INTERNATIONAL JOURNAL OF HEAT AND TECHNOLOGY

ISSN: 0392-8764
Vol. 34, No. 4, December 2016, pp. 623-629
DOI: 10.18280/ijht.340411

A publication of IIETA

International Information and Engineering Technology Association

http://www.iieta.org/Journals/IJHT

Biogas Production from Anaerobic Digestion of Manure at Different Operative Conditions

Claudia Carotenuto*, Giovanna Guarino, Mario Minale and Biagio Morrone

Dipartimento di Ingegneria Industriale e dell'Informazione, Università della Campania "Luigi Vanvitelli", via Roma 29, 81031 Aversa – CE, Italia.

Email: claudia.carotenuto@unina2.it

ABSTRACT

Anaerobic digestion is an established technology to simultaneously produce biogas and treat different kinds of wastes. This work deals with water buffalo manure digested under mesophilic (37°C) and thermophilic (55°C) conditions with initial pH varying from 6.0 to 8.7. The digestion is investigated following the evolution of the biogas composition in time, in terms of the volume fraction of CH_4, CO_2 and their ratio. The growths of the biogas products are interpolated with a Gompertz equation and in all the investigated cases the methane productivity is above 63% with a CH_4/CO_2 ratio rather high and equal to about 2. In mesophilic conditions, an initial pH of 7.0 must be preferred to optimize the methane yield and to minimize the time required to attain it. The thermophilic conditions resulted very promising since they almost halved the time required to reach the final yield. The speed up of the process at 55°C, in our case, resulted to be due to the increase of the digestion kinetic more than to the selection of a new metabolic pathway.

Keywords: Manure, Fermentation, Biogas composition, Lactating and non-lactating buffalo, CH_4/CO_2 ratio.

1. INTRODUCTION

Biomass anaerobic digestion processes to produce biogas have several advantages [1]: *i*) First, they allow converting the energy contained in biomass into a useful fuel (biogas) which may be stored and transported. Biogas is a mixture principally formed by methane (CH_4) and carbon dioxide (CO_2) and traces of other gases and organic acids of low molecular weight [2]. *ii*) Second, they represent a method of recycling the organic wastes that is transformed into stable soil fertilizers. *iii*) Third, they are a waste treatment able to reduce the pollutants release to the environment [3].

Biomass includes a large amount of material as organic fraction of municipal solid waste, sewage sludge, food waste, animal manure, etc. [4, 5]. The latter is a low cost substrate rich in carbohydrates, especially suitable to produce biogas, without the addition of any nutrient or additive [6].

Anaerobic digestion is a complex process carried out by a consortium of several different microorganisms, which in the case of manure are naturally present in the animal intestine. The metabolic pathway can be schematically divided into four main phases: hydrolysis, acidogenesis, acetogenesis and methanogenesis and each step is performed by different consortia of microorganisms [7, 8]. The microorganisms producing methane, during the last digestion phase, are called methanogens and they can be classified according to their optimal pH range [9]; in particular, to maximize the CH_4 yield, pH typically varies from 6.5 to 8.2, with optimal values of 7.0-7.2 [10]. Besides pH, the production of CH_4 from manure anaerobic digestion is principally affected by the amount of inert solids, the hydraulic retention time and the process temperature [11, 12]. Focusing on the animal manure substrate, Kalia and Singh [13] obtained a bio-methane concentration in biogas equal to 55-60 % accompanied by CO_2 concentration of 40-45%. They digested cattle dung at 23 °C and pH 8.2, in batch mode. Twelde et al. [14] digested mixtures of brewery wastes and cattle dung at 35 °C and pH = 7.5 reaching a very high level of CH_4 volume fraction equal to 69% and a CO_2 volume fraction of 30%. Abubakar and Nasir [15] used cow dung, fermented at 53 °C with neutral pH, in a semi-continuous process, producing a biogas with a methane concentration equal to 47 %; in this case, no specification of CO_2 concentration was given.

We study, in this work, the effect of temperature and pH on the biogas production from digestion of water buffalo manure, which is a substrate still poorly investigated in the literature and it is relevant in southern Italy because of the significant increase of buffalo farms related to the production of the DOP mozzarella di bufala. We treat separately manure coming from lactating and non-lactating buffaloes since the difference in their feed and hormonal phase can affect the manure characteristics. We focus not only on the production of CH_4, but also on CO_2 and on their ratio. The anaerobic digestion of water buffalo manure is performed under mesophilic (37 °C) and thermophilic (55 °C) conditions, with pH varying from acid (pH = 6.0) to basic (pH = 8.7) values.

2. MATERIAL AND METHODS

2.1 Manure

Manures from lactating and non-lactating buffaloes are collected from the farm “La Valentina s.r.l.”, in the municipality of Villa Literno, in Campania (South Italy), during a period of time covering more than three years. The manure samples are always taken in the morning; they are placed in plastic bags, transported to the laboratory and immediately stored in the fridge at 4 °C [6] to slow down the bacteria metabolism. In this way, the manure properties keep stable until the actual beginning of the digestion experiments.

The fresh manure samples used in this work are listed in Table 1. The total solids (TS), the volatile solids (VS) content, and the pH value (pH_{sub}) of each fresh sample is measured upon collection. TS and VS are determined according to the European Standard Methods [16, 17]. TS varies from about 17 to 35 % (Table 1) with a mean value of 26.8 % ± 6.3 %. This large standard deviation is ascribable primarily to the season of the year of the manure collection (rainy or dry months may affect the manure water content), to differences of the animal food supply, and to the cattle hormonal phase [18]. VS is almost constant and equal to a value of about 72 %, with the exception of the single case of sample I, which shows VS = 52.5 %. The average value that we measured is in good agreement with those reported in the literature for other kinds of manure and sewage sludge [19]. VS indicates the fraction of the organic matter in the biomass and allows estimating the effectively digestible substrate fraction. The pH value of the fresh manure substrate is always basic and, in particular, it varies from 7.1 to 8.8.

Table 1. Properties of buffalo manure samples

	TS [%]	VS [%]	pH_{sub}
Lactating buffalo			
A	28.6		8.8
B	20.6	-	8.8
C	26.9	-	7.6
D	17.1	-	7.3
E	20.7	73.9	7.6
F	33.1	72.9	7.3
Non-Lactating buffalo			
G	29.8	-	8.7
H	35.3	67.3	7.9
I	22.4	52.5	7.1
L	33.8	73.9	7.7

2.2 Process conditions

Figure 1 shows the borosilicate glass bottles, with volume of about 280 ml, used as batch digesters. Each bottle is loaded with 80 ml of substrate to leave a head volume of about 200 ml for the gases. For each process condition and for each sample, three replicates are prepared for statistical purposes.

Figure 1. Picture of batch digesters

The substrate is prepared by mixing the manure with distilled water to obtain a manure/water mass ratio equal to 30/70. This ratio was chosen as a compromise between the maximization of the biogas production and the minimization of the slurry viscosity. Indeed, the higher the manure mass fraction, the higher the biogas production, but the higher is the slurry viscosity [20-24].

The initial pH of the samples is typically corrected to achieve either the value of 6.0 or 7.0, by adding the opportune amount of 1 M HCl water solution. In this paper, we investigate also the case where the pH of the manure/water slurry is not artificially modified. In all the experiments, the pH is left to auto-evolve during the digestion and only the final value is measured. The slurries are opportunely mixed following a three steps procedure: they are firstly hand mixed, then electrically homogenized for 2 min and finally filtered with a Büchner filter equipped with a vacuum pump. Guarino et al. [25] showed that these mechanical pre-treatments, compulsories in a continuous process in lab-scale reactors, do not alter the digestion process. The manure/water mixture is loaded into the bottle and the anaerobiosis is obtained blowing nitrogen inside the hermetically closed digesters with a two-needle system. To limit the sample sedimentation, the bottles are manually shaken once a day during all the fermentation process.

The measurement of the produced gas composition is performed with the microGC Agilent 3000 equipped with two capillary columns: a MolSieve 5 A and a Poraplot U. The former is used to separate H_2, O_2, N_2 and CH_4; the injector and column temperature are respectively set at 90 °C and 110 °C and Ar is the gas carrier. The latter separates CO_2; the injector and column temperature are set at 90 °C and 85 °C, respectively, and He is the gas carrier. To dry the gas prior to its injection in the microGC a home-made water trap is used.

2.3 Gompertz growth

To quantitatively compare the results obtained with the different process conditions, the plots of the gas volume fraction growth in time are interpolated with a three parameters Gompertz sigmoidal equation [26, 27], Eq(1):

$$H = P\, exp\left\{-exp\left[\frac{R_m \cdot e}{P}\left(\lambda - t\right) + 1\right]\right\} \qquad (1)$$

where e is Euler’s number and t [h] is the digestion time. The interpolation parameters have a clear physical meaning: H [%] is the cumulative production, P [%] is the productivity, *i.e.* the volume fraction asymptotic value, R_m [h^{-1}] is the maximum production rate, and λ [h] the lag-phase time, see Figure 2.

The Gompertz growth applies to the case where the feed for the bacteria is largely abundant. In this case, the digestion products, after a lag-phase time, exponentially increase and reach a final plateau corresponding to the so called Gompertz production. On the contrary, if the feed is not so abundant, a possible decrease of the gas concentration after the plateau can be observed. Anyway, we never faced such a decrease.

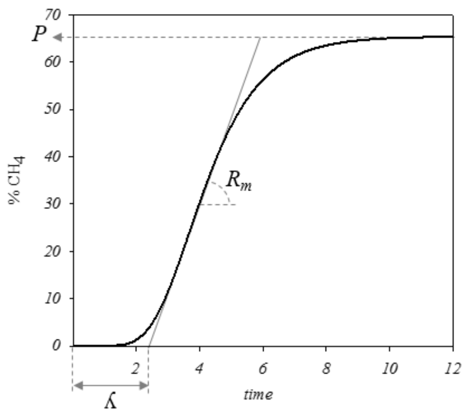

Figure 2. Three parameters Gompertz growth

3. RESULTS AND DISCUSSION

The results for each case-study are plotted in terms of the evolution in time of CH_4, CO_2 and their ratio and are shown in Figures 3-5. To keep a graphical indication of the difference between the manure coming from lactating and non-lactating buffaloes, we use empty symbols for the formers and filled ones for the latters. Since we did not detected significant differences between the two typologies of manure, the CH_4 data are interpolated altogether with a single Gompertz equation, Eq(1), and the same is done for the CO_2 data, while the curve shown in the CH_4/CO_2 plots derives from the ratio of the CH_4- and CO_2- Gompertz interpolations and it is shown to guide the eye. The estimated parameters of each case-study, P, R_m and λ, and the regression coefficient R^2 are listed in Table 2 together with the digestion parameters: initial pH_{in}, process temperature T, and final pH_{fin}, i.e. the value measured at the end of the experiments.

Figure 3 shows the results of case-study I where the samples A, B, C, G and H of Table 1 are digested at T = 37°C, starting from an initial pH equal to 6.0. The CH_4 growth in time of case-study I, Figure 3a, shows a regular sigmoidal trend with a methane productivity P ~ 63 %, a lag-phase time λ = 108 h, and a production rate R_m = 0.18 h^{-1}. These samples have a final pH_{fin} of about 6.9 ± 0.2 indicating that the slurry pH auto-evolves towards neutrality during the digestion. When this does not happen, the methane productivity remains very low, and we here do not show these results. A regular sigmoidal trend is also shown for both CO_2 data and CH_4/CO_2 ratio (Figures 3b and 3c, respectively), although some differences are evident. First, the lag-phase time of CO_2 growth is shorter than that of CH_4 and thus the interpolation parameter λ is negative. This result, though unphysical, reflects the fact that the collected experimental data do not catch the first part of the CO_2 growth, indeed the first point measured, after almost one day of digestion, already shows a finite value of CO_2 volume fraction. The lag-phase time of the ratio CH_4/CO_2 is positive and is in between those of methane and carbon dioxide because the CH_4/CO_2 ratio can be different from zero only if CH_4 volume fraction is not nil.

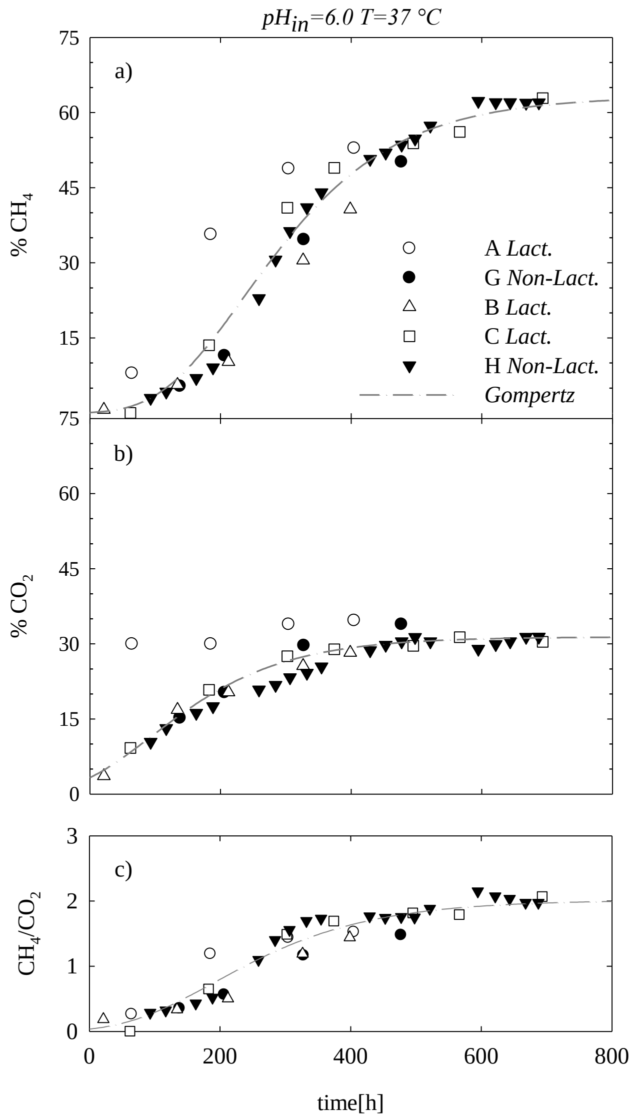

Figure 3. Case-study I: Time evolution of CH_4 and CO_2 volume fraction, and of their ratio, at pH_{in} = 6.0, T = 37 °C. Symbols are experimental data, line is the global fit curve

Table 2. Gompertz parameters

	pH_{in}	T [°C]	pH_{fin}		P [%]	λ [h]	R_m [h^{-1}]	R^2
I	6.0	37	6.9	*CH_4*	63.2	108	$1.8 \cdot 10^{-1}$	0.94
				CO_2	31.4	-21.4	$1.0 \cdot 10^{-1}$	0.86
				CH_4/CO_2	2.0	54.0	$5.5 \cdot 10^{-3}$	
II	7.0	37	7.0	*CH_4*	65.9	107	$2.5 \cdot 10^{-1}$	0.93
				CO_2	30.6	-39.2	$9.7 \cdot 10^{-2}$	0.85
				CH_4/CO_2	2.2	77.8	$8.9 \cdot 10^{-3}$	
III	7.5	37	7.0	*CH_4*	65.2	88.6	$2.1 \cdot 10^{-1}$	0.99
IV	8.1-8.7	55	7.7	*CH_4*	71.6	68.5	$4.3 \cdot 10^{-1}$	0.98
				CO_2	34.8	27.1	1.46	0.90
				CH_4/CO_2	2.1	68.3	$1.2 \cdot 10^{-2}$	

Figure 4 shows the results of case-study II where the samples D, E, H, I and F of Table 1 are digested at T = 37°C, starting from an initial pH equal to 7.0. Case-study II slightly differs from the case I: Concerning the CH_4, the value of P is slightly higher and it is equal to 66 %, and the maximum production rate is larger and equal to 0.25 h^{-1}; the lag-phase time is essentially unchanged and results equal to 107 h (Table 2). The CO_2 growths are also very similar and indeed the Gompertz parameters are almost the same.

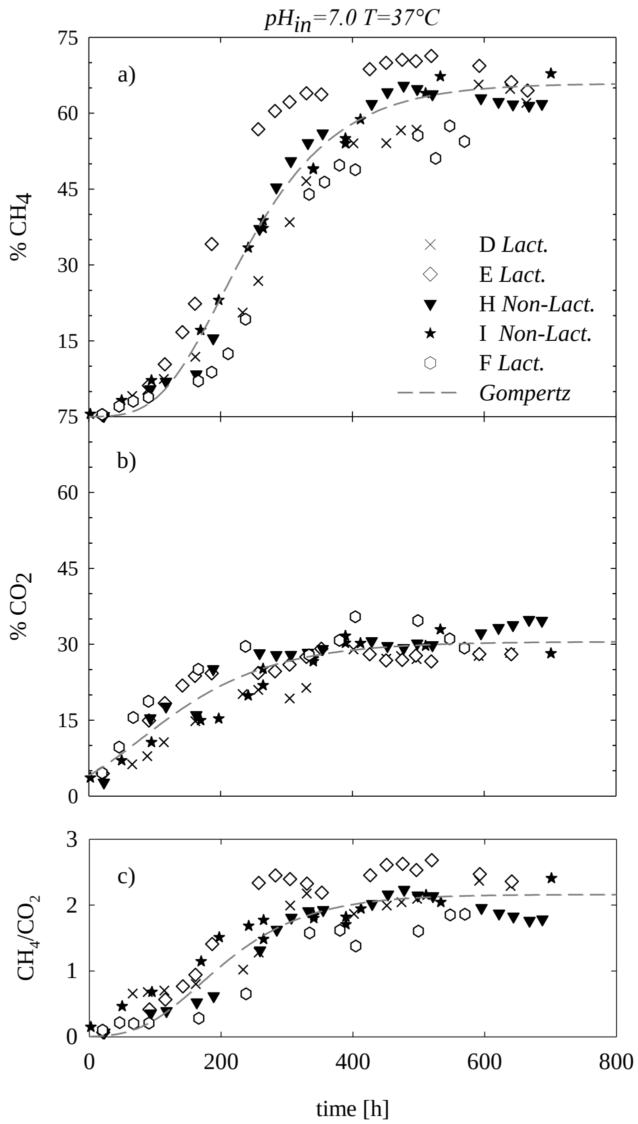

Figure 4. Case-study II: Time evolution of CH_4 and CO_2 volume fraction, and of their ratio, at pH_{in} = 7.0, T = 37 °C. Symbols are experimental data, line is the global fit curve

As regards the CH_4/CO_2 ratio, the main difference is observable in the maximum production rate parameter that for case-study II is about the 60% higher than that of case-study I. It is interesting to remark that also in this case pH_{fin} is neutral and this suggests that it remains almost constant during the entire digestion process.

The results of case-studies I and II (Table 2) suggest that all samples auto-adjust their pH during the digestion process towards neutrality, consequently the obtained CH_4 and CO_2 yields seem to be unaffected by the initial pH_{in}. It was then decided to investigate the digestion process without setting the sample pH to an initial desired value. This new process condition is imposed to sample D of Table 1, whose initial pH, *i.e.* which obtained after mixing the manure with bi-distilled water, was 7.5, only slightly different from its pH_{sub} (Table 1). We could not measure the CO_2 concentration for problems occurred with the microGC column Poraplot U that is used to separate the CO_2. The bio-methane evolution in time of this case-study III is shown in Figure 5a. The regression curves of case-studies I and II, already shown in Figures 3 and 4, respectively, are reported for comparison.

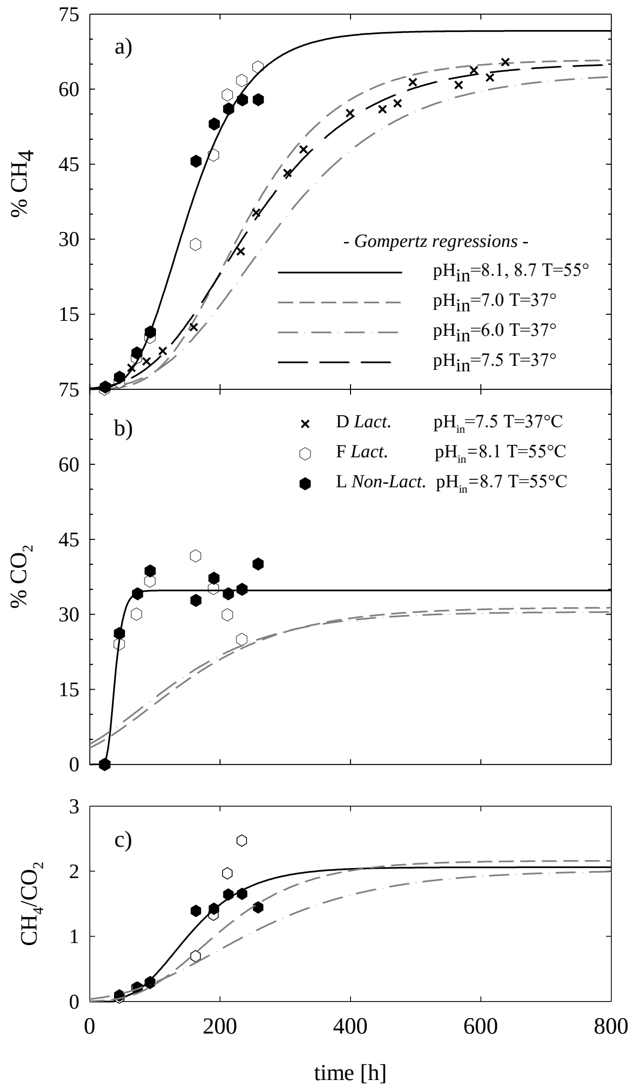

Figure 5. Time evolution of CH_4 and CO_2 volume fraction, and of their ratio, for systems digested without correcting their initial pH, at 37°C and 55°C. Comparison with results of Figures 3-4 is shown. Symbols are experimental data, lines are global fit curves

Data in Figure 5 and Table 2 indicate that the digestion of sample D starting from a pH_{in} = 7.5 shows a methane growth very similar to that of case II (pH_{in} = 7.0), but a slightly shorter lag-phase time. In particular, it has a lag-phase time λ = 88.6 h, a production rate R_m = 0.21 h^{-1}, and a productivity P equal to 65.2 %. It is interesting to remark that also in this case, pH_{fin} is neutral, thus the system reduces its pH during the digestion. The clear similarity between the CH_4 growth of case III to those of cases I and II let us imagine that also the CO_2 has a growth very similar to those shown in Figures 3b and 4b.

The digesters of wastes are typically installed within a cogeneration plant, where heat is usually available, thus a process at a temperature higher than 37 °C can be economically sustained. Moreover, in the literature there are only few papers [15, 28] indicating that bio-methane can be produced also at 53 - 55 °C. We then decided to investigate the manure digestion in thermophilic conditions, 55 °C, and since at 37°C our system auto-evolves during the digestion towards neutrality, we did not modify the initial pH (case-study IV). In Figure 5, experimental results obtained digesting the manure at 55 °C (samples F and L), without adjusting their initial pH, are shown and compared with all the results obtained at 37 °C, plotted only in terms of Gompertz regressions, for the sake of graph readability. The initial process pH_{in} resulted equal to 8.1 and 8.7 for Samples F and L, respectively, and also in this case it is slightly smaller than pH_{sub}.

The volume fractions of the biogas obtained from the digestion of samples F and L are essentially superimposed thus showing a behaviour of the system independent on the initial pH_{in}. In agreement with this observation, we measured the same final pH_{fin} for both samples that resulted only slightly basic and equal to 7.7. This shows once more that the system tends to auto-evolve towards neutrality that is only approached in mesophilic conditions, while it is reached at 37°C. Notice, however, that for samples F and L, while CO_2 shows a final plateau value, CH_4 has not yet reached it. Indeed, for technical problems, we were forced to interrupt the digestion process before the attainment of a real steady state. Thus, we may not exclude that the system pH was still evolving when we stopped the process.

In view of the similarity of the results of samples F and L, we interpolated them with a single Gompertz equation and the interpolation parameters are in Table 2. Notice that the methane productivity is only grossly estimated because the plateau experimental data that allow a good accuracy of P are missing. Nonetheless, we may observe that the methane productivity increased to a value of 71.6 % that is the highest of all the measured samples. Notice, however, that the productivities P of CH_4 and CO_2 sum to an unphysical value larger than 100%. This is due to both the grossly estimate of CH_4 productivity and the choice of fitting all the data with a single Gompertz equation. Anyway, each set of data has biogas volume fractions (CH_4, CO_2, N_2) correctly summing to 100%.

A more evident effect of the new process conditions is the reduction of the lag-phase time, which resulted equal to $\lambda = 68.5$ h, and the increase of the maximum production rate, which became $R_m = 0.43\ h^{-1}$. Consequently, the plateau value can be reached, in this case IV, in about 400 h, while it was reached in about 700 h at 37°C. Overall, the methane data indicates that the digestion kinetic is speeded up in the new process conditions. Carotenuto et al. [29] hypothesised that this may be due to not only the increase of temperature that typically enhances the chemical kinetics, but also to the higher initial pH that may promote the hydrogenotrophic methanogenesis during which CO_2 and H_2 are converted into CH_4 and H_20 [30]. Also the pH decrease suggests that the acidogenic phase is well operated; during this phase, fatty acids are released due to the degradation of substrate cellulosic material. Further insights can be now obtained looking at the CO_2 data. (Figure 5b). They show a clear speed up of the process that shows a maximum production rate one order of magnitude larger than those of the cases at 37°C, $R_m = 1.46$, and a productivity only slightly larger than the previous cases. The lag-phase time is in this case positive (Table 2), since the first the CO_2 volume fraction measured is practically nil. It is still impossible to discern whether the observed speed up is due to a simple increase of kinetic or to the selection of a different, more efficient, metabolic pathway. CH_4/CO_2 data may help with this respect (Figure 5c). Their growth is self-similar to that of the cases digested at 37°C, showing essentially the same plateau value, a very similar lag-phase time, and a maximum production rate monotonically increasing with the digestion temperature. This suggests that the metabolic pathway is essentially the same and the new process conditions act on the digestion kinetic.

Regardless the digestion temperature, the CH_4/CO_2 ratio reached in our systems is about 2. This is considered to be a high value [31] that indicates that the process involves not only the digestion of carbohydrates, but also of more complex molecules as triglycerides. Indeed, with a simple stoichiometric argument, we may consider that the biogas production from organic substrates involves an internal redox reaction that converts organic molecules to CH_4 and CO_2 according to the general Buswell equation [31]:

$$C_nH_aO_bN_d + \left(n - \frac{a}{4} - \frac{b}{2} + \frac{3d}{4}\right) H_2O \rightarrow \left(\frac{n}{2} + \frac{a}{8} - \frac{b}{4} - \frac{3d}{8}\right) CH_4 + \left(\frac{n}{2} - \frac{a}{8} + \frac{b}{4} + \frac{3d}{8}\right) CO_2 + dNH_3. \quad (2)$$

For the simplest cases, such as the conversion of carbohydrates, like starch, $(C_6H_{10}O_5)_n$, Buswell equation becomes:

$$(C_6H_{10}O_5)_n + n\,H_2O \rightarrow 3n\,CH_4 + 3nCO_2, \quad (3)$$

and thus a 1:1 ratio of CH_4 and CO_2 is obtained, as well as in the case of the digestion of a protein, $C_5H_7NO_2$, for which Buswell equation, Eq(2), reduces to:

$$C_5H_7NO_2 + 3\,H_2O \rightarrow \frac{5}{2}\ CH_4 + \frac{5}{2} CO_2 + NH_3, \quad (4)$$

while the redox stoichiometric equation of a lipid, $C_{57}H_{104}O_6$, leads to something more than a 2:1 CH_4/CO_2 ratio:

$$C_{57}H_{104}O_6 + 28\,H_2O \rightarrow 40\ CH_4 + 17CO_2. \quad (5)$$

Our results are comparable to those of Twelde et al. [14] who obtained a 2:1 ratio of CH_4/CO_2 at 35 °C, while are significantly better than those of Kalia and Singh [13] and Abubakar and Nasir [15] who chose a temperature of 23 °C and 53°C, respectively.

4. CONCLUSIONS

In this work, we compared the biogas produced by digesting water buffalo manure, in batch mode, under different process conditions. In particular, we modified two of the most important parameters affecting the process: the temperature and the initial pH_{in}. The pH is not controlled during the digestion process, but only at its beginning and it varies from 6.0 to 8.7. Since the unmodified pH of the mixture water-manure is slightly basic (Table 1), we acidified the system with 1 M HCl water solution to obtain the value of $pH_{in} = 6.0$ and 7.0, while values of $pH_{in} = 7.5$, 8.1 and 8.7 were obtained without any pH correction. The pH is always measured at the end of digestion process and for all the cases the systems auto-evolves towards neutrality. The temperature was set to 37 °C and 55 °C.

A yield of about 67% expressed in terms of methane volume fraction of the biogas is obtained regardless the initial pH value keeping the temperature at 37°C. This can be explained with the observation, already discussed, that the pH auto-evolves towards neutrality and thus the effective pH during the digestion probably is not so different. The effect of the initial pH is more pronounced on the digestion kinetic, indeed the yield is reached at different times, the shortest corresponds to $pH_{in} = 7$.

By changing the temperature, the yield seems to increase up to 70%, but the estimated production *P* has a low accuracy at 55°C because of data lacking. Anyway, a clear speed-up of the process is observable. This acceleration can be due to either a kinetic increase or a selection of different metabolic pathways. The former explanation must be preferred because of the self-similarity, under mesophilic and thermophilic conditions, of CH_4/CO_2 evolution shown in Figure 5c.

The final ratio CH_4/CO_2 of the biogas is high and equal to about 2, independently of the initial pH and of the temperature.

The results obtained at 55 °C and $pH_{in} = 8.1$ and 8.7 (samples F and L) sounds very promising, but the generalization of this experimental observations requires further studies with also other manure samples.

REFERENCES

[1] Ziemiński, K. and Frąc, M., "Methane fermentation process as anaerobic digestion of biomass: Transformations, stages and microorganisms," *African Journal of Biotechnology*, vol. 11, no.18, pp. 4127-4139, 2012. DOI: 10.5897/AJBX11.054.

[2] Lopes, W. S., Leite, V. D. and Prasad, S., "Influence of inoculum on performance of anaerobic reactors for treating municipal solid waste," *Bioresource Technology*, vol. 94, no. 3, 261-266, 2004. DOI: 10.1016/j.biortech.2004.01.006.

[3] Tafdrup, S., "Viable energy production and waste recycling from anaerobic digestion of manure and other biomass materials," *Biomass and Bioenergy*, vol. 9, no. 1, pp. 303-314, 1995. DOI: 10.1016/0961-9534(95)00098-4.

[4] Li, R., Chen, S. and Li, X., "Anaerobic co-digestion of kitchen waste and cattle manure for methane production," *Energy Sources, Part A: Recovery, Utilization and Environmental Effects*, vol. 31, no. 20, pp. 1848-1856, 2009. DOI: 10.1080/15567030802606038.

[5] Francioso, O., Montecchio, D., Salomoni, C., Caputo, A. and Palenzona, D., "Convenient renewable energy from bacterial metabolism of organic wastes," *International Journal of Heat and Technology*, vol. 27, no. 1, pp. 151-155, 2009.

[6] Guarino, G., Carotenuto, C., di Cristofaro, F., Papa, S., Morrone, B. and Minale, M., "Does the C/N ratio really affect the Bio-methane Yield? A three years investigation of Buffalo Manure Digestion," *Chemical Engineering Transaction*, vol. 49, pp. 463-468. DOI: 10.3303/CET1649078.

[7] Carillo, P., Carotenuto, C., Di Cristofaro, F., Kafantaris, I., Lubritto, C., Minale, M., Morrone, B., Papa, S. and Woodrow, P., "DGGE analysis of buffalo manure eubacteria for hydrogen production: effect of pH, temperature and pretreatments," *Molecular Biology Reports*, vol. 39, no. 12, pp. 10193-10200, 2012. DOI: 10.1007/s11033-012-1894-3.

[8] di Cristofaro, F., Carotenuto, C., Carillo, P., Woodrow, P., Morrone, B. and Minale, M., "Evaluation of CH_4 and H_2 yield with different mixtures of digested and fresh buffalo manure," *Chemical Engineering. Transactions*, vol. 37, pp. 283-288, 2014. DOI: 10.3303/CET1437048.

[9] Sibiya, N. T., Muzenda, E. and Tesfagiorgis, H. B., "Effect of temperature and pH on the anaerobic digestion of grass silage*," 6th Int'l Conf. on Green Technology, Renewable Energy & Environmental Engg. (ICGTREEE'2014),* Cape Town, South Africa 2014. Available: http://hdl.handle.net/10210/13590.

[10] Rao, M. S. and Singh, S. P., "Bioenergy conversion studies of organic fraction of MSW: kinetic studies and gas yield–organic loading relationships for process optimization." *Bioresource Technology*, vol. 95, no. 2, pp. 173-185, 2004. DOI: 10.1016/j.biortech.2004.02.013.

[11] Nozhevnikova, A. N., Kotsyurbenko, O. R. and Parshina, S. N., "Anaerobic manure treatment under extreme temperature conditions," *Water Science and Technology*, vol. 40, no. 1, pp. 215-221, 1999. DOI: 10.1016/S0273-1223(99)00387-X.

[12] Hashimoto, A. G., "Methane from cattle waste: effects of temperature, hydraulic retention time, and influent substrate concentration on kinetic parameter (K)," *Biotechnology and Bioengineering*, vol. 24, no. 9, pp. 2039-2052, 1982. DOI: 10.1002/bit.260240911.

[13] Kalia, A. K. and Singh, S. P., "Effect of mixing digested slurry on the rate of biogas production from dairy manure in batch fermenter," *Energy Sources*, vol. 23, no. 8, pp. 711-715, 2001. DOI: 10.1080/009083101316862462.

[14] Tewelde, S., Eyalarasan, K., Radhamani, R. and Karthikeyan, K., "Biogas production from co-digestion of brewery wastes [BW] and cattle dung [CD]," *Int. J. Latest Trends Agric. Food Sci*., vol. 2, no.2, pp. 90-93.

[15] Abubakar, B.S.U.I. and Nasir, I., "Anaerobic Digestion of cow dung for biogas production," *ARPN Journal of Engineering and Applied Sciences*, vol. 7, no. 2, pp. 169–172, 2012.

[16] Unificazione, E.N.I.D., "Characterization of waste - Calculation of dry matter by determination of dry residue or water content," pp. 24, 2007.

[17] Unificazione, E.N.I.D., "Characterization of waste. Determination of loss on ignition in waste, sludge and sediments," pp. 16, 2007.

[18] Carillo, P., Carotenuto, C., Di Cristofaro, F., Lubritto, C., Minale, M., Mirto, A., Morrone, B., Papa, S. and Woodrow, P., "Bacterial and archaeal communities influence on methane production," *Chemical Engineering. Transactions*, vol. 37, pp. 859-864, 2004. DOI: 10.3303/CET1437144.

[19] Gilroyed, B.H., Chang, C., Chu, A. and Hao, X., "Effect of temperature on anaerobic fermentative hydrogen gas production from feedlot cattle manure using mixed microflora," *International Journal of Hydrogen Energy*, vol. 33, no. 16, pp. 4301-4308, 2008. DOI: doi:10.1016/j.ijhydene.2008.06.016.

[20] Merola, M.C., Carotenuto, C., Gargiulo, V., Stanzione, F., Ciajolo, A. and Minale, M., "Chemical-physical analysis of rheologically different samples of a heavy crude oil," *Fuel Processing Technology*, vol. 148, pp. 236-247. DOI: 10.1016/j.fuproc.2016.03.001.

[21] Carotenuto, C., Vananroye, A., Vermant, J. and Minale, M., "Predicting the apparent wall slip when using

roughened geometries: A porous medium approach," *Journal of Rheology*, vol. 59, no. 5, pp. 1131-1149. DOI: 10.1122/1.4923405.

[22] Carotenuto, C., Merola, M.C., Álvarez-Romero, M., Coppola, E. and Minale, M., "Rheology of natural slurries involved in a rapid mudflow with different soil organic carbon content," *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, vol. 466, pp. 57-65, 2015. DOI: 10.1016/j.colsurfa.2014.10.037 10.

[23] Minale, M., "Momentum transfer within a porous medium. I. Theoretical derivation of the momentum balance on the solid skeleton," *Physics of Fluids*, vol. 26, no. 12, pp. 123101-1, 2014. DOI: http://dx.doi.org/10.1063/1.4902955.

[24] Minale, M., "Document Momentum transfer within a porous medium. II. Stress boundary condition," *Physics of Fluids*, vol. 26, no. 12, pp. 123101-1-14, 2014. DOI: http://dx.doi.org/10.1063/1.4902956.

[25] Guarino, G., di Cristofaro, F., Carotenuto, C., Morrone, B. and Minale, M., "Effect of thermal and mechanical pre-treatments on the CH4-H2 Production from water buffalo manure in different process conditions," *Chemical Engineering*, vol. 38, pp. 205-510, 2014. DOI: 0.3303/CET1438035.

[26] Khanal, S. K., Chen, W. H., Li, L. and Sung, S., "Biological hydrogen production: effects of pH and intermediate products," *International Journal of Hydrogen Energy*, vol. 29, no. 11, pp. 1123-1131, 2004. DOI: 10.1016/j.ijhydene.2003.11.002.

[27] Zhang, B., Zhao, H., Yu, H., Chen, D., Li, X., Wang, W., Piao, R. and Cui, Z., "Evaluation of biogas production performance and archaeal microbial dynamics of corn straw during anaerobic co-digestion with cattle manure liquid," *Journal of Microbiology and Biotechnology,* vol. 26, no. 4, pp. 739–747, 2016. DOI: http://dx.doi.org/10.4014/jmb.1509.09043.

[28] Aoki, K., Umetsu, K., Nishizaki, K., Takahashi, J., Kishimoto, T., Tani, M., Hamamoto, O. and Misaki, T., "Thermophilic biogas plant for dairy manure treatment as combined power and heat system in cold regions," *International Congress Series*, vol. 1293, no. 03, pp. 238-241, 2006. DOI: 10.1016/j.ics.2006.03.014.

[29] Carotenuto, C., Guarino, G., Minale, M. and Morrone, B., "Temperature and pH effect on methane production from buffalo manure anaerobic digestion," *International Journal of Heat and Technology,* vol. 34, no. 2, pp. S425-S429, 2016. DOI: 10.18280/ijht.34S233.

[30] Schink, B., "Energetics of syntrophic cooperation in methanogenic degradation," *Microbiology and Molecular Biology Reviews*, vol. 61, no. 2, pp. 262-280, 1997.

[31] Angelidaki, I. and Ellegaard, L., "Codigestion of manure and organic wastes in centralized biogas plants," *Applied Biochemistry and Biotechnology,* vol. 109, no. 1, pp. 95-105, 2003. DOI: 10.1385/ABAB:109:1-3:95.

NOMENCLATURE

TS	total solids. %
VS	volatile solids. %
pH_{sub}	original substrate pH.
pH_{in}	pH at the start of the digestion process.
pH_{fin}	pH at the end of the digestion process.
H	cumulative production. %
P	Productivity. %
R_m	maximum production rate. h^{-1}
λ	lag-phase time. h
e	Euler's number.
t	digestion time. h