MATHEMATICAL MODELING OF METHANOGENESIS

Iuliana ROGOVEANU RADOSAVLEVICI[1], Dan Niculae ROBESCU[2]

The mathematical modeling of a process, irrespectively of its nature (physical, chemical, thermal, biochemical), is an important step necessary to understand it and to use it in a judicious way. Methanogenesis is a biological process by which anaerobic microorganisms convert the sludge coming from wastewater treatment plants that contain dangerous chemical and bacteriological load in sterile sludge, which can be discharged in the environment with any danger for flora and fauna.

Keywords: methanogenesis, microorganisms, mathematical modeling

1. Introduction

The empirical analysis of the anaerobic digestion of the sludge resulted from the wastewater treatment plants was proved insufficient for increasing the process efficiency (measured by the quantity of resulted biogas), and therefore the construction, calibration and validation of a mathematical model was necessary in order to describe the relationships between the microorganism population involved in the anaerobic process and various variables of the digestion plant (volume, retention time, response time).

By using the simulation program called Stoat for the wastewater treatment plant operation, the dynamics of the methane production was thus obtained, further exported as an input of a software implemented in Matlab able to derive a mathematical model of the dynamics of the anaerobic digestion (i.e. methane production) of the sludge coming from a wastewater treatment plant

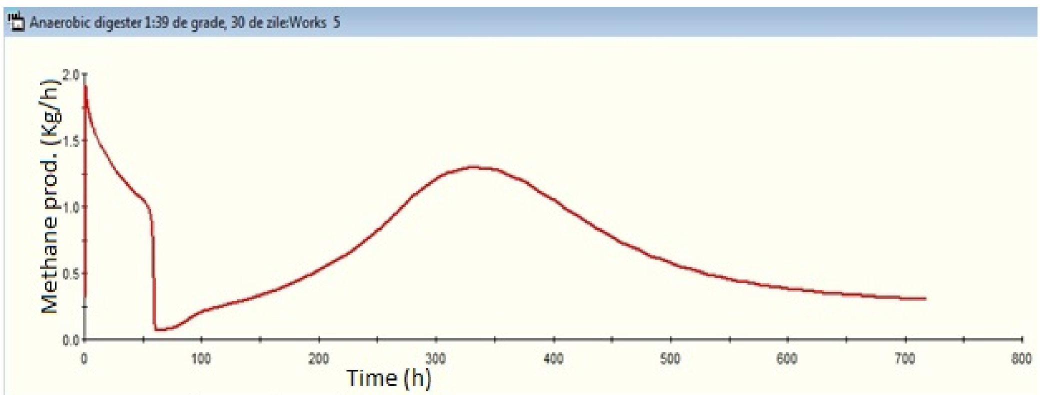
2. Paper contents

Based on the variation curves obtained by using the simulation program Stoat and an algorithm created in Matlab, a function describing the methanogenesis process and the methane content in the tank was thus obtained.

Therefore, there were performed simulations of the methane tank at three different temperatures (of the mesophilic, i.e. 35°C, 37°C, respectively 39^{o}C) for a

[1] Ph.D. student, Department of Hydraulics, Hydraulical Machinery and Environmental EngineeringUniversity POLITEHNICA of Bucharest, Romania, e-mail: rad_iu@yahoo.com
[2] Professor, Department of Hydraulics, Hydraulical Machinery and Environmental EngineeringUniversity POLITEHNICA of Bucharest, Romania

running period of 30 days, using the same organic load of influent sludge (I considered organic load that which in some previous simulations achieved highest production of methane).
Methanogenesis occurs when two processes compete, one being acetoclastic methanogenesis and the other one being hydrogenophilic methanogenesis. These two are not completely distinct, having "portions" that overlap, and therefore the function describing the entire process is obtained by summing the two different functions, whose coefficients were calculated based on data from the conducted simulations. The production of methane is shown in Fig. 1 with the digester set at a temperature of 37°C and the anaerobic process simulation set to an interval of 30 days.



	Methane production (kg/h)	
Mean	0.7	
Minimum	0.1	
Maximum	1.9	

Fig. 1. The production of methane, to 37 ° C, 30 days after the operation of the methane tank

We can see the variation of the curve shape for the production of methane (considered as a mass flow in kg / h) for the considered case. It is noted that it cannot be represented as a single function, so I proposed dividing the curve into two parts: from baseline to t1f = 63 h representing hydrogenophile methanogenesis and from t_{2i} = 64 h until the end (t_{2f} = 720 h) representing acetoclastic methanogenesis. The results that Stoat program shows(Table 18) were exported and, based on their chart it was drawn a polynomial function of degree 8, which describes the time dependence and the production of methane by hydrogenotrophic mechanism. Coefficients p_1, p_2 to p_8 are contributions of all species of hydrogenotrophic bacteria that contribute to the achievement of anaerobic fermentation of the methane tank sludge and p_9 is a coefficient that takes into account temperature and was calculated for temperature t= 37°C.

The mathematical model which best overlaps the curve in Fig. 2 is a polynomial function of degree 8 in the form:

$$F_1(x_1) = p_1{\cdot}x_1^8+p_2{\cdot}x_1^7+p_3{\cdot}x_1^6+p_4{\cdot}x_1^5+p_5{\cdot}x_1^4+p_6{\cdot}x_1^3+p_7{\cdot}x_1^2+p_8{\cdot}x_1+p_9 \quad (1)$$

where x_1 is the time and has values in the range 0-63 h and the model coefficients (with 95% confidence limit) has the values:

p_1 = -0.3531 (-1.953, 1.847)
p_2 = -0.3742 (-1.762, 1.013)
p_3 = 1.06008 (-6.45, 6.571)
p_4 = 0.7251 (-3.419, 4.869)
p_5 = -0.76372 (-7.106, 7.234)
p_6 = -0.4198 (-4.219, 3.379)
p_7 = 0.228 (-2.678, 2.723)
p_8 = -0.1796 (-1.185, 0.8256)
p_9 = 1.183 (0.913, 1.453)
Goodness of fit: SSE: 0.6019, R-square: 0.8887, Adjusted R-square: 0.833
RMSE: 0.194

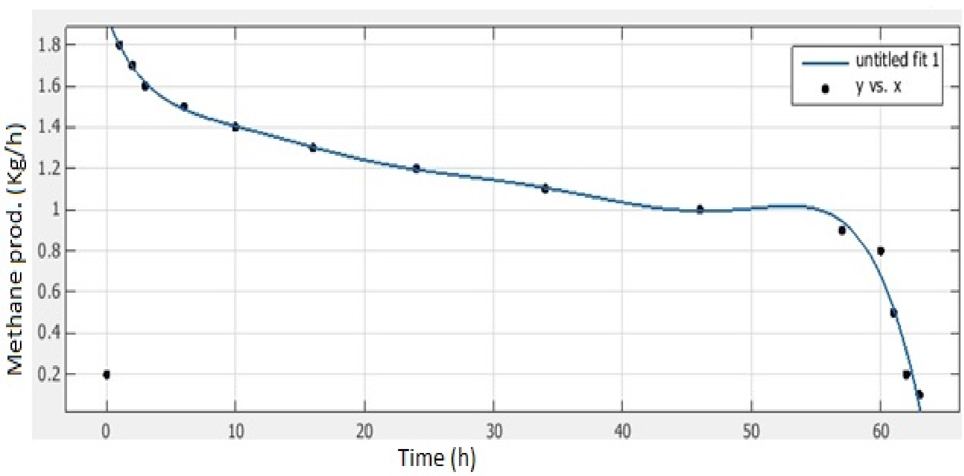


Fig. 2. Production of methane in hydrogenotrophic methanogenesis at a temperature of 37°C

For the second part of the curve in Fig. 3 there has been proposed a rational type function, of the form:

$$F_2(x_2) = (p_{10}{\cdot}x_2^4 + p_{11}{\cdot}x_2^3 + p_{12}{\cdot}x_2^2 + p_{13}{\cdot}x_2 + p_{14}) /(x_2^2 + q_1{\cdot}x + q_2) \quad (2)$$

where x_2 is the time and takes values in the range 64-719 h and the model coefficients (with 95% confidence limit) has the values:

p_{10} = -0.02515 (-0.07794, 0.02764)
p_{11} = 0.01462 (-0.04042, 0.06966)
p_{12} = 0.1784 (0.006223, 0.3505)
p_{13} = 0.239 (0.1016, 0.3764)
p_{14} = 0.5471 (0.3763, 0.7179)
q_1 = 0.7103 (0.5475, 0.8731)
q_2 = 0.4912 (0.337, 0.6455)
Goodness of fit: SSE: 0.08041, R-square: 0.9847, Adjusted R-square: 0.9823, RMSE: 0.046

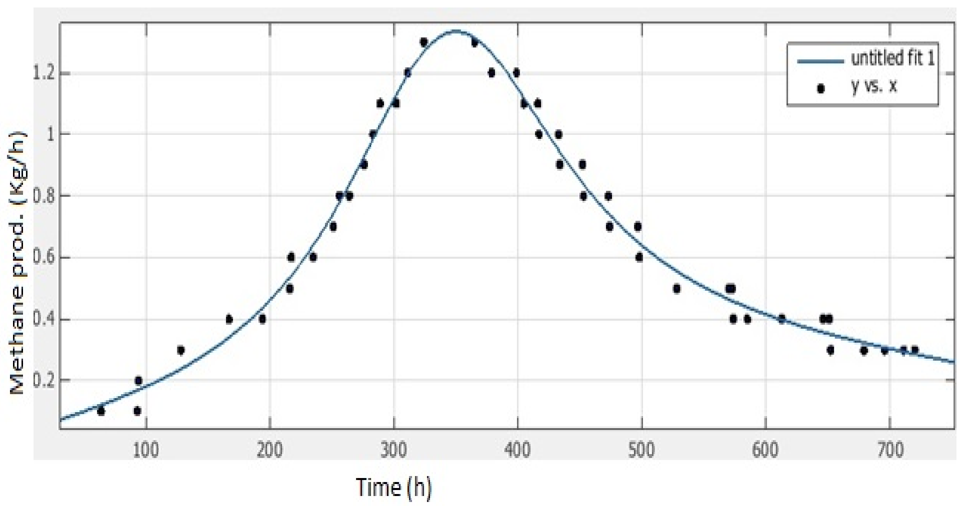


Fig. 3. Production of methane in acetoclastic methanogenesis at a temperature of 37 ° C, 30 days of operation

The entire process of methanogenesis is described by the function (the sum of the two equations (1) and (2)):

$$F(x) = p_1 \cdot x_1^8 + p_2 \cdot x_1^7 + p_3 \cdot x_1^6 + p_4 \cdot x_1^5 + p_5 \cdot x_1^4 + p_6 \cdot x_1^3 + p_7 \cdot x_1^2 + p_8 \cdot x_1 + p_9 + (p_{10} \cdot x_2^4 + p_{11} \cdot x_2^3 + p_{12} \cdot x_2^2 + p_{13} \cdot x_2 + p_{14}) / (x_2^2 + q_1 \cdot x + q_2) \quad (3)$$

where coefficients have the values explained above.

The calibration of the proposed model is done in the manner described above, by changing the value of the temperature to 39°C and set the operation time of the methane tank to 30 days, for which, the variation curve of the methane production is shown in Fig. 4:

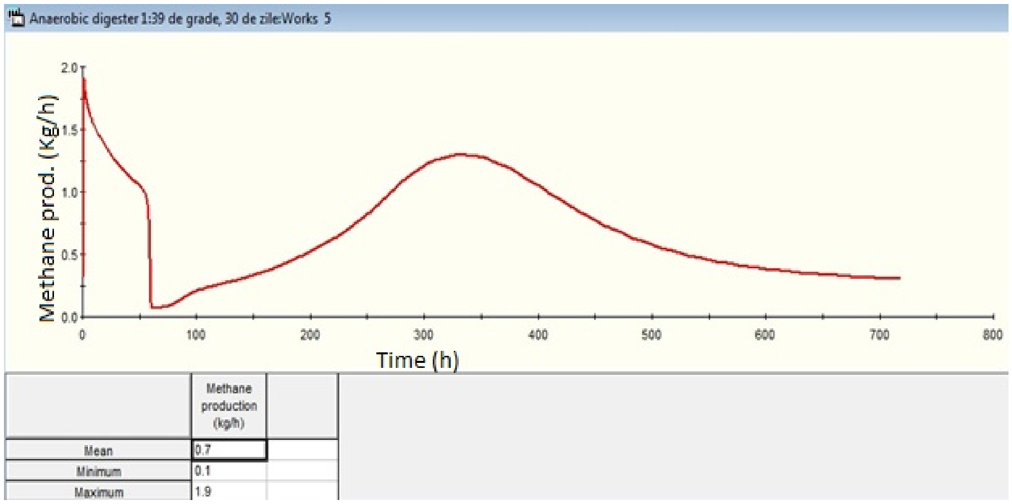


Fig. 4. The production of methane to 39°C and 30 days of operation

The curve was divided into two portions: from baseline until the hydrogenotrophic methanogenesis with t_{1f} = 60h, whose mathematical model is a polynomial function of degree 8 of the form:

$$G_1(x_1) = p_1 \cdot x_1^8 + p_2 \cdot x_1^7 + p_3 \cdot x_1^6 + p_4 \cdot x_1^5 + p_5 \cdot x_1^4 + p_6 \cdot x_1^3 + p_7 \cdot x_1^2 + p_8 \cdot x_1 + p_9 \quad (4)$$

the variable x_1 represents the length of time in which the process takes place, with values in the range of 0-60 h and coefficients (with 95% confidence limit):

p_1 = -0.3148 (-1.715, 1.085)
p_2 = -0.3639 (-1.398, 0.6697)
p_3 = 0.925 (-4.417, 6.267)
p_4 = 0.8632 (-2.45, 4.177)
p_5 = -0.7606 (-7.386, 5.865)
p_6 = -0.5798 (-3.741, 2.582)
p_7 = 0.2255 (-2.636, 3.087)
p_8 = -0.1676 (-1.045, 0.7094)
p_9 = 1.237 (0.9416, 1.532)
Goodness of fit: SSE: 0.4653, R-square: 0.8938, Adjusted R-square: 0.8231, RMSE: 0.1969 and the graph of the curve given by this function given in Fig. 5.

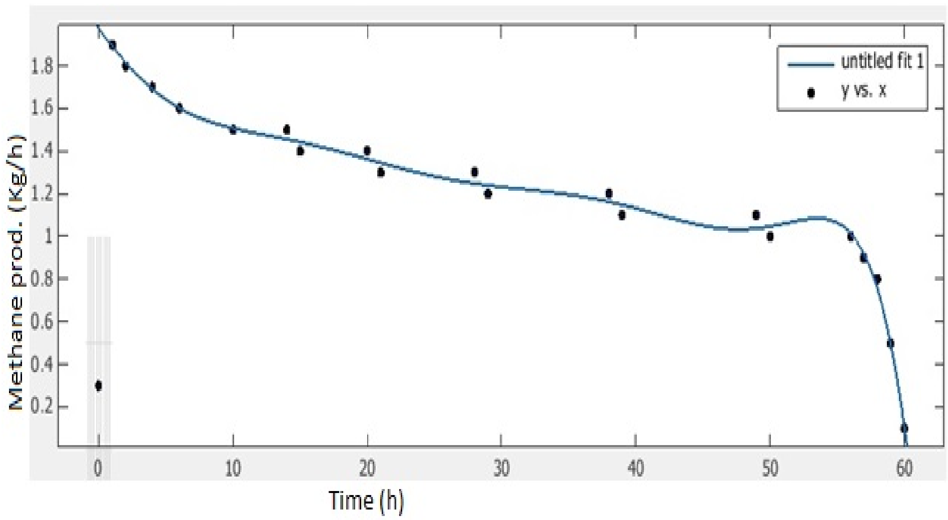


Fig. 5. Production of methane in hydrogenotrophic methanogenesis at a temperature of 39°C

For the second half of the process described by the curve of Fig. 6, curve that has been exported from Stoat simulation program representing the production of methane in the methane tank at an operating temperature of 39°C for 30 days of simulation, the function obtained using the same algorithm as in the case of above, is a rational, of the form:

$$G_2(x_2) = (p_{10} \cdot x_2^4 + p_{11} \cdot x_2^3 + p_{12} \cdot x_2^2 + p_{13} \cdot x_2 + p_{14}) / (x_2^2 + q_1 \cdot x + q_2) \quad (5)$$

In that which time (variable x_2) takes values in the range 61-719 h and the model coefficients (with 95% confidence limits) are:

p_1 = -0.0104 (-0.05444, 0.03364)
p_2 = 0.03052 (-0.01152, 0.07256)
p_3 = 0.1152 (-0.02998, 0.2605)
p_4 = 0.2108 (0.09785, 0.3237)
p_5 = 0.5911 (0.4472, 0.735)
q_1 = 0.6275 (0.4866, 0.7684)
q_2 = 0.5092 (0.3836, 0.6349)
Goodness of fit: SSE: 0.1036, R-square: 0.9861, Adjusted R-square: 0.9847, RMSE: 0.04301

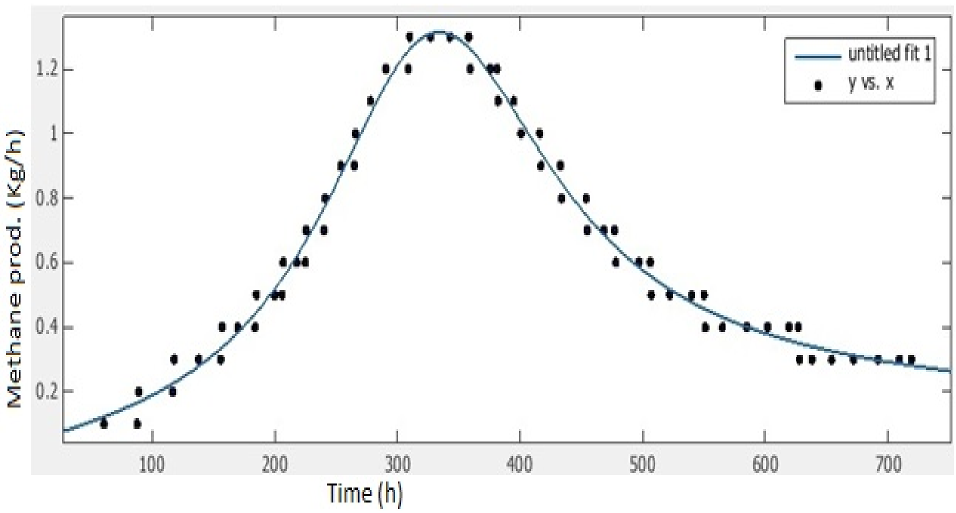


Fig. 6. Production of methane in acetoclastic methanogenesis at a temperature of 39°C

The biochemical process of anaerobic fermentation of the sludge can be considered as being described by the equation of the form:

$$G(x) = p_1 \cdot x_1^8 + p_2 \cdot x_1^7 + p_3 \cdot x_1^6 + p_4 \cdot x_1^5 + p_5 \cdot x_1^4 + p_6 \cdot x_1^3 + p_7 \cdot x_1^2 + p_8 \cdot x_1 + p_9 + (p_{10} \cdot x_2^4 + p_{11} \cdot x_2^3 + p_{12} \cdot x_2^2 + p_{13} \cdot x_2 + p_{14}) / (x_2^2 + q_1 \cdot x + q_2) \quad (6)$$

which represents the sum of the two equations (4) and (5) with x_1 and x_2 as the model variables, representing time.

For the temperature of 35°C and 30 days of operation of the methane tank, the methane production values can be found in Fig. 7.

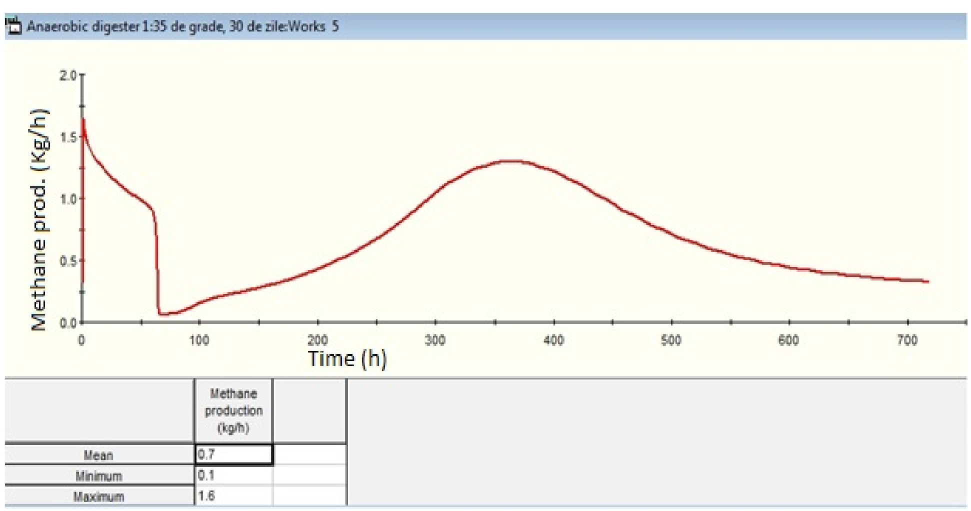


Fig. 7. The production of methane to 35 ° C and 30 days after the operation

In this figure exported from Stoat, it is shown the curve of the variation in the production of methane from the biogas resulted from the anaerobic digestion of the sludge. From the baseline until the time moment t_{1f} = 65h, the curve that describes the production of methane can be considered as a polynomial function of degree 8 of the form:

$$H_1(x_1) = p_1 \cdot x_1^8 + p_2 \cdot x_1^7 + p_3 \cdot x_1^6 + p_4 \cdot x_1^5 + p_5 \cdot x_1^4 + p_6 \cdot x_1^3 + p_7 \cdot x_1^2 + p_8 \cdot x_1 + p_9 \quad (7)$$

The variable x1 represents time, with values in the range 0-65 h and the coefficients p_1-p_9 (with 95% confidence limit) having the values:
p_1 = -0.3802 (-2.462, 1.701)
p_2 = -0.2837 (-2.524, 1.956)
p_3 = 1.077 (-5.718, 7.873)
p_4 = 0.6658 (-5.274, 6.606)
p_5 = -0.7685 (-8.445, 6.908)
p_6 = -0.4647 (-5.053, 4.123)
p_7 = 0.1385 (-3.106, 3.383)
p_8 = -0.1698 (-1.117, 0.777)
p_9 =1.129 (0.8365, 1.421)
Goodness of fit: SSE: 0.342, R-square: 0.903, Adjusted R-square: 0.8394, RMSE: 0.1688

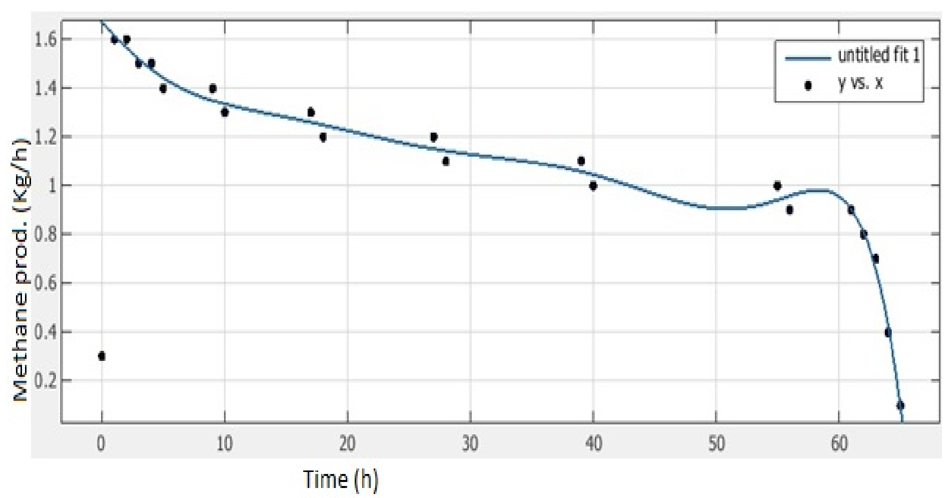


Fig. 8. Production of methane in hydrogenotrophic methanogenesis at a temperature of 35°C.

Acetoclastic methanogenesis, that which in the production of methane is described in the second part of the curve in Fig. 9, can be described mathematically by a rational type function, whose form is the following:

$$H_2(x_2) = (p_{10} \cdot x_2^4 + p_{11} \cdot x_2^3 + p_{12} \cdot x_2^2 + p_{13} \cdot x_2 + p_{14}) / (x_2^2 + q_1 \cdot x + q_2) \quad (8)$$

With x_2 being the time, that takes values in the range 66-719 h, with coefficients p_{10}-q_2 (with a 95% confidence limit) having the values:
p_{10} = -0.005337 (-0.05237, 0.0417)
p_{11} = 0.01139 (-0.03108, 0.05386)
p_{12} = 0.06541 (-0.09535, 0.2262)
p_{13} = 0.2603 (0.1434, 0.3771)
p_{14} = 0.6843 (0.5168, 0.8518)
q_1 = 0.4946 (0.361, 0.6282)
q_2 = 0.5442 (0.4064, 0.682)
Goodness of fit: SSE: 0.1015, R-square: 0.9888, Adjusted R-square: 0.9877, RMSE: 0.04047

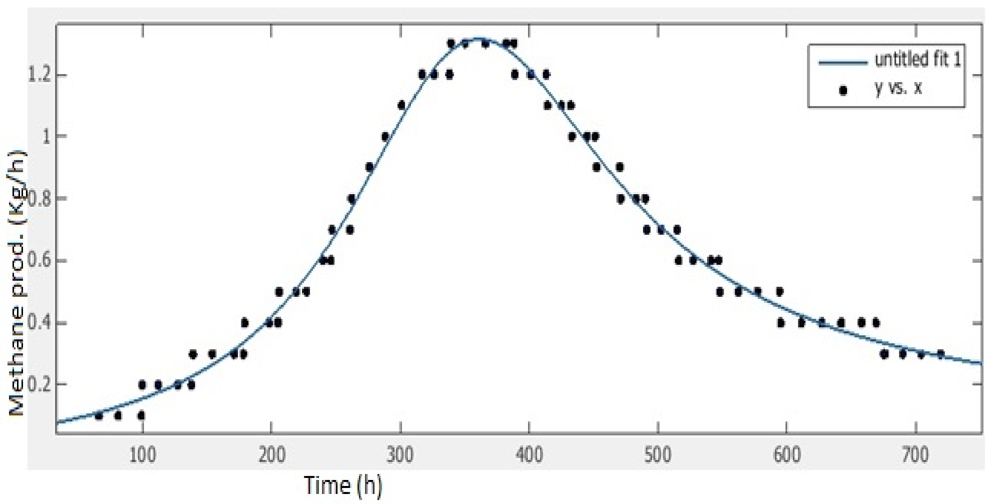


Fig. 9. Production of methane in aceotoclastic methanogenesis at a temperature of 35°C.

The mathematical model for the process of methanogenesis, when the digester temperature was 35°C and the simulation of its operation was carried out for a period of 30 days, is:

$$H(x)= p_1 \cdot x_1^8+p_2 \cdot x_1^7+p_3 \cdot x_1^6+p_4 \cdot x_1^5+p_5 \cdot x_1^4+p_6 \cdot x_1^3+p_7 \cdot x_1^2+p_8 \cdot x_1+p_9+ (p_{10} \cdot x_2^4 + p_{11} \cdot x_2^3 + p_{12} \cdot x_2^2 + p_{13} \cdot x_2 + p_{14}) / (x_2^2 + q_1 \cdot x + q_2) \quad (9)$$

Values of the coefficients of the mathematical model of methanogenesis, which is a function of the form:

$$F(x)=p_1 \cdot x_1^8+p_2 \cdot x_1^7+p_3 \cdot x_1^6+p_4 \cdot x_1^5+p_5 \cdot x_1^4+p_6 \cdot x_1^3+p_7 \cdot x_1^2+p_8 \cdot x_1+p_9+ (p_{10} \cdot x_2^4 + p_{11} \cdot x_2^3 + p_{12} \cdot x_2^2 + p_{13} \cdot x_2 + p_{14}) / (x_2^2 + q_1 \cdot x + q_2) \quad (10)$$

where explained above and the data is summarized in the Table 1.

Table 1

Coefficients of the mathematical model of the methanogenesis

Coefficient	T=35°C	T=37°C	T=39°C
p_1	-0.3802	-0.3531	-0.3148
p_2	-0.2837	-0.3742	-0.3639
p_3	1.077	1.0608	0.925
p_4	0.6658	0.7251	0.8632
p_5	-0.7685	-0.76372	-0.7606
p_6	-0.4647	-0.4198	-0.5798
p_7	0.1385	0.228	0.2255
p_8	-0.1698	-0.1796	-0.1676
p_9	1.129	1.183	1.237
p_{10}	-0.005337	-0.02515	-0.0104
p_{11}	0.01139	0.01462	0.03052
p_{12}	0.06541	0.1784	0.1152
p_{13}	0.2603	0.239	0.2108
p_{14}	0.6843	0.5471	0.5911
q_1	0.4946	0.7103	0.6275
q_2	0.5442	0.4912	0.5092

Increasing the length of time for which the simulation is carried out, from 30 to 60 days, the variation curve of the methane production is the one given by Fig. 10.

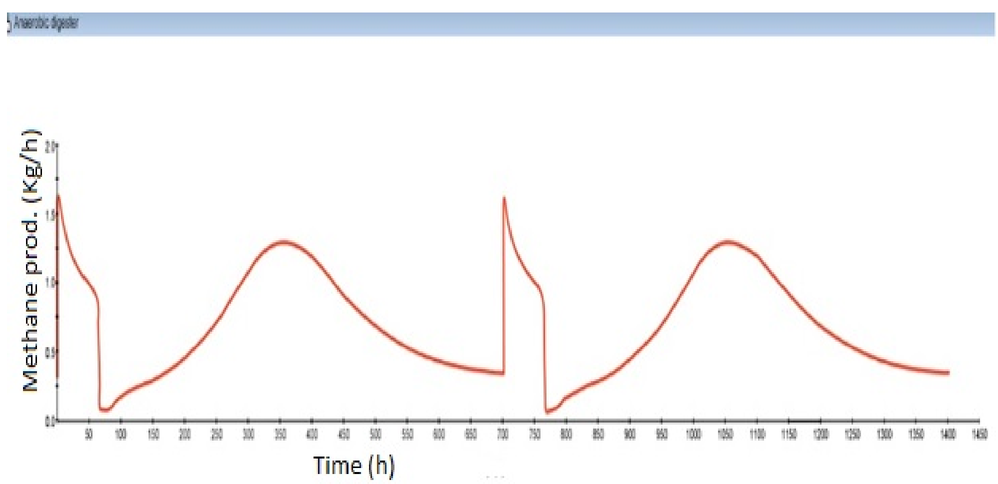


Fig. 10. Changes in the production of methane at a temperature of 37 ° C, 60 days after the operation

Following the ranges of the variables x_1 and x_2 for the three temperatures considered, the model coefficient values from Table 1, the form of the variation curve of the production of methane in the three cases considered, and as well as the shape of the curve of Fig. 10, can be pulled more conclusions.

3. Conclusions:

* There is a lag period for the duration of the process for bacteria that uses hydrogen and carbon dioxide to produce methane, which is dependent on the temperature at which the biochemical process occurs and is all the greater as the temperature is lower (29 hours at 39°C up to 35 hours at 37°C);

* The model coefficients have the same sign and values, properly close for all three temperatures used to simulate the process of methanogenesis;

* Negative coefficients, which, mathematically speaking, will induce the decrease of methane production, so inhibiting the methanogenesis, are in greater numbers in the first part of the function (p_1, p_2, p_5, p_6, p_8)

*The coefficients applied to powers 2nd, 5th and 6th of time x_1 were positive and higher, when the temperature of the methane tank is higher, which means that the biochemical process is strongly temperature dependent, being favored by its growth;

* Considering the amount of 0.3kg/h as the minimum production of methane in acetoclastic methanogenesis, so that bacteria enters into a period of regression (prior to their death), it can be seen that this minimum is reached at different times, depending on the considered temperature, the greater as the temperature is lower (652 hours at 37°C, 628 h at 39 degrees), but it can be seen that the maximum output (1.3kg/h) is carried out over a range of longer time at a temperature of 37°C (53 hours at 37°C, 50 hours for the other temperature considered), so that the methane production (considered in kg CH_4/cicle of the installation activity) is greater in the temperature range of 37°C;

* Contribution of the acetoclastic methane producing mechanism is superior to the hydrogenophile mechanism, as can be seen from the analysis of Figs. 1 and 4, which can be explained by the fact that the synthesis of methane from hydrogen and carbon dioxide is a process whose operating conditions are difficult to obtain and control than the cleavage of the molecules of acetic acid;

* Methanogenesis process is a cyclic process, as can be seen in Fig. 7, the two systems for the production of methane succeeding regular intervals, each of which is preceded and followed by a lag period, the duration of which is specific to the type of microorganisms involved in the process.

Acknowledgement

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R E F E R E N C E S

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