DETERMINATION OF THE BIOMETHANIC POTENTIAL OF CORN GRAIN

ORIGINAL SCIENTIFIC PAPER

Samra Halilović[1], Vedran Stuhli[2], Mirnesa Zohorović[2], Zoran Iličković[2]*

RECEIVED 2017-12-16
ACCEPTED 2018-05-18

[1]Institute for Chemical Engineering, Tuzla, Bosnia and Herzegovina
[2]Faculty of Technology, University of Tuzla, Tuzla, Bosnia and Herzegovina
[*]✉ samra.halilovic95@gmail.com

ABSTRACT: Although it is primarily grown as food, corn also represents a very good raw material for the production of biogas due to the favourable starch and fibre ratio that is the basis of its structure. In addition, an important fact is that there are large arable or potentially arable areas in our country that are triturated with different pollutants, so that the production of plant crops for dietary purposes on these surfaces is not possible.
The aim of this paper was to determine the biometric potential of various varieties of corn grain in laboratory conditions through a series of experimental measurements. The obtained results are based on the assessment of the possibility of applying energy plantations of corn grown on contaminated arable or recultivated surfaces in the production of biogas.

KEYWORDS: corn, biomethane potential, sludge, anaerobic digestion, biogas

INTRODUCTION

Owing to increased energy consumption and reduction of fossil fuels in the world, systems have recently been developed in order to meet renewable energy needs, which is the cause of development of new technological processes of energy production. In addition, renewable energy sources form part of the European fight against climate change, while at the same time increasing the number of employees contributes to economic growth and development of the whole region [1], [2], [3].

At the global level of biomass energy production, very high potential has been estimated that can be unambiguously linked to the potential of biogas. Existing estimates are made on the basis of different assumptions, but all the results indicate the use of a very small part of that potential. The European Biomass Association (AEBIOM) estimates that biomass energy can increase from 72 Mtoe in 2004 to 220 Mtoe in 2020 (1 Mtoe = 11.63 TWh) [4].

Biogas plants using agricultural raw materials are one of the most important examples of anaerobic digestion in the world. Compared to other biofuels, anaerobic digestion biogas is an important priority in European transport and energy guidelines, and is of increasing importance because it offers many environmental benefits and an additional source of income for farmers [5].

Maize is the most dominant crop for biogas production. It is cultivated all over the world, and the breeding area is very broad, resulting from the variety of corn utilization and abilities that can thrive on various soils and in various climatic conditions. Corn crops are the third world crops, after wheat and rice. All parts of corn can be used either as food or for industrial processing [6].

MATERIAL AND METHODS

The basic substrate was chopped corn grain (diameter 0.5-1 mm) of two varieties, hybrid maize NS 444 *Ultra* and a homemade Bosanac variety. For the purpose of achieving the production of biogas as an inoculum, sludge from the treatment plant for communal waste water in Živinice was used.

For the purposes of this paper, a laboratory reactor system for anaerobic digestion of organic matter with glass eudiometric pipes (manufacturers Šurlan-Medulin), mounted on glass bottles of 500 ml were used. Provision of anaerobic conditions was performed by sparging of nitrogen in order to displace the air from the reactor, while providing the required constant temperature of the reactor system at 35°C ± 2°C was carried out by heating in a water bath with circulating water (Figure 1). Using the eudiometric pipes, the production of biogas is simple to read off, because produced gas pushes the liquid level down, while the fluid goes back into the storage bottle.

The pressure and temperature of the ambient air were measured on the set pressure hydrometers or eudiometric tubes, whose values were used to convert the volume of the resulting biogas to normal conditions. Mixing of the substrate was realized mechanically using a magnetic stirrer.

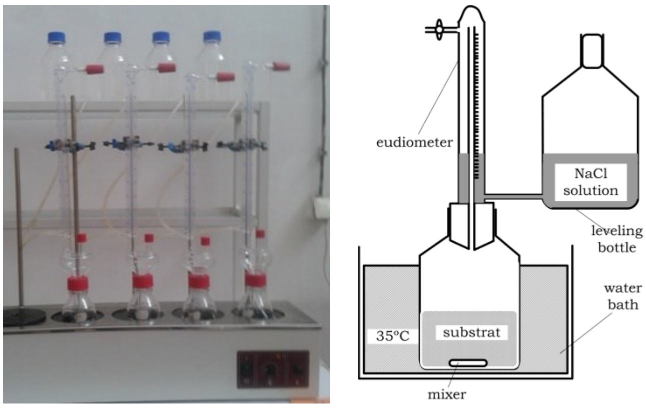

Figure 1. Laboratory reactor system: a. system layout; b. reactor block scheme

Measuring the volume of biogas produced in the reactor was performed in accordance with DIN 38 414 [7], and a gas composition analysis was performed on a gas chromatograph "PERKIN ELMER", equipped with the software package "Arnel". Helium was used as a gas carrier (flow rate 34 ml / min). A mixture of gases was used to calibrate the device which consists of CO, CO_2, CH_4 and O_2 (Messer, Germany). The gas chromatograph has two columns: 70 HayeSep N 60/80, 1/800 SF (maximum temperature 150°C) and 90 Molecular Sieve 1345-1360, 1/800 SF (maximum temperature 375°C). Conditions governing the furnace chromatograph are: initial temperature 60°C, total retention time 12 min, maximum temperature 150°C.

Because of the inhibition of anaerobic substrate degradation due to a sudden increase in the concentration of volatile fatty acids at the beginning of the process, which was reflected in a decrease of pH below 4, it was necessary to buffer the substrate by combining two bicarbonate buffers. By adding 150 mg of $NaHCO_3$ and 170 mg of $KHCO_3$ in relation to 1 g of total organic volatile matter [8] in the substrate, the optimum pH range was obtained.

To determine the necessary parameters in the substrates, the methods described below were used.

Determination of dry and volatile organic matter was performed according to Method 2540-B and 2540 Solid-Solid E. Standard Methods for the Examination of Water and Wastewater [9]. Electrometric measurement of pH was carried out by direct measurement, with the pH meter METTLER TOLEDO FE 20/EL 20. Prior to each measurement, an internal control was performed with certified reference materials of pH- value 4.01; 7.01; 10.01.

The nitrogen content by Kjeldahl was determined according to Method 4500-N_{org} B. Standard Methods for the Examination of Water and Wastewater 20[nd] edition. APHA, Washington, DC [10]. The method consists of three stages: digestion at a temperature of 340°C (boiling point of H_2SO_4) in the presence of concentrated sulfuric acid and selenium Kjeldahl catalyst; distillation in the presence of NaOH where distillate accepts in the solution of boric acid, and titration with 0.1 M HCl in the presence of indicator bromocresol green. Determination was made on Kjeldahl apparatus Gerhardt. To determine the chemical oxygen demand, the standard method was used according to the ISO 6060:2000 [11].

RESULTS AND DISCUSSION

The anaerobic digestion experiment of two grain varieties and waste sludge from municipal wastewater treatment plants was carried out at mesophilic conditions (36 ± 1°C). When experimenting with the mixture of corn grain substrate and waste sludge, experimental data [12] were used as a blank test waste sludge was used without additives (Table 1).

Table 1. Composition of the cosubstrate in the formed blends (2&3) and the blank test (1)

Test	sludge mas%	*Bosanac* mas %	*NS 444 Ultra* mas %	H_2O mas %
1	100	0	0	0
2	49.67	0.33	0	50
3	49.64	0	0.36	50

The values of the physico-chemical parameters of the treadmill are shown in the Table 2.

Table 2. Physico-chemical characteristics of the cosubstrates used at the beginning of the experiment

Parameter	Unit	1	2	3
TS	%	5.05	2.83	2.84
VS	%	3.36	1.96	1.99
VS/TS	-	0.66	0.69	0.70
pH	-	6.41	6.21	6.09
COD	g/kg	48.6	102.58	117.96
TKN	g/kg	2.80	2.20	2.00

TS – total solids; VS – volatile solids; COD - chemical oxygen demand; TKN - total Kjeldahl nitrogen

The ratio of VS / TS to the blank test sample (1) and the formed coagulates (2 and 3) approx. 0.7 the condition of the presence of sufficient quantity of organic matter in the reactors is satisfied. The content of dry matter in reactors 2 and 3 is lower than the content of dry matter in the control sample (1).

The optimum ratio of organic matter and nitrogen in the ratio of 30:1 in this case is expressed through HPK:TKN and ranges from 17:1 in the control sample up to 60:1 in reactor 3 (HPK reactor: TKN = 47:1). It is clear that substrates are not loaded with nutrients especially nitrogen.

The graphs show daily biogas production (Figure 2) and cumulative yield of biogas (Figure 3) in reactors 1, 2 and 3. On the biogas daily production diagram, discontinuous biogas production is observed.

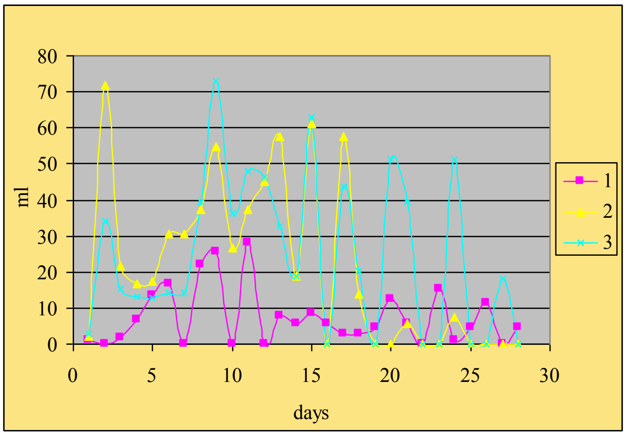

Figure 2. Daily biogas production diagram

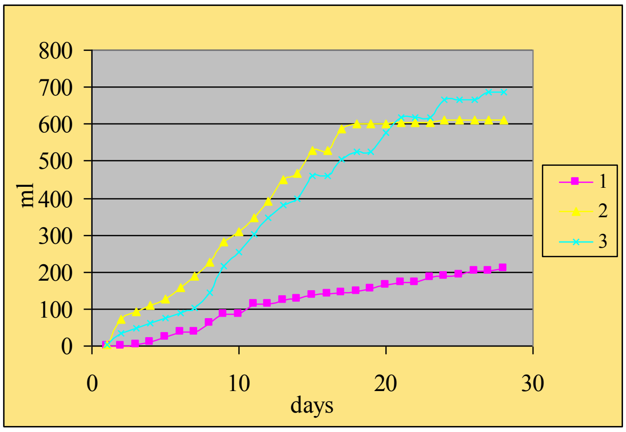

Figure 3. Cumulative biogas yield

The cumulative yield of the biogas (Figure 3) confirms the adaptation phases and the beginning of hydrolysis in the first days of the process. The diagram clearly shows a significantly larger biogas production in reactors 2 and 3 compared to the controlled sample 1.

Table 3 gives characteristics of the digested residue (digestate) which remains after the experiment has been realized. If we compare the content of dry and volatile organic matter before and after the process, it is easy to conclude that a certain part of the matter has been transformed into gas products. Also, the value of HPK for all three samples is significantly lower in the digestate (Table 2) compared to HPK values in substrates prior to the decomposition process (Table 1). In addition, the lower value of TKN content in digestates can be noted with respect to the TKN values in the initial coagulants. Based on the proportion of methane in biogas and biogas production, a calculation of methane production was performed for all three analyzed cases (Figure 4).

Table 3. Final results of batch anaerobic digestion after experiment

Parameter	Unit	1	2	3
TS	%	2.79	2.22	2.19
VS	%	1.36	1.26	1.09
pH	-	7.57	7.44	7.47
HPK	g/kg	14.43	15.12	10.47
TKN	g/kg	1.06	1.35	1.15
V biogas	ml	208.2	612.84	685.75
V methane	ml	64.77	366.05	411.38
W methane	%	31.11	59.73	59.99
spec. gas yield	ml CH_4/gVS	14.49	466.90	524.72

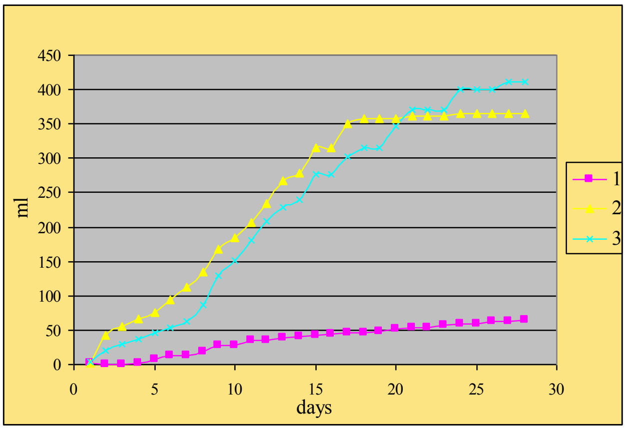

Figure 4 Cumulative yield of methane

Similarly to the case of cumulative production of biogas and methane production from cobblestone 2 and 3, it is considerably higher than methane production of controlled sample 1. In addition, the share of methane in biogas in samples 2 and 3 is almost identical and is close to 60 % while the share in the biogas of the sample is almost twice as small.

CONCLUSIONS

Based on the physical-chemical analysis of waste sludge from the municipal wastewater treatment plant and the maize hybrid cultivar "NS 444 Ultra", as well as the preserved Bosanac variety, all three types of substrates represent potential biogas raw materials owing to very favourable VS content and HPK representing the amount of organic matter from which methane is obtained, and a favourable ratio of the macronutrient expressed through the ratio HPK: TKN.

By comparing the content of dry and volatile organic matter before and after the process, it is easy to conclude that a certain part of matter has been transformed into gas products. Also, the value of HPK and TKN for all three samples is significantly lower at the end of the process compared to the HPK and TKN values in the substrates prior to the decomposition process, which is particularly relevant for the 2 and 3 blends. Methane production from both substrates 2 and 3 is considerably larger in comparison to the methane production of the controlled sample 1. In addition, the proportion of methane in the biogas in samples 2 and 3 is almost identical and is close to 60 % while the biogas fraction of the blank test sample is almost twice as small.

The specific production of methane produced from the sands and grains of hybrid maize NS 444 Ultra is 524.72 ml of CH_4/gVS, while the sludge and the Bosanac grain is 466.90 ml of CH_4/gVS.

REFERENCES

[1] T. Amon, B. Amon, V. Kryvoruchko, W. Zollitsch, K. Mayer, L. Gruber, "Biogas production from maize and dairy cattle manure-Influence of biomass composition on the methane yield", *Agriculture, Ecosystems and Environment*, pp. 173-182, 2007.

[2] P. Balsari, P. Bonfanti, E. Bozza, F. Sangiorgi, "Evaluation of the influence of animal feeding on the performances of a biogas installation (mathematical model)", *Proceedings of the 3rd International Symposium "Anaerobic Digestion*, Boston, 1983.

[3] P. Vindiš, P. Muršec, C. Rozman, F. Cus, "A multi-criteria assessment of energy crops for biogas production", *Journal of Mechanical Engineering*, 2009.

[4] Z. Osman, "Projekt biolinskog postrojenja", Diplomski rad, 2015.

[5] T. Al Seadi, D. Rutz, H. Prassl, M. Kottner, T. Finsterwalder, S. Volk, R. Janssen, *Priručnik za bioplin*, Intelligent Energy Europe, 2008.

[6] D. Čakija, "Proizvodnja silažnog kukuruza na OPG-u Čakija za potrebe bio-plinskog postrojenja bioplinara Ogranica, Gregurovec" Diplomski rad, 2-5, 2016.

[7] DIN 38 414-S1-1986-11 (1986): *Analyses of Water, Drinking Water, Waste Water, Sludge, Sediments and Residues*.

[8] A. Flor, L. Arroja, I. Capela, "Anaerobic co-digestion of organic fraction of municipal solid waste and waste activated sludge at different ratios", *Proceedings Sardinia 2003, Ninth International Waste Management and Landfill Symposium S. Margherita di Pula*, Cagliari, Italy, 2003.

[9] Method 2540-B and 2540 Solid-Solid E. *Standard Methods for the Examination of Water and Wastewater*.

[10] Method 4500-N_{org} B. *Standard Methods for the Examination of Water and Wastewater 20nd edition*. APHA, Washington, DC, 1998.

[11] BAS ISO 6060 *Određivanje hemijske potrošnje kisika*, 2000.