Experimental and Modelling Approach of Biogas Production by Anaerobic Digestion of Agricultural Resources

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Anaerobic digestion processes of agricultural resources, as single substrates (wheat bran and barley) or as combination of substrates (75 % corn & 25% corn cob – named MIX1 and 40 % corn & 40 % wheat & 20 % sunflower husks – named MIX2), were performed, at a mesophilic temperature in a batch reactor, at pilot scale. The results proved that the higher quantity of biogas yield was achieved for barley, followed by MIX1, and finally MIX2. The same order was obtained when the total methane production was evaluated. The performances of digesters were mathematically evaluated by using the modified Gompertz equation. The kinetic parameters, such as the methane production potential (M_p), the maximum methane production rate (R_m) and the extent of lag phase (λ) were calculated, for each experimental case. The values of the performance indicators confirmed that all the models fitted well with the experimental data.

Keywords: agricultural resources, anaerobic digestion, biogas, modified Gompertz model

Nowadays, one of the most important issues worldwide represents the usage of renewable sources of energy in order to obtain clean fuels and secure the sustainable development. Biomass, for example, is widely available, under different forms, and its utilization for energy production has a great potential to reduce carbon dioxide (CO_2) emissions and consequently to prevent global warming [1]. In 2014, the share of renewable energy in final gross energy consumption in the EU was 16 %, representing 80 % of the 20 % target set in the EU for 2020. 63.1 % of renewable energy produced in 2014 came from biomass and wastes [2].

In this context, one of the feasible processes of generating renewable energy (fuel), using biomass as a base substrate is the biogas production, by using anaerobic fermentation processes. Biogas technology offers a very attractive route to use certain categories of biomass for satisfying partial energy needs [3-5].

Biogas represents a versatile renewable energy source, entering the chain for the replacement of fossil fuels in power and heat production; it can be used also as gaseous vehicle fuel [6]. 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 [7]. Biogas is a mixture of combustible gases produced during the digestion of organic matter, composed mainly by 60–65 % by volume methane (CH_4) and 35–40 % by volume carbon dioxide (CO_2), hydrogen sulfide (H_2S), nitrogen (N_2), hydrogen (H_2) and traces of oxygen (O_2), carbon monoxide (CO), ammonia (NH_3), argon (Ar_2) and other volatile organic compounds (VOC) or trace gases [8].

The composition of biogas depends on the type and concentration of organic matter to be digested, on the physicochemical conditions in the digester (pH, alkalinity, temperature) and on the presence of other anions such as sulfates and nitrates [9-10].

This technology has been successfully implemented in the treatment of agricultural wastes, food wastes, and wastewater sludge, due to its capability of reducing chemical oxygen demand (COD) and biological oxygen demand (BOD) from waste streams and producing renewable energy [11,12].

In order to understand and control the complex biochemical processes that take place during the anaerobic digestion of various biomass types, different mathematical models have been developed over the years. The pioneers were Graef and Andrews [13-14] in the late 1960's. Since then, kinetic models have been reported in the literature for the simulation of anaerobic biodegradation process. By 2002, the International Water Association (IWA) group developed the Anaerobic Digestion Model No.1 (ADM1) [15]. The main advantage of ADM1 model is its capability of simulating the anaerobic digestion of different biomasses. The disadvantage is represented by the complexity of the model, that needs many input parameters. This aspect is for sure time consuming and expensive from experimental point of view. In order to eliminate such inconveniences, statistical linear and non-linear regression models (modified Gompertz model, Logistic function, Transference function – Reaction curve type model, etc.) were developed to describe and predict the anaerobe digestion performances [16-20].

The present study investigates the anaerobic digestion performances (in terms of biogas and methane production) of different agricultural biomasses, used as single substrate or in combination. Also a simplified mathematical model was used to reach edifying simulations and predictions.

Experimental part

Substrates

Four different agricultural degraded biomasses: wheat bran (WB), barley (B), mix of 75 % corn and 25% corn cob (Mix1) and a cereal mix (40 % corn, 40 % wheat and 20 % sunflower husks) (Mix2) were used as substrates in an anaerobic digestion process. The substrates were previously stored at room temperature, until further use. All % compositions were expressed by volume.

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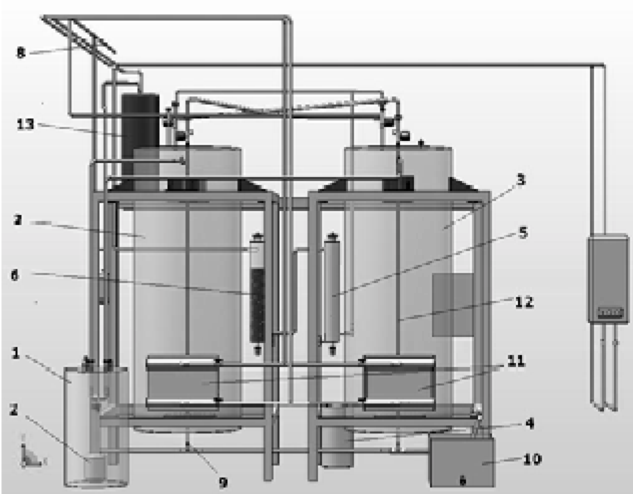

Fig. 1. Schematic configuration of the pilot plant used to produce biogas from biomass

Description of the Pilot Plant

The pilot plant used for producing biogas from biomass through anaerobic digestion is presented in figure 1.

The used input material was passed through a mill, and then sent to the tank where the preparation of the suspension of biomass occurs (1). The suspension transported with the help of the pump (2) is introduced into the fermentation reactors (3). The correction agent tank for the *p*H (4) ensures, through the control system, the conditions for the process of anaerobic fermentation. The resulted biogas is sequently passed through a filter for retaining the H_2S (5) and further, through a system used for retaining CO_2 (6). The CO_2 desorption and the compression of the CO_2 occur in the adjacent system (7 – separate system) and the purified biogas is finally sent to (8), for being used. The digestate is discharged through the means of a gravimetric system (9). The solid material is retained for being dried by a natural process, and after that it is sent to a compost deposit for being used as a soil fertilizer. A part of the resulting liquid is neutralized if necessary, in the system (10) and sent to the sewerage network, or it is transported by the recirculation pump (2) from the suspension preparation tank (1). The fermentation reactors are thermostat heated with the system (11). A bubbling system (12) made by polypropylene pipes is used for the homogenization of the suspension. Also, for capturing small quantities of biogas for analysis purposes, the installation is equipped with a small tank (13), placed at the top of the reservoirs.

Analytical Methods

Biogas production of each digester was measured daily by means of a gas counter, with indicated temperature and pressure values. Methane (CH_4) and carbon dioxide (CO_2) compositions (v/v) were measured by using a Delta 1600 IV gas analyzer. Temperature and pH were also continuously measured; the temperature by means of J thermocouples connected to AD-025V2DS-C temperature controllers and *p*H by means of pH sensors, model HI 1210, connected to *p*H controllers, model BL 981411.

The samples collected from each substrate were analyzed for moisture, ash and volatile matter content by using standard methods EN 14774, 14775 and 15148. The calorific values were determined with an IKA C 5000 Calorimeter. The elemental analyzer used to determine the carbon, hydrogen and nitrogen content of samples was a LECO TruSpec CHN model.

Mathematical Model

In order to calculate and compare the methane production during anaerobic digestion of different biomasses, the modified Gompertz model was used [16, 20]:

$$M = M_P \cdot \exp\left(-\exp\left(R_m \cdot \frac{\exp(1)}{M_P} \cdot (\lambda - t) + 1\right)\right) \quad (1)$$

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 anaerobic digestion and the 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 [21].

The software used to determine those parameters was Matlab R2008b (version 7.7.0.741). The appropriateness of the model was first evaluated graphically and then the Pearson correlation coefficient (r) and the root mean square deviation (RMSD) were calculated.

Table 1
THE CUMULATIVE BIOGAS PRODUCTION DURING ANAEROBIC DIGESTION OF FOUR SUBSTRATES INVESTIGATED IS PRESENTED IN FIGURE 2

Biomass	Wheat bran, WB	Barley, B	Mix, Mix1	Cereal mix, Mix2
Moisture content (db) (%)	9.72	10.6	9.67	10.7
Ash content (db) (%)	5.54	2.52	1.35	1.53
Net calorific value (db)(J/g)	17520	17291	16904	16820
Carbon content (db) (%)	41.3	40.2	41.3	40.7
Hydrogen content (db) (%)	6.2	6.2	6.4	6.7
Nitrogen content (db) (%)	2.06	1.44	1.29	1.16
Volatile matter content (db) (%)	78.4	82.5	84.9	84.9
C/N ratio	20.05	27.92	32.02	35.08

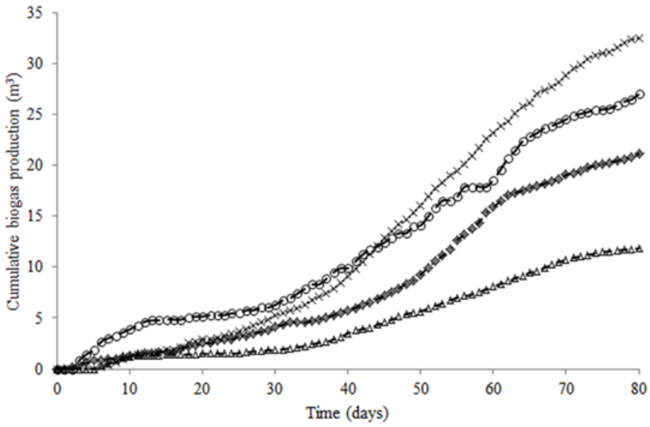

Fig. 2. Cumulative biogas production during anaerobic digestion of four biomasses: —◆— wheat bran, ...x.... barley, -o- 75% corn + 25% corn cob, - - △- - cereal mix

Results and discussions

The general characteristics of substrates used in the anaerobic digestion process are given in the table 1. Among the substrates used, the Mix1 had the lowest content of ash, while the ash content of WB was four times higher. The ash content is important to be determined, in order to determine the potential possibilities of using the residual sludge in co-firing processes. Of course, high ash contents are not generally suitable for this type of applications.

The carbon to nitrogen ratio (C/N) for WB and B were within the optimal range (20 – 30) for anaerobic digestion. The Mix1 and Mix2 had higher C/N ratio. A higher value indicates a rapid consumption of nitrogen by methanogens and results in lower gas production. A lower C/N ratio generates accumulation of ammonia in the digester, which may lead to the inhibition of methanogenic bacteria [22-23].

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

In the case of barley (B) and cereal mix (Mix2), the biogas production started after 5 days of digestion, while, for wheat bran (WB) and 75% corn + 25% corn cob (Mix1) the gas production began in the second day of the digester operation.

The cereal mix (Mix2) digester process had a very low biogas production, until day 32 when it reaches a cumulative biogas production of 2 m^3. This amount of biogas was generated after 17 days of digestion for wheat bran and barley substrates and after 6 days based on the Mix1 digester process. After day 32, the biogas production from Mix2 digester increases slowly and reaches 11.9 m^3 of biogas on day 80. Even if barley and wheat bran behaved similarly at the beginning of the experiment, after 17 days of digestion they showed different biogas production pattern. The increase of cumulative biogas production was significantly higher in the barley digester. At the end of digestion period, the amount of biogas generated by anaerobic digestion was 21.2 m^3 for wheat bran and 32.6 m^3 for barley. As concerns the Mix1 digester, the cumulative gas production at the end of anaerobic digestion was 27 m^3. The order of investigated substrates, in terms of total amount of biogas generated during anaerobic digestion process was: B > Mix1 > WB > Mix2.

The methane content of biogas produced during anaerobic digestion of investigated substrates is presented in figure 3. The methane content of biogas formed during anaerobic digestion process proved the same evolution for barley and cereal mix substrates. The values of methane concentration in biogas increased rapidly until day 30, reaching a value of 75% by volume and then decrease slowly till a constant value of 70 %.

As concern the other two substrates, the methane content in the biogas had a different behavior. The biogas from Mix1 started to present a methane content only after 22 days of digestion. Then the methane concentration in biogas increased continuously till 69% in day 60 and remained constant for the rest of digestion process. The methane content in the biogas generated by wheat bran (WB) digester showed the same progress. The difference was at the beginning of the process, the biogas from wheat bran having 0.15 % methane after 5 days.

The experimental data about the biogas yield and its methane content were used to calculate the cumulative equivalent methane for each of the four substrates subjected to anaerobic digestion.

The modified Gompertz equation is the basic for the mathematical model used to estimate the performance of the digestion process. Figure 4 illustrates the experimental data (markers) and the results of the mathematical model (solid lines).

The values of mathematical model parameters are presented in the table 2.

Previous studies reported the existence of three characteristic zones during cumulative methane production process as a result of different biomasses anaerobic digestion [24]. A lag zone corresponding to the period before gas generation started can be noticed at the beginning of the digestion process. This zone is followed by a rapid methane production phase, named exponential

Table 2
PARAMETERS OF THE CONSIDERED MATHEMATICAL MODEL

Biomass used	Model parameters			r^a	RMSD^b
	M_P (m^3)	R_m (m^3/days)	λ (days)		
Wheat bran	13.1297	0.3767	39.4911	0.9984	0.0652
Barley	28.3019	0.4941	29.1578	0.9997	0.0363
75% corn+25% corn cob Mix1	17.1661	0.3518	35.9153	0.9986	0.0632
Cereal mix Mix2	10.1124	0.1820	32.2488	0.9994	0.0094

[a] Pearson correlation coefficient; [b] the root mean square deviation [20]

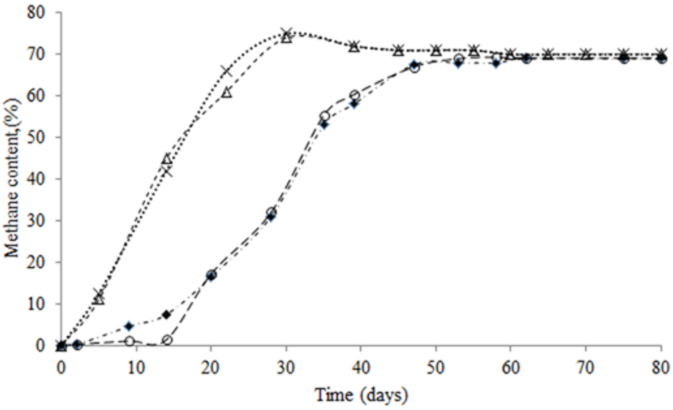

Fig. 3. Methane content of biogas produced during anaerobic digestion of four biomasses: ····x···· wheat bran, ...x.... barley, —o— 75% corn + 25% corn cob, --△-- cereal mix

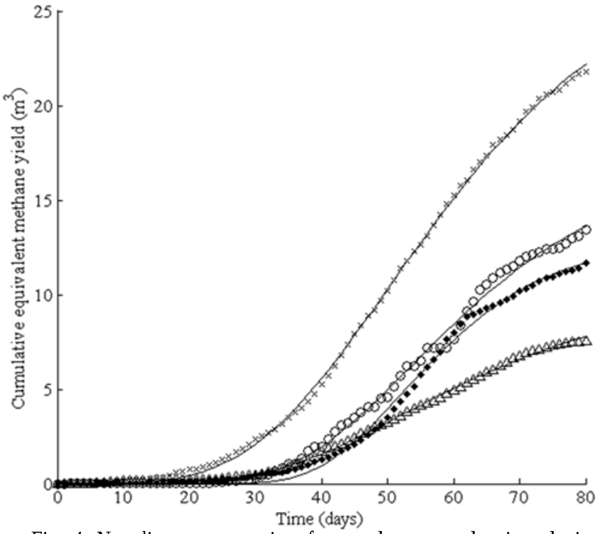

Fig. 4. Non-linear regression for methane production during anaerobic digestion of substrates investigated: ♦ wheat bran, x barley, o 75% corn + 25% corn cob, △ cereal mix, _____ modified Gompertz model

zone. In the end of the process, the production of methane is reduced drastically and the cumulative methane quantity will experience a steady state zone. These zones are well highlighted in our study.

From the figure 4 and the table 2 it results that the highest methane production potential is exhibited by the barley substrate (B); The effect is further depicted for Mix1 (75% corn + 25% corn cob), wheat bran (WB) and cereal mix (Mix2), in this order. The maximum methane rate (R_m) is shown in the case of anaerobic digestion of barley, while the minimum was observed for cereal mix. The largest lag phase (λ) was observed for the wheat bran, fact which suggests that the initial microbiological composition of this sample is not adequate for anaerobic digestion. The shorter lag phase was exhibited by the barley sample.

The good values of the Pearson correlation coefficient and of root mean square deviation indicate that the modified Gompertz kinetic model describes very well the phenomena that took place during anaerobic digestion of the investigated substrates. The results of the mathematical modeling indicate that among the studied substrates, barley (B) is the most appropriate material to be used for anaerobic digestion, followed by Mix1, wheat bran (WB) and cereal mix (Mix2).

Conclusions

The results demonstrate that barley is the most suited substrate for anaerobic digestion processes, based on its high potential of generating biogas with high methane content. The modified Gompertz kinetic model was used to describe the cumulative methane production during the digestion process. Comparison of the obtained kinetic parameters showed that barley digestion led to the shorter lag time and the highest potential for cumulative methane production. The accuracy of the model was confirmed by the good values of the performance indicators (r = 0.9984 – 0.9997, RMSD = 0.0094 – 0.0652).

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