# Factors Affecting the Performances of Biomass Anaerobic Digestion Process

A.E. Cioabla<sup>\*</sup>, G.A. Dumitrel<sup>\*\*</sup> and D. Tucu<sup>\*</sup>

<sup>\*</sup> POLITEHNICA University of Timisoara, Faculty of Mechanical Engineering, Bv. M. Viteazu, nr. 1, 300222, Timisoara, Romania, adrian.cioabla@upt.ro

\*\* POLITEHNICA University of Timisoara, Faculty of Industrial Chemistry and Environmental Engineering, Bv. Vasile Parvan, nr. 6, 300223, Timisoara, Romania

**Abstract:** The effect of heavy metals and light metals ions on anaerobic digestion of three agricultural biomasses (two row barley, wheat bran and a mixture of 75 % corn kernels and 25 % corncobs) was investigated in this study. The raw materials were characterized from physico-chemical point of view and their heavy metals content (copper, chromium, nickel, lead and zinc) and light metals ions content (potassium, magnesium, calcium and aluminum) was measured. The effects of these substances on the anaerobic activity were analyzed by measurements of cumulative biogas production and the methane content of the obtained biogas.

Keywords: biomass, anaerobic digestion, heavy metals.

# 1. Introduction

Nowadays, the usage of renewable sources of energy in order to obtain clean fuels is one of the most important issues with which humanity confronts itself. Relative to the matter at hand, one of the means of obtaining renewable fuels is biogas production using anaerobic fermentation processes. This method can be applied both at small and large scale using as substrate, relatively any biodegradable material which has as a source of origin agriculture, domestic activities or industry.

Biogas is considered a carbon dioxide-neutral biofuel and if used as vehicle fuel, emits lower amounts of nitrogen oxide, hydrocarbon and carbon monoxide emissions than petrol or diesel engines [1].

The production of methane through the microbial degradation of organic wastes, which leads to so-called biogas (i.e., a wet mixture of  $CH_4$  and  $CO_2$  with hydrogen sulfide and hydrocarbons as minor compounds), is appealing [2].

Biogas production has become an important branch of agriculture, mainly due to continuously growing usage of agricultural raw materials for anaerobic digestion (AD) [3].

Assessment of environmental impact of operating biogas plants has been reported by Bachmaier et al. [4]. Results showed that assessed biogas plants contributed significantly to the reduction of greenhouse gas (GHG) emissions. In Michel et al. [5], the effects of inclusion of a biogas plant into organic cropping systems were assessed using life cycle assessment (LCA) methodology. It was found that the main benefits are reduction of GHG and energy recovery, as well as increase of yields of agricultural products by manuring the farmland with the digested residue.

The failure of an anaerobic digestion process can be due to inhibitory substances, among which heavy metals and light metal ions play an important role. The presence of heavy metals in the substrates can be due to natural or anthropogenic sources. The most dangerous heavy metals are: cadmium, chromium, copper, iron, lead, nickel and zinc. The light metal ions that influence the anaerobic digestion are sodium, potassium, calcium, magnesium and aluminum.

Heavy metals influence the bio-chemical reactions that take place in the anaerobic digestion process [6]. According to Lin [7] and Yenigun et al. [8], the acidogenesis and methanogenesis of an anaerobic process are easily affected by Cd, Cu, Cr, Zn, Pb and Ni.

The aim of this study was to investigate the effect of heavy metals and light metals content from three agricultural biomasses (two row barley, wheat bran and a mixture of 75 % corn kernels and 25 % corncobs), on the anaerobic digestion efficiency of these substrates. The cumulative biogas production and the methane content of biogas were the efficiency indicators used.

## 2. Experimental

## 2.1. Chemical analysis

Three different agricultural biomasses: two row barley, wheat bran and a mixture of 75 % corn kernels and 25 % corncobs were used for this study.

The samples collected were successively subjected to physical and chemical analyses. The laboratory analyses were made according to the following standards:

- EN 14774 – Solid biofuels – Determination of moisture content – Oven dry method (parts 2 and 3) [9];

- EN 14775 - Solid biofuels - Determination of ash content [10];

- EN 14918 - Solid biofuels - Determination of

calorific value [11];

- EN 15290 – Solid biofuels – Determination of major elements [12];

- EN 15297 – Solid biofuels – Determination of minor elements [13];

- EN 15104 – Solid biofuels – Determination of total content of carbon, hydrogen and nitrogen – Instrumental methods [14];

- EN 15148 – Solid biofuels – Determination of the content of volatile matter [15].

All analyses were performed in duplicate.

#### 2.1. Description of pilot plant

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

From the biomass deposit, the used material is passed through a mill, and then it's sent to the tank where the preparation of the suspension of biomass is made (1). The biomass suspension is transported with the help of the pump (2) and introduced into the fermentation reactors (3). The correction agent tank for the pH assures, through the control system, the conditions for the process of anaerobic fermentation. The resulted biogas is passed through a filter for partially retaining the  $H_2S$  (5) and after that, through a system used for partially retaining  $CO_2$  (6), after which takes place the CO<sub>2</sub> desorption and the compression of the CO<sub>2</sub> in the adjacent system and the purified biogas is sent for being used (8). The used material is discharged through the means of a gravimetric system (9), and the solid material is retained for being dried using the natural drying, and after that is sent to a compost deposit for being used as a soil fertilizer. A part of the resulting liquid is neutralized when the case, in the system (10) and sent to the sewerage network, or is transported by the recirculation pump (2) from the suspension preparation tank (1). The fermentation reactors are thermostat heated with the system (11). For the homogenization of the suspension is used a bubbling system (12) made by polypropylene pipes to avoid the possible corrosion. Also, for depositing small quantities of biogas of the purpose of analyzing, the installation is equipped with a small tank (13) positioned at the top of the reservoirs.

The reactors were fed at the beginning of the experiment with approximately 75 kg dry biomass and 2000 L water. Biogas production was measured daily, the pressure difference being dropped with the help of a semiautomated system and afterwards through a gas counter. Methane (CH<sub>4</sub>) and carbon dioxide (CO<sub>2</sub>) compositions (v/v) were measured using a Delta 1600 IV gas analyzer. Temperature and pH were also continuously measured.

## 3. Results and Discussion

Before starting the anaerobic digestion experiments, each agricultural biomass were characterized from a physical and chemical point of view: moisture content, ash content, gross and net calorific value, volatile matter content, carbon content, nitrogen content, hydrogen content. The corresponding values are presented in table 1.

The values listed in table 1 suggested that the properties of three substrates are closer one to each other. In light of the fact that the properties of raw materials influence the effectiveness of anaerobic digestion, we can expect to similar biogas production for the three biomasses considered in this study.

Investigation of heavy metals (Cu, Cr, Ni, Pb, Zn) and light metals ions (K, Mg, Ca, Al) presence in the substrates revealed the value presented in table 2 and 3.

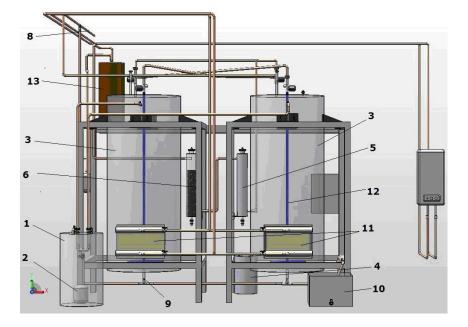


Figure 1. Anaerobic digestion pilot plant

| Biomass                          | Two Row Barley | Wheat bran | Mixture of 75 % corn kernels<br>and 25 % corncobs |
|----------------------------------|----------------|------------|---|
| Moisture content (db) [%]        | 10.7           | 9.72       | 9.67  |
| Ash content (db) [%]             | 2.22           | 5.54       | 1.35  |
| Gross calorific value (db)[J/g]  | 18354          | 19034      | 18470   |
| Net calorific value (db)[J/g]    | 16763          | 17520      | 16904   |
| Carbon content[%]                | 40.1           | 41.3       | 41.3  |
| Hydrogen content [%]             | 6.5            | 6.2        | 6.4   |
| Nitrogen content [%]             | 1.38           | 2.06       | 1.29  |
| Volatile matter content (db) [%] | 82.4           | 78.4       | 84.9  |

TABLE 2. Heavy metal content of biomasses used in the anaerobic digestion process

|    | Biomass  | Two Row Barley | Wheat bran | Mixture of 75 % corn kernels and 25 % corncobs |
|----|----------|----------------|------------|--|
| Cu | ι [mg/L] | <5             | 10         | <5   |
| Cr | · [mg/L] | <5             | <5         | 11   |
| Ni | [mg/L]   | <5             | <5         | 10   |
| Pb | [mg/L]   | 450            | 440        | 440  |
| Zn | [mg/kg]  | 30             | 70         | 20   |

TABLE 3. Light metals content of biomass used in the anaerobic digestion process

| Biomass    | Two Row Barley | Wheat bran | Mixture of 75 % corn kernels and 25 % corncobs |
|------------|----------------|------------|--|
| K [mg/kg]  | 4590           | 11300      | 4110   |
| Mg[mg/kg]  | 540            | 1750       | 860  |
| Ca [mg/kg] | 1150           | 950        | 660  |
| Al [mg/kg] | 80             | 60         | 110  |

According to the results from table 2, the two row barley was clear of copper, chromium and nickel. Copper was identified in wheat bran substrate and chromium and nickel was present in the mixture of corn kernels and corncobs. Lead and zinc were present in all three substrates. In the review of Mudhoo et al. [6] the influence of heavy metals on the acetogenesis and methanogenic stages of anaerobic digestion is presented. The effect of heavy metals on the hydrolysis stage was not sufficiently studied till now. The performance of acidogenesis stage is severely affected by Cd and Cu, while Pb and Ni were the least toxic heavy metals [6]. The results of studies performed on the heavy metals effects on methanogenic stage are contradictory. These data suggested that the severity of heavy metal inhibition depend upon many uncontrollable factors.

The presence of light metals (table 3) in the substrate are necessary for stimulation of microbial growth, but a higher concentration can harm this process. An excessive amount of aluminum can inhibit the acetogenic and methanogenic microorganisms. The role of calcium is to stimulate the growth of certain strains of methanogens and the formation of microbial aggregates. Large amounts of calcium lead to precipitation of carbonate and phosphate which are toxic to anaerobic degradation. Moderate concentration of potassium (less than 400 mg/L) increases the anaerobic digestion processes that operate at both mesophilic and thermophilic temperatures. Higher concentration of potassium has a negative effect, more visible in thermophilic conditions [16].

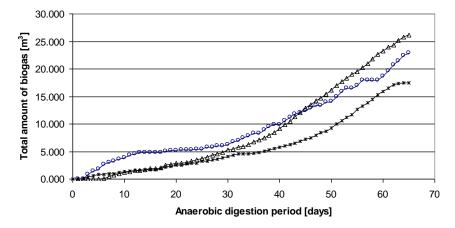
The amount of biogas generated by anaerobic digestion of studied substrates is depicted in figure 2.

Even the condition of digestion were the same, the total quantity of biogas after a period of 65 days was different. The higher production of biogas was obtained for two row barley digestion (26.198 m<sup>3</sup>), follow by the mixture of 75 % corn kernels and 25 % corncobs digestion (22.835 m<sup>3</sup>). The wheat bran substrate produced the lowest quantity of biogas at the end of 65 days of digestion (17.773 m<sup>3</sup>). Because the anaerobic digestion was made in the same conditions and the compositions of biomasses are similar, the differences on the total biogas yield can be due to the different amount of heavy metals and light metals ions in the studied biomasses.

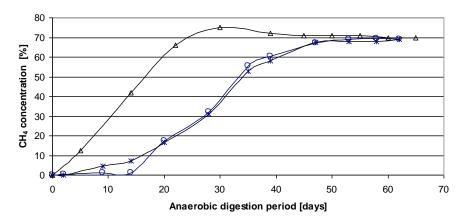
The quality of produced biogas was evaluated by measuring the amount of  $CH_4$  and  $CO_2$ . These values are presented in figures 3 and 4.

From figure 3, is obviously that the quality of biogas is superior for two raw barley digestion. The biogas from digestion of the other two biomasses has similar methane composition.

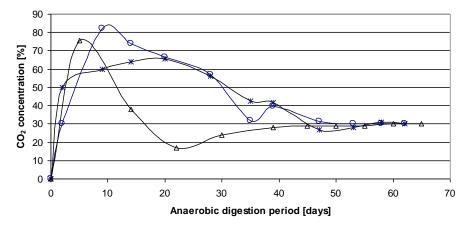
As concern the carbon dioxide composition of the three biogases, the lowest concentration is found in the case of two row barley digestion.

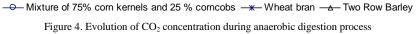


→ Mixture of 75% corn kernels and 25 % corncobs → Wheat bran → Two Row Barley Figure 2. Cumulative biogas production



-O Mixture of 75% corn kernels and 25 % corncobs ——— Wheat bran ——— Two Row Barley Figure 3. Evolution of methane concentration during anaerobic digestion process





## 4. Conclusions

The performances of anaerobic digestion process of three types of agricultural biomasses (two row barley, wheat bran and a mixture of 75 % corn kernels and 25 % corncobs) was studied in this paper. Even if the compositions of biomasses were similar and the anaerobic digestion was achieved in the same conditions, the total biogas yield and its methane composition was different. The higher amount of biogas yield was obtained for two row barley substrate follow by wheat bran and the mixture of corn kernels and corncobs. As concern the quality of this biogas, the CH<sub>4</sub> concentration in the biogas from two row barley digestion was superior to the CH<sub>4</sub> yields by the digestion of the other two substrates. These differences can be due to the different amount of heavy metals and light metals ions in the studied biomasses, because it is well known that higher amounts of these substances inhibit the biochemical reactions that take place during anaerobic digestion process of organic matter.

#### REFERENCES

1. Wellinger A. and Lindbergh A., Biogas upgrading and utilization, IEA Bioenergy Task, vol. 24. Paris, France: International Energy Association, **2000**, 3-20.

- 2. Favre E., Bounaceur R. and Roizard D., J.Membr.Sci., 328, 2009, 11-12.
- 3. Djatkov D., Effenberger M., Lehner A., Martinov M. and Tesic M., *Renew Energ.*, 40, **2012**, 104 112.

4. Bachmaier H., Effenberger M. and Gronauer A., International scientific conference "Biogas Science 2009-Science Meets Practice". Erding, Germany, **2009**, 417-427.

5. Michel J., Weiske A. and Möller K., *Renew. Agr. Food Syst.*, 25(3), 2010, 204 -218.

6. Mudhoo A. and Kumar S., J. Environ. Sci. Technol., 10, 2013, 1383-1398.

7. Lin C.Y., Water Res., 27(1), 1993, 147-52.

8. Yenigun O., Kizilgun F. and Yilmazer G., *Environ. Technol.*, 17, **1996**, 1269–1274.

9. EN ISO 14774/2009. Solid biofuels – Determination of moisture content – Oven dry method, **2009**.

10. EN ISO 14775/2009. Solid biofuels - Determination of ash content, 2009.

11. EN ISO 14918/2010. Solid biofuels – Determination of calorific value, **2010**.

12. EN ISO 15290/2011. Solid biofuels – Determination of major elements, **2011**.

13. EN ISO 15297/2011. Solid biofuels – Determination of minor elements, **2011**.

14. EN ISO 15104/2011. Solid biofuels – Determination of total content of carbon, hydrogen and nitrogen – Instrumental methods, **2011**.

15. EN ISO 15148/2010. Solid biofuels – Determination of the content of volatile matter, **2010**.

16. Chen Y., Cheng J.J. and Creamer K.S., *Biores. Technol.*, 99, 2008, 4044-4064.

Received: 15 May 2013 Accepted: 20 June 2013