	19.00	351.17	158.86
V-B	62.03	18.43	239.58	100.81
-A	55.39	*	162.50	*
VI-B	55.33	14.52	162.92	381.80

* There was no analysis in this sub-period.

Table 10. Methane (%) and pH and temperature (°C) in the influent (I-UASB) and effluent (E-UASB)

Period and sub-period	CH ₄	pH	Temp	pH	Temp
		I-UASB	I-UASB	E-UASB	E-UASB
IV-A	63.98	6.93	26.47	7.34	26.59
IV-B	57.22	5.35	25.01	6.73	24.78
V-A	55.14	4.79	23.34	6.29	22.10
V-B	62.03	6.34	23.22	6.97	21.46
VI-A	55.39	6.50	22.50	7.34	20.90
VI-B	55.33	6.56	22.82	7.19	20.31

Table 11. Methane (%) Ripley and acidity and alkalinity (mg L⁻¹ of CaCO₃) in the I-UASB

Period and sub-period	CH ₄	PA	IA	TA	IA/PA	AVT
IV-A	63.98	431.30	485.87	917.17	1.3	118.01
IV-B	57.22	0.00	492.16	492.16	∞	209.14
V-A	55.14	36.47	308.88	345.35	3.8	248.71
V-B	62.03	175.31	576.86	752.17	3.6	101.75
VI-A	55.39	340.07	917.35	1,257.42	2.7	168.39
VI-B	55.33	356.03	1,005.11	1,361.15	3.8	154.55

Table 12. Methane (%) Ripley and acidity and alkalinity (mg LCaCO₃⁻¹) in E-UASB

Period and sub-period	CH ₄	PA	IA	TA	IA/PA	AVT
IV-A	63.98	752.16	321.04	1,073.20	0,4	76.36
IV-B	57.22	604.88	286.98	891.86	0,5	92.13
V-A	55.14	317.88	256.16	574.04	1,2	113.84
V-B	62.03	460.89	315.44	776.34	0,7	50.18
VI-A	55.39	1,048.76	366.39	1,415.15	0,4	49.39
VI-B	55.33	922.67	675.00	1,597.67	0,8	100.01

Table 13. Methane (%) and lateral solids (mg L⁻¹) in the UASB

Período e sub-period	CH ₄	TS	TFS	TVS
IV-A	63.98	26,729	10,646	16,083
IV-B	57.22	32,467	10,600	21,777
V-A	55.14	48,927	14,952	33,975
V-B	62.03	44,228	12,971	31,257
VI-A	55.39	*	*	*
VI-B	55.33	50,021	12,863	37,157

* There was no analysis in this sub-period.

The pH, acidity and alkalinity are directly related (Pereira et al. 2009). It was found that the highest concentrations of methane in the biogas were obtained during periods when the pH was as close to neutrality (7.00) and the acidity was lower, resulting in a ratio IA/PA minor. It is evident, therefore, the importance of adding NaOH to increase the alkalinity PA, contributing to a lower value of IA/PA. The alkalinity is due to PA that ensures the bicarbonate buffer in the reactor, a condition of utmost importance to maintaining good

microbial activity in the reactor, with a satisfactory production of methane.

The simple correlation coefficient (r) was -0.660 for CH₄/ST; to CH₄/STF was -0.520 and, for CH₄/TVS; was -0.667, indicating medians, negative correlations, in which the concentration of methane was opposed to the increase of biomass in reactor.

The values of the concentration of methane and theoretical methanogenic activity (TMA) of biomass, can be seen in Table 14.

Table 14. Methane (%) and TMA (m³CH₄ kg⁻¹TVS d⁻¹) in the UASB

Period e sub-period	CH ₄	TMA
IV-A	63.98	0.051
IV-B	57.22	0.073
V-A	55.14	0.061
V-B	62.03	0.049
VI-A	55.39	0.099
VI-B	55.33	0.167

The simple correlation coefficient (r) for CH₄/TMA was -0.601, indicating a negative correlation median, where the concentration of methane was opposed to the increase in TMA. This demonstrates that the increase of methane production did not necessarily imply increasing the percentage of this component in biogas, which occurred concomitant increase of other components of biogas, like CO₂, H₂S and other gases. One must consider that:

- During periods IV-A and V-B, it was obtained the highest values of methane concentration. During these periods, one can verify that with the addition of NaOH in the CWP, the pH in the I-UASB remained with values closer to neutrality, the ratio IA/PA was the lowest obtained in both influent and effluent of the UASB, and acidity had the lowest values;

- During periods V-B and VI-B were also adding NaOH, but from the V period, due to the

increased loading, the pipes began clogging varying the flow.

The temperature was maintained within the mesophilic range throughout the treatment process and there was a good removal efficiency of COD and BOD₅ in all periods.

The lowest concentration of methane were obtained from the VI period and may be related to the occurrence of low pH, high values IA/PA and frequent variations in discharge, resulting from blockage. In this period, the concentration of phenolic compounds in the CWP was higher than in

previous periods, which may have interfered with the metabolism of anaerobic bacteria.

Results of theoretical calculations of the calorific values

For the calculations of lower calorific value or net calorific value (NCV), and higher calorific value or gross calorific value (GCV), it was considered the concentration of methane in the biogas from 68.14%, with a density of 0.61 kg.m⁻³. The values of GCV and NCV of the biogas can be seen in Table 15.

Table 15. Calorific values of biogas

Calorific values	Kcal kg ⁻¹	Kcal m ⁻³	kJ m ⁻³	kWh m ⁻³
GCV	10,051.41	6,131.36	25,654.23	7.11
NCV	9,315.85	5,682.67	23,776.86	6.59

It was considered: 1J = 0.2390 cal = 2.773 x 10⁻⁷ kWh. The values obtained are close to the reference values of mean of 23,380 kJ m⁻³ (6.5 kWh m⁻³) for the biogas from urban sewage, with 70% methane, and 21,610 kJ m⁻³ for biogas (CASSINI, 2003; STAFFORD et al. 1980).

Calculation results of interchangeability

For the calculations of interchangeability through the Wobbe number (W), considered the GCV of the gases. The values obtained are shown in Table 16.

Table 16. Calculating the number of Wobbe

Fuel	GCV (kcal m ⁻³)	Density (kg m ⁻³)	W (kcal m ⁻³)
LPG	26,860	1.77	20,189.42
Natural gas	9,850	0.64	11,945.19
Pipe gas	4,700	0.57	6,225.17
CWP Biogas	6,131.36	0.61	7,850.65

The results have shown that it is not feasible, energetically, in the same proportion, the substitution of LPG or natural gas by biogas from the CWP, but is feasible with respect to piped gas. However, the biogas from the CWP can be used as additional gas in cases where using LPG and natural gas.

The significant results of the NCV and GCV of the biogas, their interchangeability and the concentration of methane, demonstrating the feasibility of the treatment of CWP in UASB reactor and its energy use in agro-industrial properties of coffee. Biogas can be used in various stages of post-harvest processing of coffee as a supplementary energy source, using its thermal energy and the possibility of mixing it with another fuel gas for heating the air in the drying process of product.

The increasing production and profitability of farms, need conserving energy. One of important actions that contribute to energy conservation would be developing ways to reduce losses in raw materials and energy utilization of waste, and thus an additional source of energy, such as the

exploitation of biogas from CWP. One should also take into consideration that the treatment of CWP and the use of biogas contributes to the preservation of natural resources (soil and water) and the reduction of environmental pollution (soil, water and atmosphere), both by treatment of the CWP as by reducing the emission of methane into the atmosphere.

In general, the results stood close to the values referenced in the literature, may be concluded that the production of biogas from the treatment of CWP in UASB reactor is a viable alternative to the use of residues from coffee processing, contributing to energy conservation and the preservation of natural resources.

CONCLUSIONS

The parameters that influence the changes in concentrations of methane in the biogas were temperature, pH, acidity and concentration of phenolic compounds in the CWP. Temperature variations with a magnitude of 8.9 at full term,

correlated positively with the concentration of methane, which increased with increasing temperature, even if in all periods it was maintained within the mesophilic range.

Should take into account also the negative interference of variations in flow, caused by blockage of the system and shock loads and wash-outs occurred during the increased concentrations of the flows.

There is a need for operating the reactor with a systematic control of the parameters that are directly linked to biomass in the reactor, such as temperature, pH, alkalinity and acidity and other physical-chemical parameters of operation of the reactor, as the flow and loads, avoiding shock loads

and scans so that they obtain best values of methane concentration. However, the results of methane concentration in biogas demonstrated to be close to the theoretical framework and are consistent.

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RESUMO: O metano é o principal constituinte do biogás, sendo o responsável pelo seu poder calorífico. Neste trabalho, são apresentadas as análises da concentração de metano no biogás produzido a partir do tratamento das águas residuárias do processamento por via úmida do café (ARC) em sistema de tratamento anaeróbico em escala de laboratório, sendo utilizado o café coco para a produção destas ARC. As análises foram realizadas por cromatografia gás-sólido (CGS), sendo o sistema composto de uma coluna Restek RT-Q-PLOT, tendo como fase fixa, o divinil-benzeno; do nitrogênio como fase móvel e um detector de ionização de chama (DIC). Os resultados da concentração de metano no biogás variaram de 48,60 a 68,14 %, sendo estas variações obtidas em função dos parâmetros do processo de tratamento. Os poderes caloríficos superior e inferior foram de 25.654 e 23.777 kJ.m⁻³, respectivamente. Para a permutabilidade, obteve-se um número de Wobbe de 7.851 kcal.m⁻³, resultando na sua permutabilidade com o gás canalizado (gás da cidade).

PALAVRAS-CHAVE: Bioenergia. Metano. Anaerobiose. Poder calorífico. Energia renovável.

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