Evaluation by Kinetic Models of Anaerobe Digestion Performances for Various Substrates and Co-substrates

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Anaerobic digestion is a complex process that allows the conversion of organic wastes into biogas with minimal costs and benefits for the environment. The goal of this study is to evaluate the anaerobic digestion potential of two common agricultural biomass wastes (degraded corn and degraded wheat) used as single substrates or as co-substrates together with wastewater from a waste water treatment plant. The results reveal that the co-digestion is an improved solution, both in terms of biogas amount produced and its methane concentration. Two kinetic models (modified Gompertz model and logistical growth model) were applied to study the methane production. For each case, the kinetic parameters were estimated. One demonstrates that the modified Gompertz model fitted very well the measured methane potential, for all studied cases.

Keywords: anaerobic digestion, waste biomass, biogas, digestion potential, kinetic models

According to the National Institute of Statistics, 61.3% of the Romanian territory is covered with agricultural lands (arable, orchards and vineyards, pasture and meadows) [1]. Due to this fact, agricultural biomass (such as animal and vegetable wastes) is produced in a significant amount. According to the Romanian Association of Biomass and Biogas (ARBIO), in 2014, Romania produces 200 million tons of wastes. However, biomass and biogas have a share of only 0.62% of the total energy source generated in the country [2].

In the past few years, Romania has been supported by the European Union to build wastewater treatment plants. From this process results sludge, waste which is a valuable raw material for anaerobic digestion. In Romania, only 2% of sludge from wastewater treatment plants (estimated at a total of approximately 171 086 t/year) is used in agriculture and the rest is disposed to landfills or stored inside the plants [3]. These options are not sustainable to be applied further as they do not fit to sustainable development option; neither are allowed by European regulations. Anaerobic digestion of sludge can thus be a valuable solution and option to contribute efficiently to the decrease of organic waste deposits and to the production of biogas [4-7], as a country specific renewable resource.

It is fully attested that Romania has a considerable biomass reserve - formed mainly from wood waste, agricultural waste, domestic waste and energy crops – that can represent a valuable renewable energy resource.

Anaerobic digestion is a capitalization alternative of these organic wastes. By using this technique, the organic wastes are converted to biogas, a fuel mainly composed by methane and carbon dioxide [8-11].

Mathematical modeling is a valuable tool used to predict methane production during anaerobic digestion. It allow to investigate the influence of different parameters on biogas quantity and quality and thus to optimize the process without performing expensive and time-consuming experiments. In the literature are found different types of mathematical models [12-17].

The aim of this study was to investigate the anaerobic digestion biogas potential of two common agricultural biomasses used as single substrates or as co-substrates together with wastewater from a treatment plant. Based on experimental data obtained in the pilot plant, a series of kinetic models were developed in order to predict the methane production of investigated substrates in batch anaerobic digesters under mesophilic conditions.

Experimental part

Substrates

Two agricultural biomasses (degraded corn – C and degraded wheat - W) were tested for their biogas production – as single substrates or as co-substrates with wastewater from treatment plant (WTP) – in a pilot plant anaerobic digestion system.

Description of the Pilot Plant

The pilot plant anaerobic digestion system used for the studies is presented in figure 1. The operation of the plant is describe in previous articles [18].

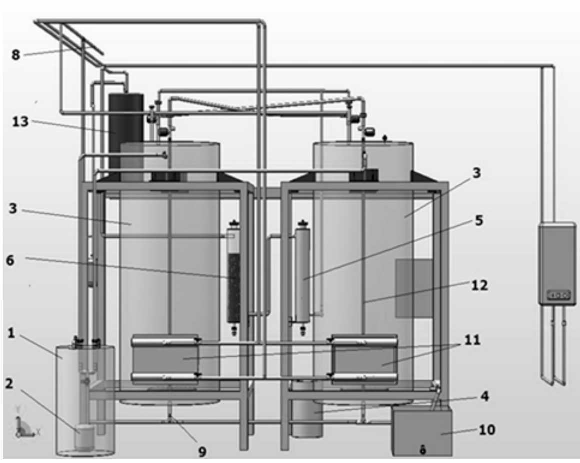

Fig. 1. Pilot plant anaerobic digestion system

where: 1- tank for biomass suspension preparation; 2- pump; 3 - fermentation batch reactors; 4 - tank with *p*H correction agent; 5 – filter for H_2S removal; 6 - CO_2 retention system; 8 -pipes; 9- system for digestate download; 10 - system for neutralization of digestate solid fraction; 11- temperature controllers; 12 - bubbling system; 13- tank for

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biogas collection.

The reactors were operated under mesophilic temperature conditions. 75 kg of dry biomass and 2000 Liter water were used to prepare the suspension for anaerobic digestion. The quantity of biogas produced was measured daily. The temperature was measured with J thermocouple continuously, controlled with temperature controllers (AD-025V2DS-C). The *p*H value was detected and controlled by a pH sensor (HI 1210) and a pH controller (BL 981411).

Mathematical models

The mathematical models used to calculate and compare the methane production during anaerobic digestion of different substrates are [19]:

a)Logistical growth model

$$M = M_p/(1 + b * \exp(-k * t)) \quad (1)$$

where: M is the cumulative equivalent methane yield at time t, in m^3, M_p is the methane production potential in m^3, b is a dimensionless constant, k is kinetic hydrolysis reaction rate constant, day^{-1}, t is the time, expressed in days of the process, and exp(1) is 2.7183.

b)The modified Gompertz model [16]:

$$M = M_p * \exp(-\exp(R_m * \exp(1)/M_p * (\lambda - t) + 1)) \quad (2)$$

where: M is the cumulative equivalent methane yield at time t, m^3, M_p is the methane production potential, m^3, R_m is the maximum methane production rate, m^3/days, λ is the period of lag phase, days, t is the time expressed in days of the process, and exp(1) =2.7183.

The parameters of the model were calculated by non-linear unconstrained optimization method, using the Nelder-Mead algorithm, which minimizes a scalar-valued nonlinear function of *n* real variables, by using only function values [20, 21].

One applied Matlab R2008b (version 7.7.0.741) software in order to determine the mentioned parameters. The quality and appropriation of the model were first evaluated graphically and further, the Pearson correlation coefficient (r) and the root mean square deviation (RMSD) were calculated.

Results and discussions

The cumulative biogas production during anaerobic digestion of the substrates investigated is presented in figure 2.

According to data presented in figure 2, the biogas production for degraded corn mixed with wastewater from treatment plant (CWTP) and degraded wheat mixed with wastewater from treatment plant (WWTP) started very quickly, already in the second day of the digestion process.

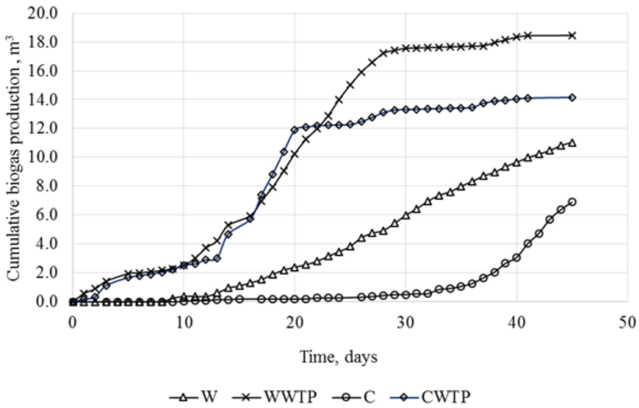

Fig. 2. Cumulative biogas production during anaerobic digestion

The CWTP and WWTP showed a low biogas production until day 9, when both digestion reactors reached a cumulative biogas production of 2 m^3. After day 9, the biogas production from CWTP and WWTP digesters increased slowly and reached by day 45 a value of 14.5 m^3 biogas for CWTP and, respectively, 18.5 m^3 of biogas for WWTP. By comparative analyzing the fermentation process of degraded corn (C) and degraded wheat (W), one notices that the biogas production started very late (in the 9th day of the process). The degraded wheat digestion (W) reached a cumulative biogas production of 2 m^3 by day 19, while for the degraded corn (C) 38 days were needed ,to reach a cumulative biogas production of the same amount (2 m^3).

The amount of biogas generated after 45 days of anaerobic digestion varies with the substrate used, in the following order (from high to low): WWTP, CWTP, W, C.

The methane content of biogas produced during anaerobic digestion of investigated substrates is presented in figure 3.

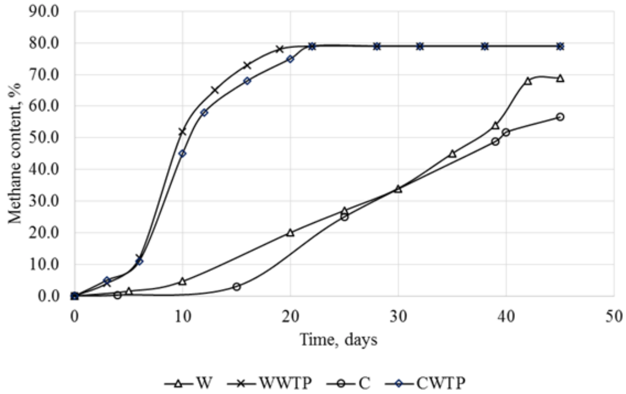

Fig. 3. Methane content of biogas produced during anaerobic digestion

The methane content of biogas increased rapidly for CWTP and WWTP until day 22, when it reached the maximum value of 79 % from biogas content. Concerning the other substrates (C and W), the methane content in the biogas had a slowly evolution. The lowest concentration of methane was found in biogas produced from anaerobic digestion of degraded corn. The methane concentration in the biogas produced from anaerobic digestion of degraded wheat was a little bit higher that in the case when the biogas was generated by the degraded corn digestion.

In order to calculate and compare the methane production during anaerobic digestion of investigated substrates, two mathematical models were used: logistical growth model and modified Gompertz model [16,19].

The results of logistical growth models together with the experimental results are presented in figure 4. The model parameters and the values of model performances are presented in table 1.

By analyzing figure 4 and table 1 it is noticed that the logistical growth model describes very well the methane production during anaerobic digestion of degraded wheat (W) and degraded wheat mixed with wastewater from a water treatment plant (WWTP). The methane production potential for these two co-substrates (W and WWTP) is closed to the experimental quantity of the produced methane. The kinetic hydrolysis reaction rate constant is higher for the case when using WWTP than for W. In reference to the other two co-substrates (C and CWTP), the experimental data showed inferior agreements with the model results.

The results of modified Gompertz models, as well the experimental results are presented in figure 5. The model

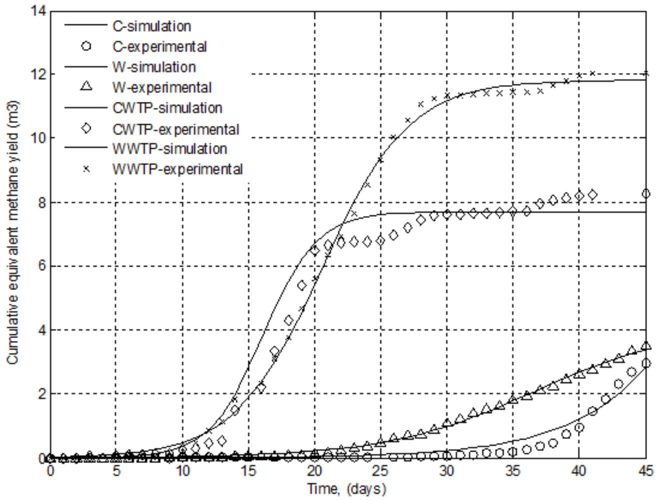

Fig. 4. Experimental data (different markers) and logistical growth models (solid lines) for methane production during anaerobic digestion of investigated substrates

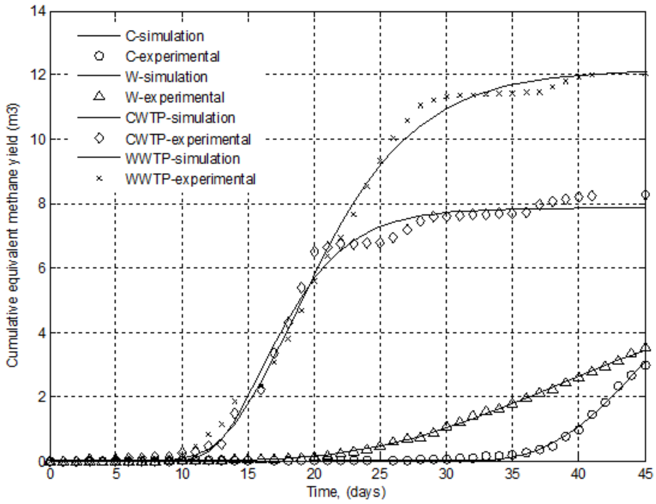

Fig. 5. Experimental data (different markers) and associated modified Gompertz models (solid lines) for methane production during anaerobic digestion of investigated substrates

parameters and the values of model performances are presented in table 2.

Figure 5 and table 2 highlight that the highest methane production potential is exhibited by degraded wheat mixed with wastewater from a WWTP. Further, the production is attested, at lower quantities, by using degraded corn mixed with wastewater (CWTP), degraded wheat (W) and degraded corn (C), in this order. The maximum methane rate (R_m) is revealed in the case of anaerobic digestion of degraded wheat mixed with wastewater from treatment plant (WWTP). The largest lag phase (λ) was observed for degraded corn (C). Thus, one suggests that the soluble degradable materials are not available and the initial microbiological composition of this sample is not adequate for anaerobic digestion. The use of wastewater from water treatment plant influenced that situation and the shorter lag phase was exhibited by the action of CWTP. These model results are in agreement with the experimental data (r = 0.9967 – 0.9996, RMSD = 0.0008 – 0.0858).

Based on the kinetic results and the values of statistical indicators one states that the modified Gompertz model is the best suitable model to fit the methane yields for the tested substrates.

Table 1
PARAMETERS FOR THE LOGISTICAL GROWTH MATHEMATICAL MODEL AND THE VALUES OF THE OBTAINED MODEL PERFORMANCES

Substrate used	Model parameters			r^a	RMSD[b]
	M_P (m^3)	b	k (day^{-1})		
Corn (C)	24834	$1.8216*10^7$	0.1696	0.9806	0.0285
Wheat (W)	4.1262	657.5424	0.1776	0.9987	0.0034
Corn + wastewater from treatment plant (CWTP)	7.7000	3184.3000	0.5000	0.9898	0.2874
Wheat + wastewater from treatment plant (WWTP)	11.8170	506.0154	0.3031	0.9993	0.0342

[a] Pearson correlation coefficient; [b] the root mean square deviation [16]

Table 2
PARAMETERS OF THE MODIFIED GOMPERTZ MATHEMATICAL MODEL AND THE VALUES OF THE MODEL PERFORMANCES

Substrate used	Model parameters			r^a	RMSD[b]
	M_P (m^3)	R_m (m^3/day)	λ (days)		
Corn (C)	3.0891	0.4343	37.9495	0.9980	0.0024
Wheat (W)	4.4748	0.1699	24.4987	0.9996	0.0008
Corn + wastewater from a water treatment plant (CWTP)	7.8577	0.8405	12.6843	0.9967	0.0765
Wheat + wastewater from a water treatment plant (WWTP)	12.1759	0.8683	13.3293	0.9983	0.0858

[a] Pearson correlation coefficient; [b] the root mean square deviation [16]

Conclusions

The results demonstrate that the co-digestion of degraded corn and degraded wheat with wastewater from treatment plant enhance the anaerobic digestion process and the achieved biogas production, respectively. By far, the most suitable co-substrate for anaerobic digestion is the mixture of degraded wheat and wastewater from treatment plant. One found out that, after 45 days of this co-substrate digestion process, the biogas production was increased by 68%, compared to situation when the fermentation of degraded wheat occurred alone. The methane concentration of biogas was clearly superior, showing a large potential of using this fuel for renewable energy and heat production.

The kinetic study of methane production proved that there are different evolution patterns of digestion processes, due to substrate characteristics. The modified Gompertz model was found to be the best model for predicting of the methane potential for all investigated substrates.

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