

Experimental Aspects Connected with Agricultural Biomass Behavior during Anaerobic Fermentation Process

A.E. Cioabla* and G.A. Dumitrel**

*"Politehnica" University of Timisoara, Mechanical Engineering Faculty, Bd. M. Viteazu, No. 1, 300222, Timisoara, Romania, cioablaadrianeugen@yahoo.com

**"Politehnica" University of Timisoara, Faculty of Industrial Chemistry and Environmental Engineering, Victoriei Square, No. 2, 300006, Timisoara, Romania, dumitrelalina@yahoo.com

Abstract: The main focus of this paper is to underline some of the general characteristics of different sorts of biomass related with substrate analysis before the anaerobic fermentation process, influence of external parameters (temperature regime, pH, degradation aspect of the material) during the fermentation and also a correlation between theoretical and experimental results of pH variation related with temperature and time for two different sorts of degraded biomass. The conclusions will underline aspects underlining substrate characteristics, influence parameters and visual observations related with the general aspect of the material during a 40 days period of time.

Keywords: vegetal biomass, anaerobic fermentation, degradation process.

Introduction

In the last decades, biomass was starting to play an important role as an alternative source of energy, while the theoretical and experimental studies increased in number and results were obtained using different types of substrates.

In today's energy demanding life style, need for exploring and exploiting new sources of energy which are renewable as well as eco-friendly is a must. In rural areas of developing countries various cellulosic biomass (cattle dung, agricultural residues, etc.) are available in plenty which have a very good potential to cater to the energy demand, especially in the domestic sector [1].

Details regarding the anaerobic fermentation process as one of the used technologies for obtaining biogas from different types of materials are presented in many materials from literature.

It is considered that the anaerobic fermentation process represents the process of decomposition of organic matter by a microbial consortium in an oxygen-free environment [2-4]. It is a process found in many naturally occurring anoxic environments including watercourses, sediments and waterlogged soils [3].

Anaerobic fermentation could convert complex organic substances in excess sludge into value-added products, such as volatile fatty acids and other low molecular weight soluble carbon compounds [5].

Already established as a reliable technology in Europe and Asia, anaerobic fermentation is used to treat more than 10% of organic waste in several European countries [6].

Anaerobic fermentation processes are classified by critical operating parameters and reactor design such as continuity (batch versus continuous), operating temperature (psychrophilic, mesophilic and thermophilic), reactor design (plug-flow, complete-mix, and covered lagoons), and solid content (wet versus dry) [4].

The biogas production process is complex and sensitive since several groups of microorganisms are involved. The important processes in anaerobic digestion are hydrolysis, fermentation, acetogenesis, and methanogenesis, where hydrolysis is subject to the fermentation process, while acetogenesis and methanogenesis are linked. The hydrolysis step is an extracellular process where the hydrolytic and fermentative bacteria excrete enzymes to catalyse hydrolysis of complex organic materials into smaller units [7].

Once produced, biogas is generally composed of ca. 48–65% methane, ca. 36–41% carbon dioxide, up to 17% nitrogen, <1% oxygen, 32–169 ppm hydrogen sulphide, and traces of other gases [8]. Both carbon dioxide and methane are potent greenhouse gases and possibly 18% of global warming is thought to be caused by anthropogenically derived methane emissions [9]. Carbon dioxide released through natural mineralisation is considered neutral in greenhouse gas terms as the carbon has been recently removed from the atmosphere by plant uptake, to be released again as part of the carbon cycle [3].

Related with the existing literature, the presented study will underline the process parameters and influence factors for two different types of material (degraded two row barley and degraded rye) during anaerobic fermentation in mesophilic conditions (30 - 37°C) in a small scale installation.

2. Experimental

In Figure 1 is presented the general schematics for a small scale installation built in order to analyze some of the process characteristics of different substrates during the anaerobic fermentation process.

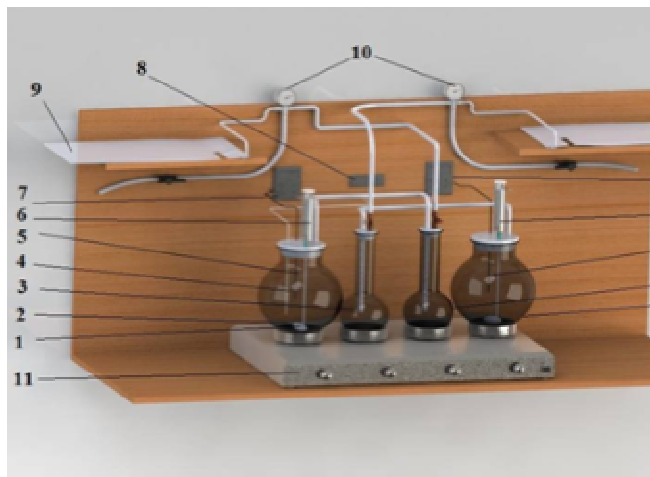


Figure 1. General schematics for the small scale installation

1 – glass reactor with a total volume of 6 l; 2 – magnet placed on the bottom of the 6l glass reactors for magnetic stirring; 3 – small glass reactor for biogas washing with water, with a total volume of 500 mL; 4 – thermocouple; 5 – pH sensors; 6 – system for pH correction and sample collecting; 7 – pH controllers; 8 – temperature controller; 9 – gas bags for biogas samples; 10 – pressure gauges; 11 – heating system.

Working principle of installation: inside the glass reactors (1) is inserted a semi-fluid suspension composed from fine-granulated biomass and water. Each glass reactor has on the bottom part a magnet (2) used for the magnetic stirring process in order to have a relatively homogenous material. From the glass reactors, the formed biogas will pass into the smaller glass reactors (3) half filled with water in order to “wash” the impurities of the biogas.

Each of the glass reactors (1) has inside a pH sensor (5) which is controlled with pH controllers (7), and also a thermocouple (4) controlled with the help of a temperature controller (8) in order to assure the necessary temperature for the process. The installation is equipped with special gas bags (9) in order to take samples if necessary and pressure control with the help of pressure gauges (10) in case of overpressure.

The temperature regime is assured with the help of the heating device (11) which allows 2 batches to be analyzed separately. The installation was built in order to support two batches of material under the same temperature conditions in order to better observe and make comparisons over the general particularities of each used material.

The materials which were used in this study are presented in figures 2 and 3.



Figure 2. Degraded two row barley



Figure 3. Degraded rye

For the analyzed materials there were determined some of the characteristics which are presented in Table 1.

TABLE 1. General characteristics for the two sorts of biomass

No.	Name	Water content [%]	Ash content [%]	Carbon content [%]	Nitrogen content [%]
1	Degraded two row barley	13.0	3.7	45.19	2.18
2	Degraded rye	12.9	2.9	45.74	1.82

From Table 1 it can be observed that the C / N ratio for degraded two row barley is close to 21/1 while for the degraded rye the C/N ratio is around 25/1, being an indicator for the suitability of those materials regarding their potential during the anaerobic fermentation process.

3. Results and Discussion

The two batches of materials were subject to anaerobic fermentation process for a period of 40 days, in which the temperature, pH and general aspect of the material structure was observed.

In Figures 4 and 5 are presented the temperature and pH variation during the 40 days period of time.

From Figure 4 it can be observed that the temperature regime is between 34 and 36 °C with an average value of 35°C which is a corresponding value for the mesophilical temperature regime.

The pH variation presented in Figure 5 shows a starting acid tendency in the first time frame related to the initial biomass pH value which needs to be corrected using lime water and after a period of approximately 10 days the value starts to increase to neutral levels which are maintained until the end of the batch.

Connected with the pH variation there were made some theoretical observations in order to better understand the phenomena. In this direction there were made correlations between pH values and other parameters considered to generate pH variation.

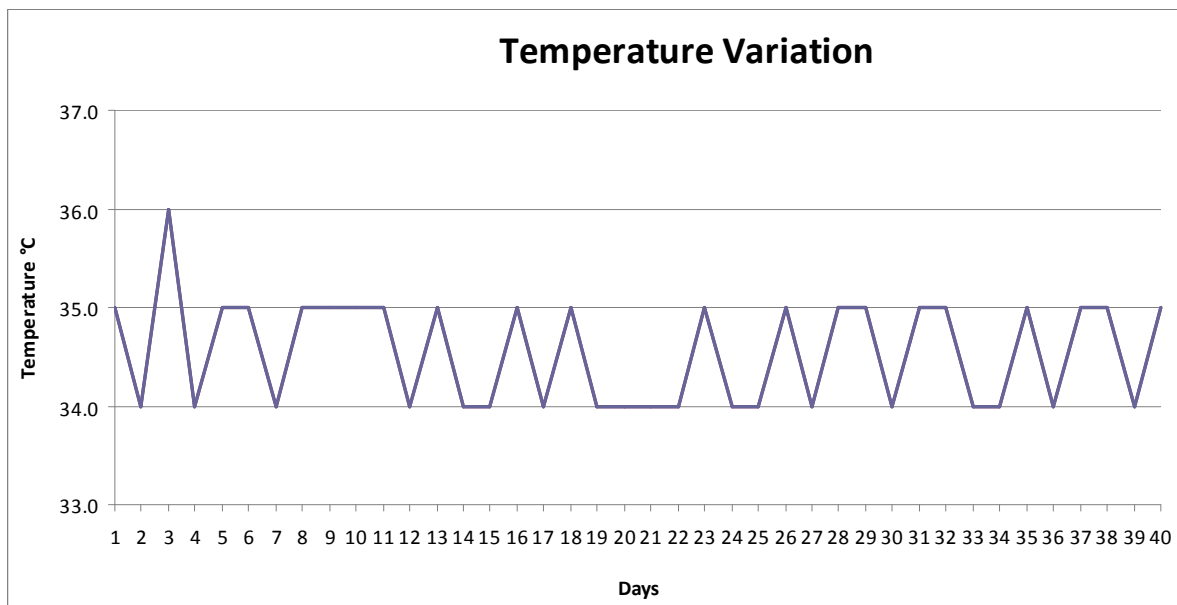


Figure 4. Temperature variation

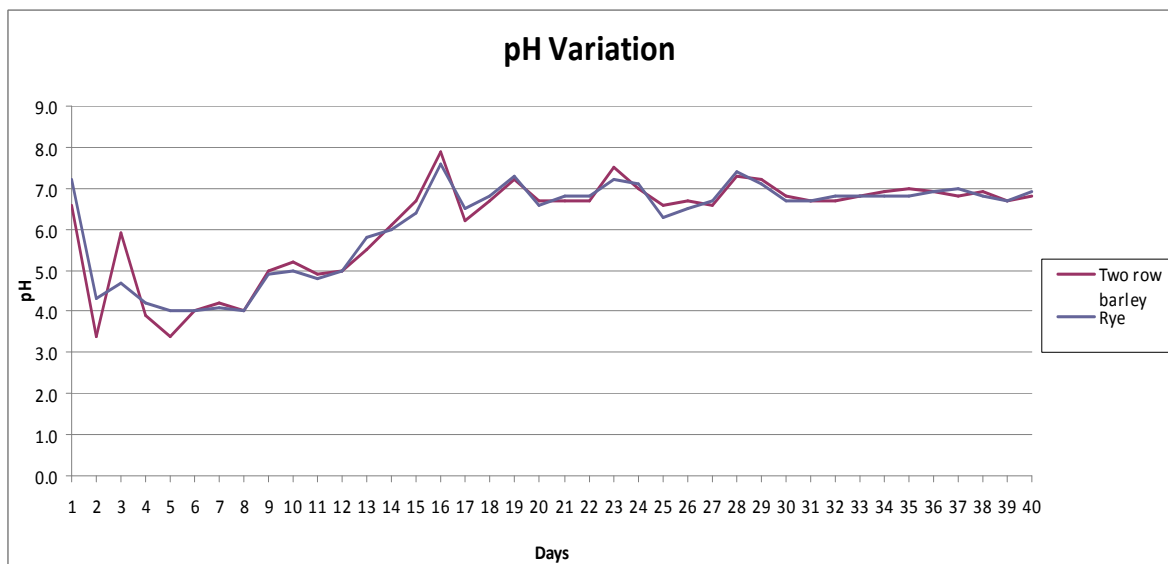


Figure 5. pH variation

For an accurate description of pH variation with temperature and time it was proposed a polynomial equation of second degree expressed by equation 1 [10, 11].

$$y = a_0 + a_1 \cdot x_1 + a_2 \cdot x_2 + a_3 \cdot x_1 \cdot x_2 + a_4 \cdot x_1^2 + a_5 \cdot x_2^2 \quad (1)$$

where: a_i – equation coefficients; y – pH; x_1 – temperature [°C]; x_2 – time, [days].

The coefficients values in the case of second degree polynomial regression are corresponding to the minimum of the function:

$$S = \sum_{j=1}^m (\hat{y}_j - (a_0 + a_1 \cdot x_{1j} + a_2 \cdot x_{2j} + a_3 \cdot x_{1j}^2 + a_4 \cdot x_{1j} \cdot x_{2j} + a_5 \cdot x_{2j}^2))^2 \quad (2)$$

Through annullment of the partial derivates of S function in connection with a_i coefficients, a linear equations system is obtained. The coefficient matrix of the system A and the free coefficients vector, B are:

$$A = \begin{bmatrix} \sum_{j=1}^m 1 & \sum_{j=1}^m x_{1j} & \sum_{j=1}^m x_{2j} & \sum_{j=1}^m x_{1j}^2 & \sum_{j=1}^m x_{1j} \cdot x_{2j} & \sum_{j=1}^m x_{2j}^2 \\ \sum_{j=1}^m x_{1j} & \sum_{j=1}^m x_{1j}^2 & \sum_{j=1}^m x_{1j} \cdot x_{2j} & \sum_{j=1}^m x_{1j}^3 & \sum_{j=1}^m x_{1j}^2 \cdot x_{2j} & \sum_{j=1}^m x_{1j} \cdot x_{2j}^2 \\ \sum_{j=1}^m x_{2j} & \sum_{j=1}^m x_{1j} \cdot x_{2j} & \sum_{j=1}^m x_{2j}^2 & \sum_{j=1}^m x_{1j}^2 \cdot x_{2j} & \sum_{j=1}^m x_{1j} \cdot x_{2j}^2 & \sum_{j=1}^m x_{2j}^3 \\ \sum_{j=1}^m x_{1j}^2 & \sum_{j=1}^m x_{1j}^3 & \sum_{j=1}^m x_{1j}^2 \cdot x_{2j} & \sum_{j=1}^m x_{1j}^4 & \sum_{j=1}^m x_{1j}^3 \cdot x_{2j} & \sum_{j=1}^m x_{1j}^2 \cdot x_{2j}^2 \\ \sum_{j=1}^m x_{1j} \cdot x_{2j} & \sum_{j=1}^m x_{1j}^2 \cdot x_{2j} & \sum_{j=1}^m x_{1j} \cdot x_{2j}^2 & \sum_{j=1}^m x_{1j}^3 \cdot x_{2j} & \sum_{j=1}^m x_{1j}^2 \cdot x_{2j}^2 & \sum_{j=1}^m x_{1j} \cdot x_{2j}^3 \\ \sum_{j=1}^m x_{2j}^2 & \sum_{j=1}^m x_{1j} \cdot x_{2j}^2 & \sum_{j=1}^m x_{2j}^3 & \sum_{j=1}^m x_{1j}^2 \cdot x_{2j}^2 & \sum_{j=1}^m x_{1j} \cdot x_{2j}^3 & \sum_{j=1}^m x_{2j}^4 \end{bmatrix}$$

$$B = \begin{bmatrix} \sum_{j=1}^m \hat{y}_j \\ \sum_{j=1}^m x_{1j} \cdot \hat{y}_j \\ \sum_{j=1}^m x_{2j} \cdot \hat{y}_j \\ \sum_{j=1}^m x_{1j}^2 \cdot \hat{y}_j \\ \sum_{j=1}^m x_{1j} \cdot x_{2j} \cdot \hat{y}_j \\ \sum_{j=1}^m x_{2j}^2 \cdot \hat{y}_j \end{bmatrix} \quad (3)$$

Using MATLAB software the equation system was solved and there were analyzed the experimental data.

The obtained data together with the generated surfaces from the statistical mathematical models are presented in Figures 6.

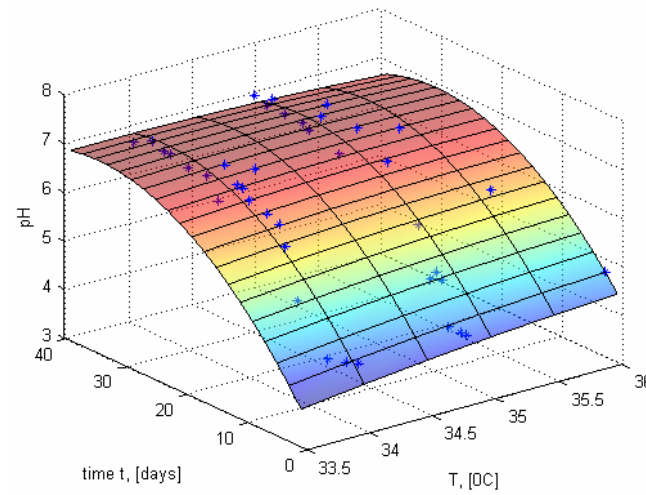


Figure 6. pH evolution in connection with temperature T and time t for a batch containing and degraded two row barley and degraded rye

From the graphics it can be observed that the pH variation has an evolution form acid to neutral or basic levels in time. This process can be explained by the characteristic pH values connected with the phases from

which the material starts to degrade (acid phase) until the biogas production where the degradation process is much more intense and the pH tends for a neutral / slight basic value. Also, in order to assure a corresponding value, during the process was used correction liquid (lime based suspension).

The equation for the obtained mathematical statistical models after the linear multiple regressions are presented in Table 2. They are valid on the studied field of values.

TABLE 2. Equations of the obtained statistical models

Batch	Equation for the statistical mathematical model
Degraded two row barley – degraded rye	$y = - 53.03 + 3.03 \cdot x_1 + 0.48 \cdot x_2 - 0.008 \cdot x_1 \cdot x_2 - 0.04 \cdot x_1^2 - 0.003 \cdot x_2^2$

After the computation of the model coefficients it is necessary to make a comparison between model predictions and experimental data. For adequacy indicators there were used the dispersion and R correlation coefficient (Table 2)

- dispersion :

$$\sigma^2 = \frac{\sum_{i=1}^n (y_{i \text{ exp}} - y_{i \text{ calc}})^2}{n - 1} \quad (4)$$

- R correlation coefficient:

$$R = \sqrt{1 - \frac{\sum_{i=1}^n (\hat{y}_i - y_{i \text{ calc}})^2}{\sum_{i=1}^n (\hat{y}_i - \bar{y})^2}} \quad (5)$$

TABLE 3. Adequacy indicators for determined statistical model

Batch	Dispersion, σ^2	Correlation coefficient, R
Degraded two row barley – degraded rye	0.5079	0.7747

The values for the presented adequacy coefficients in Table 3 are indicating a satisfactory correlation between the determined statistical model and experimental data. This confirms the fact that obtained mathematical equations describe with sufficient accuracy the pH evolution in time as a function of temperature.

During the 40 days period of time the general aspect of the material was observed with the help of a microscope at a period of 10 days in order to better observe the degradation rate of the material. Those pictures are presented in Figures 7 to 16.



Figure 7. Degraded two row barley 10X – first stage



Figure 8. Degraded rye 10X – first stage



Figure 9. Degraded two row barley 15X – second stage

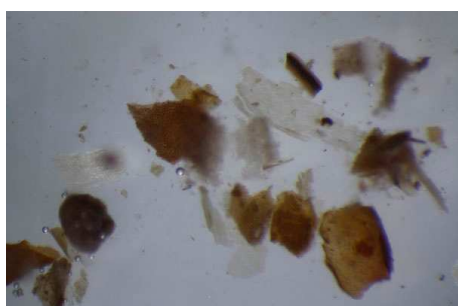


Figure 10. Degraded rye 15X – second stage



Figure 11. Degraded two row barley 40X – third stage

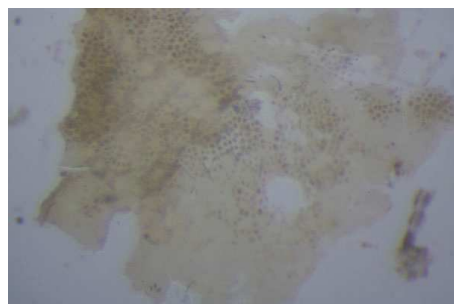


Figure 12. Degraded rye 40X – third stage



Figure 13. Degraded two row barley 40X – fourth stage

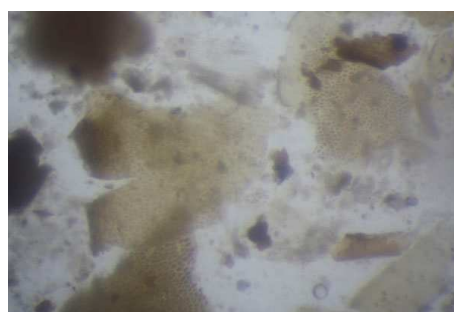


Figure 14. Degraded rye 30X – fourth stage

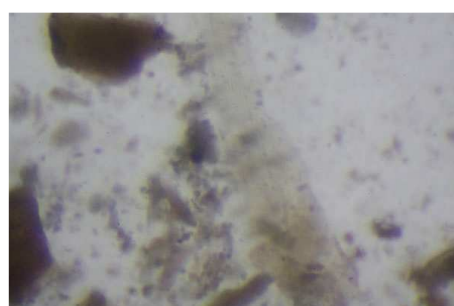


Figure 15. Degraded two row barley 50X – final stage

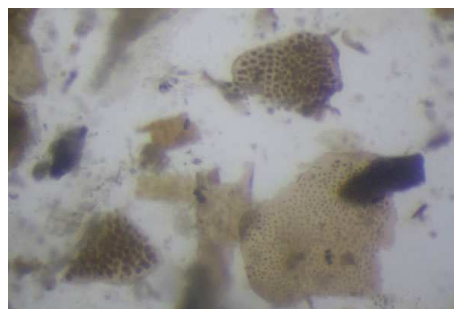


Figure 16. Degraded rye 40X – final stage

From the figures presented above one can observe the gradual degradation process which takes place inside the substrates. First figures (7 and 8) present the material unaltered by bacterial influence. The general structure and color is constant in the batch mass. The second set of pictures (9 and 10) underlines the beginning of the degradation process, the material is still colored and the general aspect is relatively unchanged. This suggests that the process has a slow evolution related with the temperature and pH influence. In the third stage (Figures 11 and 12) it can be observed that the degradation process has evolved, the general structure of the material is deteriorating, the color starts to disappear in some areas, which is a sign of preferential degradation inside the mass of material. The fourth stage (Figures 13 and 14) underlines an extended degradation process in all the mass of the batch, the cellular structure of material without color and superficial layers can be observed in detailed images as a sign of advanced stage of degradation. In the last phase (Figures 15 and 16) one can observe that the material is attacked by bacterial formations, cellular aspect is revealed, impurities from the degradation process are presented and the general structure is without any color related to the beginning of the process. This is a good indicator that the fermentation process takes place in good conditions.

4. Conclusions

Cereal degraded materials can be used in anaerobic fermentation processes with good results related to the behavior during the fermentation and potential in obtaining biogas in large quantities and good quality in larger scale installations.

It has to be kept in mind that the general properties of the material (C/N ratio for example) are good indicators of the general potential during the anaerobic fermentation.

The correlation between the theoretical and experimental results shows a good evolution of pH in time related with the temperature regime that was chosen in the presented case.

Both batches of material have shown good indicators of degradation from a visual point of view with a relative preferential degradation of the starch based structure relative to the external part of the grains which is denser and harder to degrade.

ACKNOWLEDGMENTS

This paper was supported by the project "Development and support of multidisciplinary postdoctoral programmes in major technical areas of national strategy of Research – Development – Innovation" 4D-POSTDOC, contract no. POSDRU/89/1.5/S/52603, project co-funded by the European Social Fund through Sectorial Operational Programme Human Resources Development 2007-2013.

REFERENCES

1. Yadvika S., Sreekrishnan T.R., Sangeeta K. and Vineet R., *Bioresource Technol.*, 95, **2004**, 1 – 10.
2. Pain B.F. and Hephred R.Q., In: Pain, B.F., Hephred, R.Q. (Eds.), *Anaerobic Digestion of Farm Waste*. NIRD Technical Bulletins, Reading, **1985**, pp. 9–14.
3. Ward A.J., Hobbs P.J., Holliman P.J. and Jones D.L., *Bioresource Technol.*, 99, **2008**, 7928 – 7940.
4. Yebo L., Park S. Y. and Zhu J., *Renewable and sustainable energy reviews*, 15, **2011**, 821 – 826.
5. Elefsiniotis P. and Oldham W.K., *Biotechnol. Bioenerg.*, 44, **1994**, 7–13.
6. De Baere L., *Water Sci. Technol.*, 41(3), **2000**, 283–290.
7. Karellas S., Boukis I. and Kontopoulos G., *Renewable and sustainable energy reviews*, 14, **2010**, 1273 – 1282.
8. Rasi, S., Veijanen, A. and Rintala, J., *Energy*, 32, **2007**, 1375–1380.
9. Ghosh, S., In: 8th International Conference on Anaerobic Digestion., Sendai International Center, Sendai, Japan **1997**, 9–16.
10. Todinca T. and Geanta M., *Modelarea si simularea proceselor chimice. Aplicatii in MATLAB*, Politehnica, Timisoara, **1999**.
11. Borse G.J., *Numerical Methods with MATLAB®*, PWS Publishing Company, Boston, **1997**.

Received: 18 February 2011

Accepted: 25 October 2011