Modeling of anaerobic digestion of Canary grass

Anna Kacprzak [1]*, Liliana Krzystek L., Stanisław Ledakowicz *

[1]*Department of Bioprocess Engineering, Faculty of Process and Environmental Engineering, Technical University of Lodz, Wolczanska 213, 90-924 Lodz, Poland.*

**Corresponding author: anna.kacprzak@wipos.p.lodz.pl, tel. +48 42 631 36 97, fax. +48 42 631 37 38.*

Keywords: biochemical methane potential, Canary grass, biogas

Biological conversion of biomass (energy crops, agricultural waste) and various organic waste (organic fraction of the municipal solid waste-OFMSW) for continuous production of renewable energy-biogas has a great potential in order to reduce carbon dioxide (CO_2) emissions and to protect the environment [1]. During the last few decades, anaerobic digestion of organic matter has been presented as a suitable technology used for treatment of organic wastes and production of biogas [2]. In anaerobic digestion, co-digestion is the term used to describe the combined treatment of several wastes with complementary characteristics, being one of the main advantages of the anaerobic technology. There is abundant literature about utilization of co-digestion, such as co-digestion of OFMSW and agricultural residues, organic solids wastes or more specific wastes [2].
Energy crops, i.e. plants grown specifically for the purpose of producing energy, are a carbon-neutral source of domestic renewable energy. The most important parameter in choosing crops for methane production in net energy per hectare, which is defined mainly by biomass yield and convertibility of the biomass to methane [4]. A Biochemical Methane Potential (BMP) assay provides a measure of the anaerobic digestibility of a given substrate. The use of BMPs provides a relatively inexpensive and repeatable method to make relative comparisons of the anaerobic digestibility and potential biogas production between various substrates. Biochemical methane potential assays are used to 1) determine the concentration of organics in a wastewater that can be anaerobically converted to CH_4, 2) to evaluate the potential efficiency of the anaerobic process with a specific wastewater, 3) to measure residual organic material amenable to further anaerobic treatment, and 4) to test for non-biodegradables remaining after treatment [5]. Literature related to BMP assays for agricultural wastes shows that these assays have been widely used. Labatut and Scott (2008) used BMPs to determine which available food residues could be co-digested with manure from a dairy and at what ratio the residue should be mixed to improve the economic viability of the on-farm digester. Similarly, BMPs were used by Lovanh et al. (2008) to determine the effect amending swine manure with poultry litter had on methane production rates. Kirk and Bickert (2004) utilized BMPs to evaluate manure slurry from multiple points in a dairy manure treatment system to determine the optimal location of the digester within the treatment system for maximum gas production and pathogen reduction [5].
In the anaerobic fermentation it is necessary to maintain proper composition of the feedstock for efficient plant operation, thus the C:N ratio in feed should remain within desired range. It is generally found that during anaerobic digestion microorganisms utilize carbon 25–30 times faster than nitrogen [9]. Co-digestion can improve an important nutrient balance by adding large quantity of carbon being readily degradable and as a result an increase of biogas yields and the quality of fertilizer [3].
The benefits of codigestion also include dilution of potential toxic compounds, synergistic effects of microorganisms and increased load of biodegradable organic matter (Sosnowski et al., 2003). In the literature many examples of the successfully conducted co-fermentation processes of different substrates can be found [3]. The anaerobic co-digestion of OFMSW and fats of animal and vegetable origin was examined by Fernandez et al. (2005). Lehtomäki et al. (2007) studied co-digestion of energy crops and crop residues with cow manure. Bouallagui et al. (2009) worked on

the improvement of fruit and vegetable waste anaerobic digestion performance and stability with co-substrate addition.
The knowledge of the anaerobic co-digestion has significantly expanded, nonetheless, more research is needed on the effects of various compositions of co-substrates and their influence on the process stability [10,11]. This is why the presented investigations aimed not only at extension of the anaerobic co-digestion potential, but also at optimization. Kinetic models may be a useful tool to optimize co-digestion processes [12]. A model can be defined as a set of relationships between the variables of interest in the system being investigated. It may be expressed in the form of equations [3,13]. This paper presents results of both BMP assay of Canary grass (*Phalaris canariensis)* and its co-digestion with cheese whey and glycerin fraction in large laboratory scale as well as mathematical modelling of such quasi-continuous anaerobic co-digestion and batch anaerobic digestion processes.

MATERIALS AND METHODS

1. BMP assays

The BMP assays of Canary grass from first and second swath were determined in batch experiments in 1 dm^3 glass bottles (liquid volume 0.5 dm^3) incubated statically at 37±1°C, Figure 1. The crops material was used in the form of silage.

Inoculum (sludge after anaerobic digestion) and substrate were added into the bottles, distilled water was refilled to produce a liquid volume of 0.5 dm3. The contents of the bottles were flushed with N_2/CO_2-gas for 5 minutes and the bottles were then sealed with rubber stoppers. Daily methane production from each digester was measured by using a water displacement. Biogas production is given in norm litre per kg of volatile solids (Ndm^3 kg^{-1} VS). The content of methane and carbon dioxide was performed using gas analyzer LMS GAS DATA. The bottles were shaken at 80 rpm. The reactors ran until no further methane production could be detected.

Figure 1. Experimental set-up

2. Co-digestion process

The process of co-fermentation of Canary grass and cheese whey together with waste glycerin fraction was carried out in 25dm^3 bioreactor operated mesophically in quasi-continuous mode, Fig. 2. Inoculum (sludge after anaerobic digestion) came from anaerobic digestion chambers of Municipal Wastewater Treatment Plant in Lodz, Poland.

The mixture of substrates (Canary grass, whey, glycerin fraction) in specified weight ratio was fed to the digester once a day, after withdrawing the same amount of fermentation broth. Every three days the ratio was increased in percentages until the highest yield of biogas and methane content were obtained. When the steady state was reached the sample from the bioreactor was taken every 1 hour during day and night (the 24-hour-period between feeding) and analyzed. Basing on this experimental data the kinetic model was proposed.
Mixed samples drawn from the bioreactor was measured to determine:
volatile fatty acids (steam distillation - BÜCHI B-324, chemical oxygen demand (COD) on centrifuged samples (Hach-Lange, method 435).
Continuously – biogas flow rate (flowmeter Ritter) and pH (pH-meter electrode WTW pH 540 GLP) were measured and biogas content (gas content analyzer LMS GAS DATA).

Figure 2. Bioreactor scheme: *1-stub pipe for pouring the fermentation broth ; 2-heating jacket; 3-thermostating system; 4-stirrer; 5-valve for fermentation broth withdrawal; 6-Biogas meter Ritter; 7- Redox and pH electrodes*

RESULTS AND DISCUSSION

1.Biochemical Methane Potential (BMP) assays

Data obtained from batch anaerobic processes was used to determine the kinetics of methane production. In table 1 the yields of biogas and methane production are presented.
When calculated against wet weights, the methane yields from first and second swath were similar 55 and 47 Ndm^{3}CH$_4$/kg wet weight, respectively, in contrary to biogas yield, which was significantly higher from the first swath 102 Ndm^3/kg wet weight, comparing to that from the second one: 66 Ndm^3/kg wet weight.

Table 1. The yield of biogas production

	BIOGAS			METHANE		
	Ndm^3/ kg wet weight	Ndm^3/ kg dry weight	Ndm^3/ kg VS	Ndm^3CH_4/ kg wet weight	Ndm^3CH_4/ kg dry weight	Ndm^3CH_4/ kg VS
Canary grass I	102	551	622	55	295	333
Canary grass II	66	223	266	47	158	189

The cumulative methane production data from the experiments was fitted to the modified Gompertz equation that describes the cumulative methane production in batch assays assuming that CH_4 production is a function of bacterial growth, i.e.

$$M = P \times \exp\left\{-\exp\left[\frac{R_m \times e}{P}(\lambda - t) + 1\right]\right\} \quad (1)$$

where M is cumulative methane production, P the methane production potential [ml], R_m the maximum methane production rate (ld^{-1}), λ the duration of lag phase and t is the duration of the assay at which cumulative methane production M is calculated [9].

Fitting the kinetic model to the experimental data and the estimation of kinetic parameters was carried out in MATLAB software. The equations were integrated using the ODE45 solver, which is a built-in function in MATLAB. Table 2 shows the values of kinetic parameters obtained by fitting the model to experimental data with their corresponding standard deviations. The high values obtained for R^2 demonstrates the suitability of the proposed model for the realistic estimation of the anaerobic digestibility of the given substrate.

Table 2. Summary of kinetic parameters

	Canary Grass I	Canary Grass II
P [ml]	648.44	223.21
R_m [dm^3CH_4/d]	15.64	18.47
λ [day]	14.67	1.75
R^2	0.99256	0.99952

Figures 3 and 4 show fitting of the the kinetic model to experimental data for Canary grass I and II respectively. The proposed model describes well the production of biogas.

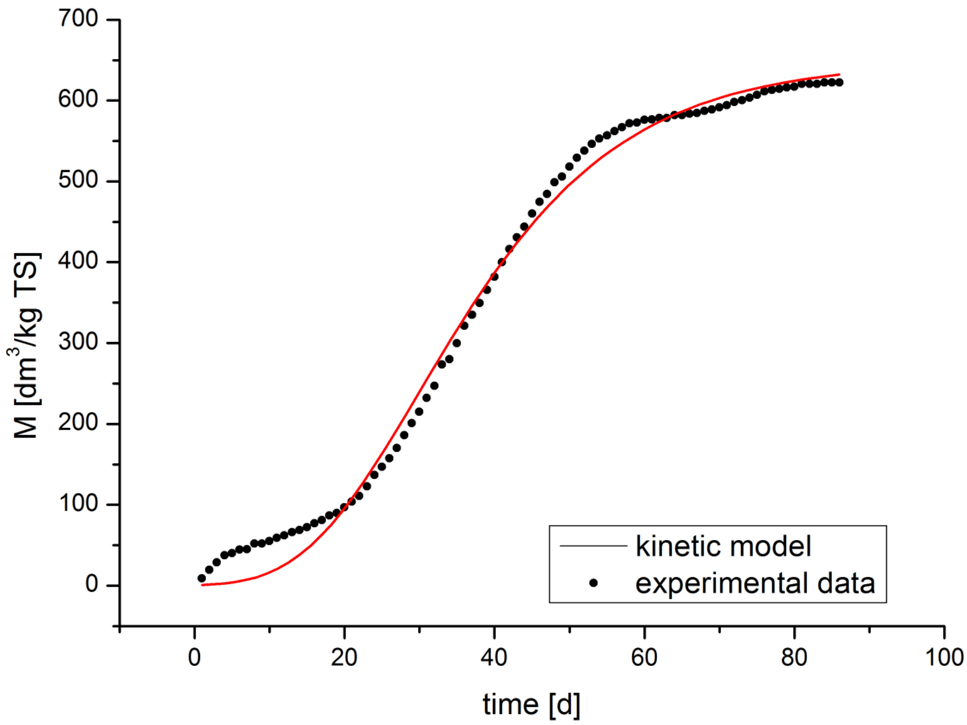

Figure 3 Fitting of experimental data to the kinetic model (Canary grass I)

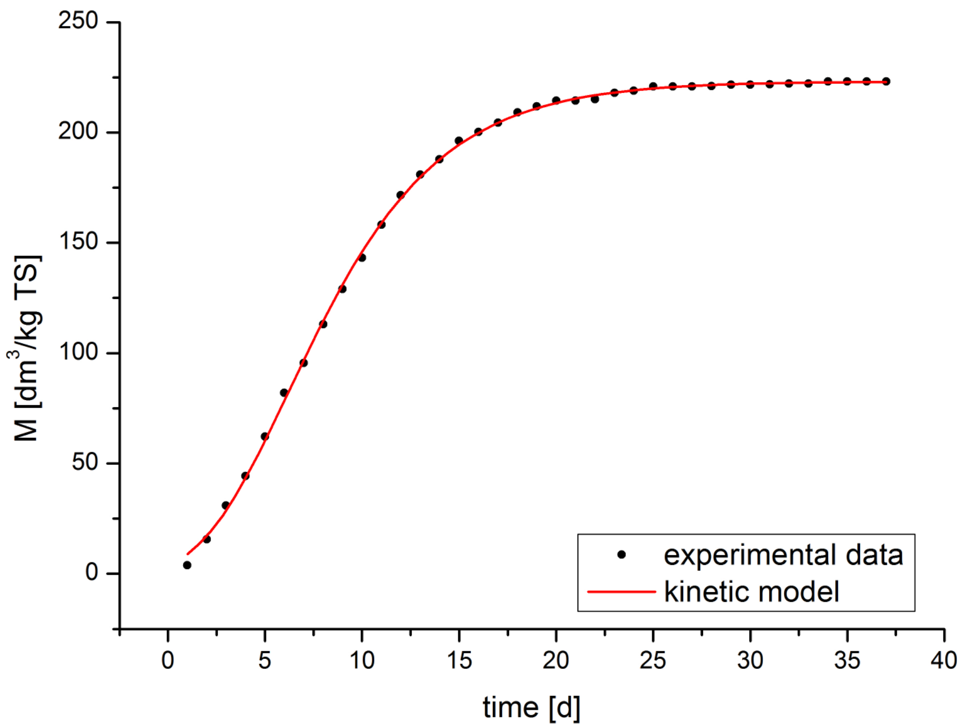

Figure 4 Fitting of experimental data to the kinetic model (Canary grass II)

3. **Co-digestion process**

The experiments of co-digestion of Canary grass I with cheese whey and glycerin fraction were performed. On the basis of the experimental data obtained on the way of the co-digestion processes the kinetic model describing changes of organic carbon and was proposed.
Fitting kinetic models and the estimation of kinetic parameters were made using the optimization procedure which combines the Gauss Newton method and quasi-Newton - called DFNLP (Schittkowski, 1998), built-in program EasyFit (Schittkowski, Germany). This procedure requires the boundary conditions - initial ones. As the initial conditions experimental data determined at the start of processes was assumed. Selected optimization method consisting in finding the minimum deviation calculated as the sum of squared deviations from the experimental data from the function divided by the sum of the squares of the experimental data - equation (1).

$$R = \frac{\sum_{j=1}^{n}\sum_{i=1}^{m}\left(y_{ji} - f_j(x_i,k)\right)^2}{\sum_{j=1}^{n}\sum_{i=1}^{m} y_{ji}^2} \qquad (1)$$

Other calculations were performed using Microsoft Excel 97
The rate of oxidation of dissolved organic matter to volatile fatty acids is treated as a significantly higher than the rate of hydrolysis - volatile fatty acids (A) are formed directly by hydrolysis of organic matter contained in the fermented plant material (S). Similarly acetogenesis and methanogenesis are described as a single stage - biogas (G) is formed from volatile fatty acids. Generally, it was assumed that the substrate undergoes the following changes:

$$S \text{ (solid)} \rightarrow A \text{ (liquid)} \rightarrow G \text{ (gas)} \qquad (2)$$

Assumed that the hydrolysis process is a reaction of pseudo-first order reaction - equation (3), while the process of methane production takes place with the participation of methane bacteria.

$$\frac{dS}{dt} = -k_S \cdot S \qquad (3)$$

During the first trials of fitting of the model to experimental data it was found that the saturation constant has reached very high values. Therefore, an attempt to describe the production of biogas as a pseudo-first order reaction. As a result, biogas production is described by equation (4).

$$\frac{dG}{dt} = k_A \cdot A \qquad (4)$$

Changes in the concentration of volatile organic acids have been described by the equation:

$$\frac{dA}{dt} = k_S \cdot S - k_A \cdot A \qquad (4)$$

All the values have been converted to mgC • dm^{-3}. In the course of the process one did not determined the organic matter content in the fermented plant material. Changes in the amount of carbon contained in it, was estimated by the following equation:

$$S = S_o - A - G \qquad (5)$$

This model with sufficient precision describes the experimental data - the value of the sum of squared deviations of experimental data on the value of the function of a numerical simulation was less than 0.02. Figure 5 also confirms the good agreement of numerical simulation results with experimental data - a model well describes the increase in concentrations of VFA and its use for biogas production.

In Table 3 the values of the kinetic constants obtained from the adjustment of the model to the experimental data are presented. The kinetic model which is proposed defines the experimental data in a satisfactory way.

Table 3. Kinetic constants

	Process 1	Process 2
k_S	1,2	1,2
k_A	0,03	0,04
Residuals [-]	0,0150	0,0079

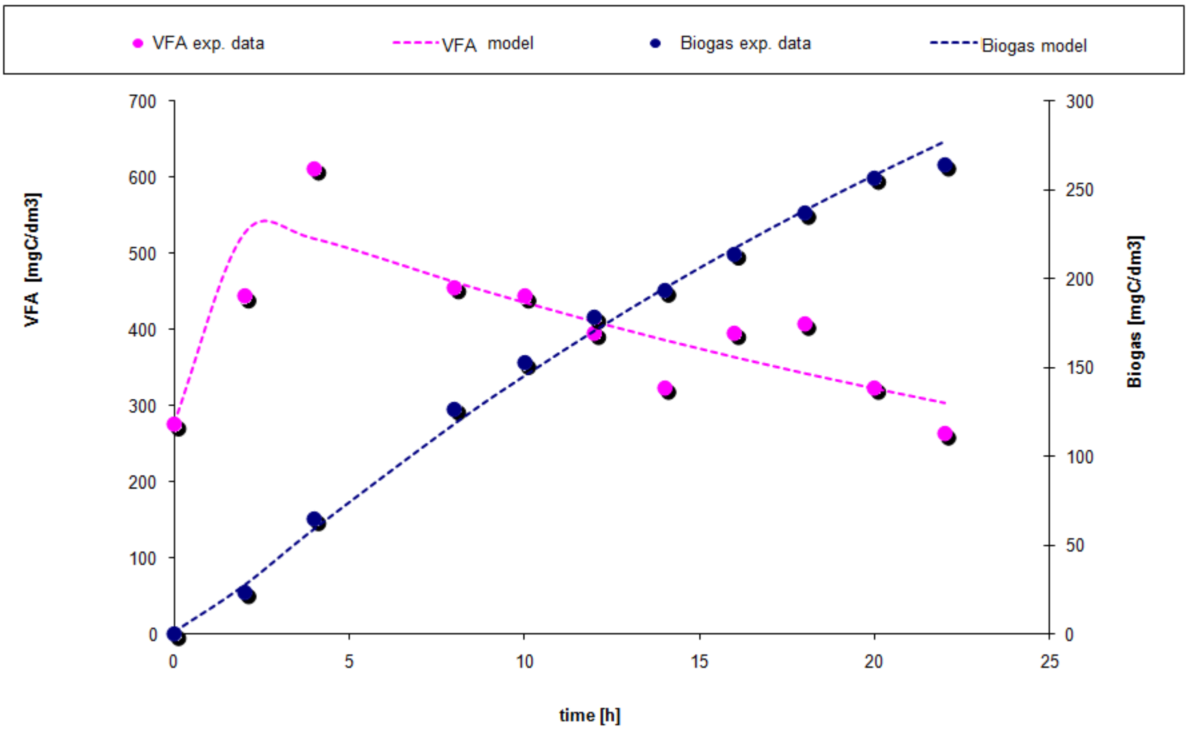

Figure 5. Adjustment of the kinetic model with the experimental data

CONCLUSIONS

Anaerobic digestion benefits have led to increased interest and use of the technology. However, capital costs of anaerobic digestion systems are high and careful planning and accurate system design are necessary to optimize performance and maximize return. Biochemical methane potential assays (BMPs) provide a realistic estimate of the anaerobic digestibility of a given substrate.

The proposed kinetic models defined the experimental data in a satisfactory way and was validated with the real anaerobic co-digestion process. The models can be useful instruments for the prediction of the process performance and the behavior of methane digestion.

References

[1] Demirel B., Scherer P. (2009) Bio-methanization of energy crops through mono-digestion for continuous production of renewable biogas. Renewable Energy 34, 2940-2945

[2] Fernández A., Sánchez A., Font X. (2005) Anaerobic co-digestion of a simulated organic fraction of municipal solid wastes and fats of animal and vegetable origin. Biochemical Engineering Journal 26, 22-28.

[3] Sosnowski P., Klepacz-Smółka A., Kaczorek K., Ledakowicz S. (2008) kinetic investigations of methane co-fermentation of sewage sludge and organic fraction of municipal solid waste. Bioresource Technology 99, 5731-5737.
[4] Lehtomäki A., Viinikainen T.A., Rintala J.A. (2008) Screening boreal energy crops and crop residues for methane biofuel production. Biomass and Bioenergy 32, 541-550.
[5] Moody L., Burns R., Wu-Haan W, Spajiš R. (2009) Use of Biochemical Methane Potential (BMP) Assays for Predicting and Enhancing Anaerobic Digester Performance. 44th Croatian & 4th International Symposium on Agriculture.
[6] Labatut, C., Scott N. (2008) Experimental and predicted methane yields from the anaerobic co-digestion of animal manure with complex organic substrates. ASABE Paper No. 085087. St. Joseph, Mich. U.S.A. ASABE.
[7] Lovanh N., Loughrin J., Ruiz-Aguilar G., Sistani K. (2008) Evaluation of methane potential from swine slurry with poultry litter amendments. ASABE Paper No. 083989. St. Joseph, Mich. U.S.A. ASABE.
[8] Kirk D., Bickert W. (2004) The use of biochemical methane potential tests to evaluate the digestibility of processed dairy manure. ASABE Paper No. 044066. St. Joseph, Mich. U.S.A. ASABE.
[9] Yadvika, Santosh (2004) Enhancement of biogas production from solid substrates using different techniques – a review. Bioresource Technology, 95, 1–10.
[10] Murto, L., Bjornsson, B., Mattiasson, (2004) Impact of food industrial waste on anaerobic co-digestion of sewage sludge and pig manure. J. Environ. Management, 70, 101–107.
[11] Gelegenis, J., Georgakakis, D., Angelidaki, I., Christopoulou, N., Goumenaki, M., (2007) Optimization of biogas production from olive-oil mill wastewater, by codigesting with diluted poultry-manure. Appl. Energ. 84, 646–663.
[12] Gavala, N.H., Angelidaki, I., Ahring, B.K.(2002) Kinetic and modeling of anaerobic digestion process. Adv. Biochem. Eng. Biotechnol. 81, 57–93.
[13] Coker, K.A. (2001) Modeling of Chemical Kinetics and Reactor Design. Gulf Professional Publishing.