Experimental approach on degradation process during anaerobic fermentation for different agricultural biomass properties

A. E. Cioablă, G. A. Dumitrel, F. Popescu, D. G. Călinoiu, and A. Țenchea

Abstract—Relative to the existing technologies for using renewable sources in order to produce clean energy, the use of biomass for biogas production is one of the means to replace at least partially the existing natural gas which represents a fossil fuel. There will be presented the influence of degradation process, during anaerobic digestion on agricultural materials in terms of process indicators during the process and chemical parameters evolution before and after the anaerobic fermentation.

Keywords—chemical parameters, anaerobic fermentation, agricultural biomass.

I. Introduction

NOWADAYS, the main problem of present society is connected with decrease of fossil fuels in the context of energetic consumption increasing worldwide.

Rapid development in technology and industry in recent years causes an increase in environmental problems. Today, negative effects of solid wastes on nature that increase rapidly in respect to both content and quantity in parallel to technological development, industrialization and urbanization have been an important environmental problem [1].

In this context, strategic plan and budget may be considered as the primary tools of sustainable development of regions. Strategic plan basically allows or facilitates the creation, implementation and evaluation of regional policies [2].

Depletion of fossil fuel reserves and associated global climate changes caused by the net increase in atmospheric CO_2 due to combustion of fossil fuels [3] are leading to search for alternative, renewable, carbon-neutral energy sources [4].

Primary energy sources include domestic mined fuels, hydro and wind power, nuclear heat, the balance of imports and exports and changes to stocks of fuel and energy [5].

In 2030, it is estimated that in terms of source used, the structure of energy production will be: 75…85 % of conventional fuel combustion, 10…20 % of nuclear fission, 3…5 % of waterpower, approx. 3 % of solar and wind energy [6].

In the present context of obtaining clean energy, biomass represents one of the most used renewable sources of energy with potential to be applied using different technologies.

Alongside combustion, the biomass based fuels were put to a variety of uses as solvents, greases, cleaners or as basic chemicals for the emerging chemical industry [7].

Also in regards with biomass, the large amounts of animal manure and slurries produced today by the animal breeding sector as well as the wet organic waste streams represent a constant pollution risk with a potential negative impact on the environment, if not managed optimally [8].

In this context, the use of anaerobic digestion or anaerobic fermentation represents a viable solution for partially solving the problem of using residual materials, with vegetal, animal or industrial origins.

Anaerobic digestion is the process of decomposition of organic matter by a microbial consortium in an oxygen-free environment [9].

Anaerobic digestion involves the degradation and stabilization of organic materials under anaerobic conditions by microbial organisms and leads to the formation of biogas (a mixture of carbon dioxide and methane, a renewable energy source) and microbial biomass [10].

Anaerobic digestion effluent typically contains high amounts of ammonium, phosphate, suspended solid (SS), and persistent organic substrate, which has been generally applied as a fertilizer for recycling the nutrients in agricultural field [11],[12].

Even if this process has its advantages, one of the problems which can appear is the appearance of foaming.

Anaerobic digestion (AD) foaming has been recorded in many sewage treatment works (STWs) for over a decade with severe impacts on the overall digestion process [13],[14].

Foaming can result in an inverse solids profile having higher solids concentrations at the top of a digester, creation of dead

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zones and reduction of the active volume of the digester hence resulting in sludge, which has not received the same degree of stabilization [15].

Connected with the previous presented aspects, the present paper underlines the influence of anaerobic fermentation on different agricultural materials during tests at small scale and using a pilot installation for different amounts of time as residence periods inside the installations.

Conclusions will be traced in regards with process parameters and variation of general material properties before and after the process.

II. MATERIALS AND METHODS

A. Experimental installation

The next paragraph will take into consideration the installations used for testing.

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

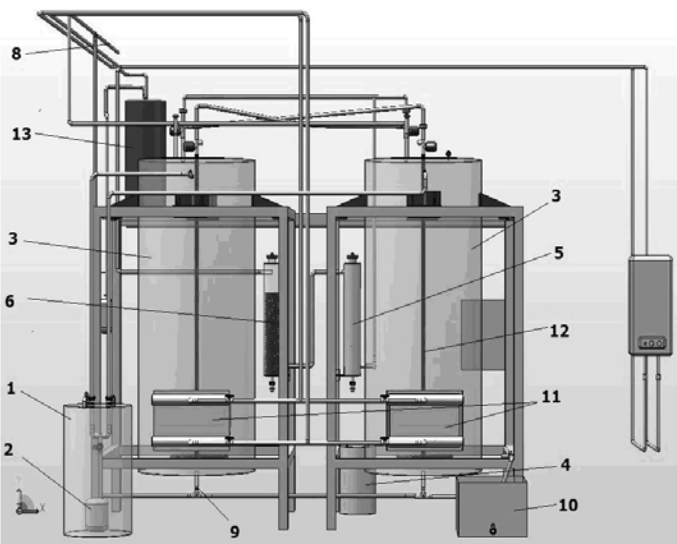

Fig. 1 Pilot installation general schematics

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 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_2 desorption and the compression of the CO_2 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 semi-automated system and afterwards through a gas counter. Methane (CH_4) and carbon dioxide (CO_2) compositions (v/v) were measured using a Delta 1600 IV gas analyzer. Temperature and pH were also continuously measured.

The small scale installation is presented in Fig. 2.

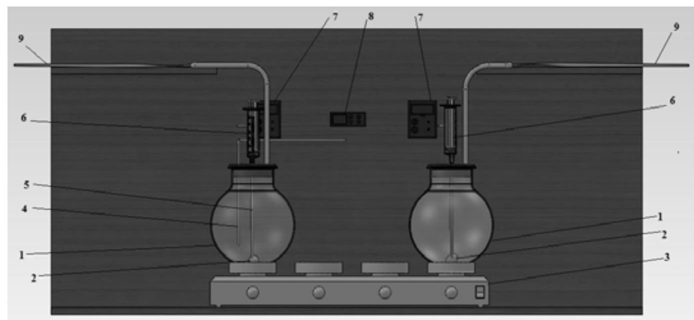

Fig. 2 Schematics of the small scale installation

The components of the small scale installation are identical with the ones described above.

1 – thermal glass vessels with a total volume of 6 l used for dark fermentation;

2 – magnets positioned at the bottom of the glass vessels used for magnetic stirring of the used material suspensions; this system allows also the manual stirring / agitation;

3 – device used for heating the suspension inside the glass vessels;

4 – thermocouple used for temperature control inside the fermentation vessels;

5 – system for sampling and pH correction of the suspensions inside the vessels;

6 – syringe used for sampling and pH correction system

7 - pH controllers connected to pH sensors inside the glass vessels in order to determine in real time the pH value of the suspension;

8 – temperature controller connected with the thermocouple inside the glass vessel for temperature control to a determined range;

9 – gas bags with a total volume of 2 l dedicated for sampling the obtained biogas from the fermentation process.

B. Chemical analysis

The samples collected were successively subjected to physical and chemical analyses. The standards used for laboratory determinations were: EN 14774 – Solid biofuels – Determination of moisture content – Oven dry method (parts 2 and 3) [16]; EN 14775 - Solid biofuels - Determination of ash content [17]; EN 14918 - Solid biofuels – Determination of calorific value [18]; EN 15290 – Solid biofuels – Determination of major elements [19]; EN 15297 – Solid biofuels – Determination of minor elements [20]; EN 15104 – Solid biofuels – Determination of total content of carbon, hydrogen and nitrogen – Instrumental methods [21]; EN 15148 – Solid biofuels – Determination of the content of volatile matter [22].

All analyses were performed in duplicate.

III. Results and discussion

Four different agricultural biomasses: wheat (W), wheat bran (WB), barley (B), two-row barley (TB) used as ingestates in an anaerobic digestion process were characterized from physico-chemical point of view: moisture content, ash content, gross and net calorific value, volatile matter content, carbon content, nitrogen content, hydrogen content and heavy metal concentrations. The corresponding values are presented in table I.

Table I. Main parameters of biomasses used in the anaerobic digestion process

Biomass	Wheat	Wheat bran	Barley	Two Row Barley
Moisture content (db) (%)	9.92	9.72	10.6	10.7
Ash content (db) (%)	1.63	5.54	2.52	2.22
Gross calorific value (db)(J/g)	18125	19034	18667	18354
Net calorific value (db)(J/g])	16566	17520	17291	16763
Carbon content (%)	40.1	41.3	40.2	40.1
Hydrogen content (%)	6.4	6.2	6.2	6.5
Nitrogen content (%)	1.35	2.06	1.44	1.38
Volatile matter content (db) (%)	84.1	78.4	82.5	82.4
Cr (ppm)	<5	<5	<5	<5
Pb (ppm)	450	440	440	450

These biomasses were subjected to an anaerobic digestion process during 40 and 65 days. In the end, the corresponding digestate samples were collected for analysis: wheat digestate after 40 days (WD40), wheat bran digestate after 40 days (WBD40), barley digestate after 40 days (BD40), two-row barley digestate after 40 days (TBD40), wheat digestate after 65 days (WD65), wheat bran digestate after 65 days (WBD65), barley digestate after 65 days (BD65), two-row barley digestate after 65 days (TBD65). The samples were subjected to same characterization as the raw materials, in order to see the evolution of parameters during anaerobic digestion process.

The temperature regime for the material batches was the mesophilic one with temperatures between 27 – 37 °C. In the graphics below (Fig. 3 – 6) is presented the pH variation for the batches during 40 days and 65 days of process.

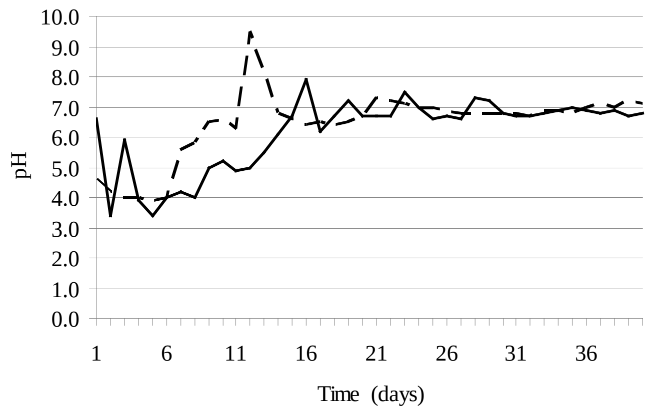

Fig. 3 pH variation at 40 days for barley (— —) and two row barley (——)

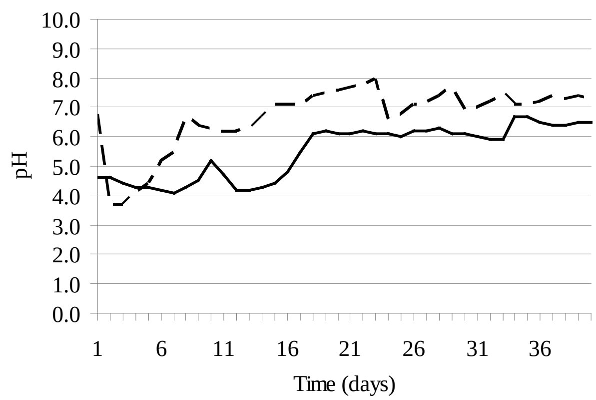

Fig. 4 pH variation at 40 days for wheat (——) and wheat bran (— —)

From the two graphics presented above it can be observed that the materials had different pH behavior during the anaerobic fermentation from the initial acid phase to the final neutral phase, the most stable material being wheat bran.

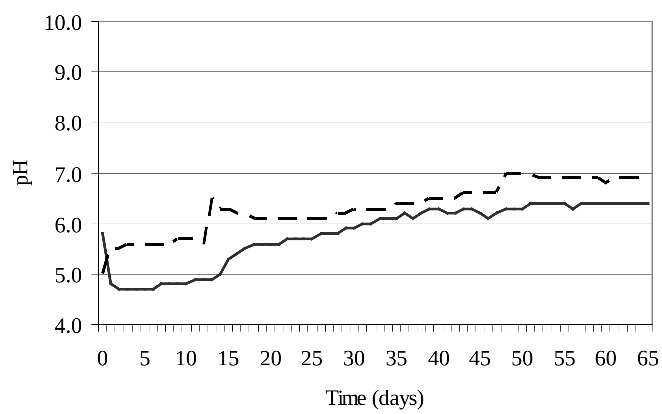

Fig. 5 pH variation at 65 days for wheat (——) and wheat bran (— —)

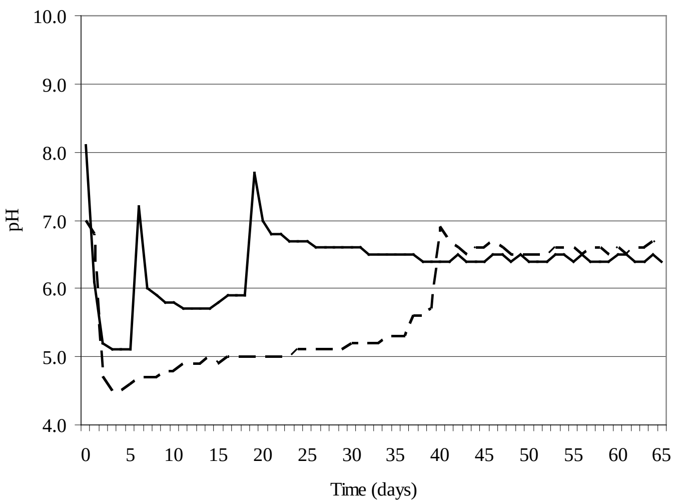

Fig. 6 pH variation at 65 days for barley (— —) and two row barley (——)

Also for this case, the wheat bran material had the most stable behaviour during the process, reaching the neutral pH values faster than the rest of materials.

The lowest pH was observed for the barley batch.

For the process at 65 days fermentation there was determined also the produced biogas quantity for the used materials as follows:

- wheat batch: 17 m^3
- wheat bran batch: 17 m^3
- barley batch: 13.5 m^3
- two row barley batch: 27 m^3.

After the fermentation process the next step was to analyze the obtained residues in order to determine the overall influence of the process on the material general properties. The determined values are presented below.

The variation of digestates ash content in regard to initial biomasses is presented in Fig. 7.

Fig. 7 Variation of substrate ash content during anaerobic digestion process: 0 -, 40 -, 65 -

From the figure it can be noticed that the ash content of resulted digestates is higher that of the initial material. Only the barley digestate obtained after 40 days of anaerobic digestion has a lower value. Among the digestates resulted after 65 days of anaerobic digestion, the one corresponding to wheat substrate has the lower ash content. The high percent of ash content indicates that the digestates are not suited to be capitalized in the combustion process as a biofuell.

The gross and net calorific values of substrates and digestates are presented in Fig. 8 and 9.

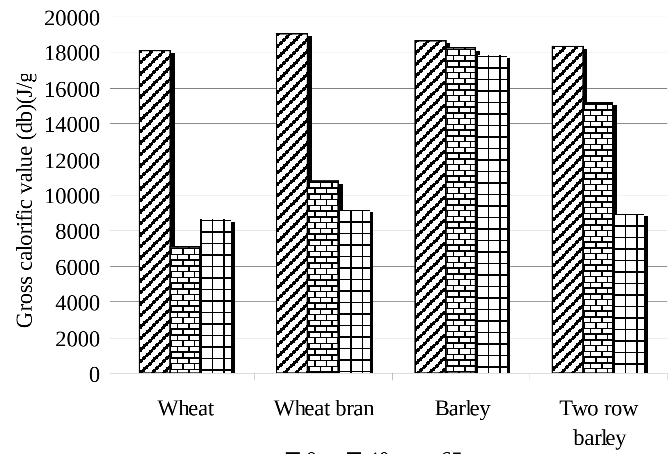

Fig. 8 Variation of substrate gross calorific value during anaerobic digestion process: 0 -, 40 -, 65 -

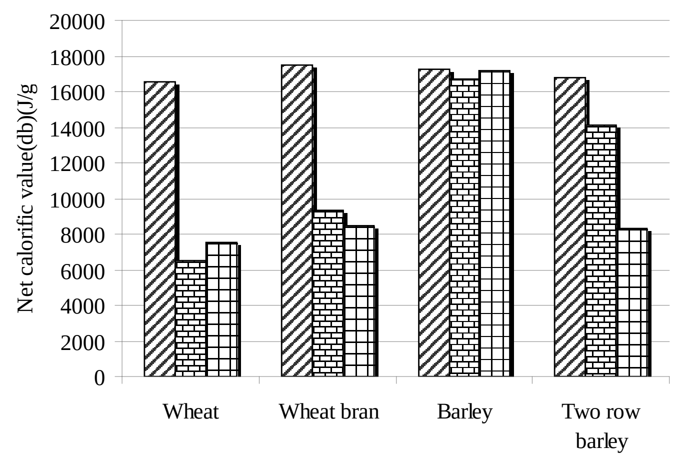

Fig. 9 Variation of substrate net calorific value during anaerobic digestion process: 0 -, 40 -, 65 -

The figures revealed that there were not significant differences in calorific energy of the different agricultural crops used as substrate in anaerobic digestion process. Contrary, this is changing when it comes to digestates. Wheat digestates have the lowest values of gross and net calorific energy. As concern barley digestates, even after 65 days of anaerobic digestion, their gross and net calorific values do not change from the values of the substrate. This indicates that these digestates can be used further in biogas production field.

The chemical characteristics of fresh biomasses and corresponding digestates are reported in table II.

Table II. Chemical characteristics of fresh biomasses and digestates

No.	Material	Carbon content, (%)	Hydrogen content, (%)	Nitrogen content, (%)	Volatile matter content (db), (%)
1.	W	40.1	6.4	1.35	84.1
2.	WD40	23.0	2.5	2.45	54.3
3.	WD65	40.3	5.2	1.00	47.3
4.	WB	41.3	6.2	2.06	78.4
5.	WBD40	57.1	6.4	11.0	62.1
6.	WBD65	27.6	3.2	1.67	58.4
7.	B	40.2	6.2	1.44	82.5
8.	BD40	55.7	6.2	1.62	81.8
9.	BD65	26.4	3.0	1.38	35.4
10.	TB	40.1	6.5	1.38	82.4
11.	TBD40	36.7	4.7	3.87	64.8
12.	TBD65	27.4	3.0	1.09	59.1

At the end of anaerobic digestion process, the volatile matter content of digestates was significantly lower relative to fresh biomass. This can be due to consumption of sugars, proteins, amino acids and fatty acids during the anaerobic digestion. The decrease level of volatile matter content of digestates can be a measure of the depletion degree of fresh biomass. Thus, the lowest value of volatile matter content was found for barley digestate (BD65) according to the following order: BD65 < WD65 < WBD65 < TBD65.

In order to be used as nutrient fertilizer or organic amendments, the content of heavy metals in the digestates have to be lower. The heavy metal concentration of substrates before and after anaerobic digestion is presented in table III.

Table III – Heavy metals concentration of substrates before and after anaerobic digestion

No.	Material	Cr, (ppm)	Pb, (ppm)
1.	W	<5	450
2.	WD40	20.0	190
3.	WD65	5	<5
4.	WB	<5	440
5.	WBD40	10.0	260
6.	WBD65	10.0	240
7.	B	<5	440
8.	BD40	10.0	440
9.	BD65	<5	<5
10.	TB	<5	450
11.	TBD40	10.0	370
12.	TBD65	30.0	230

As shown in table III, the highest concentrations of Cr and Pb can be found in the digestates of wheat bran and two row barley.

IV. Conclusions

The results presented in this study revealed the influence of the raw materials on the digestate characteristics, which mean that each digestate must be analyzed before deciding their future uses.

From the used materials, from the point of view of pH variation, the most stable is wheat bran for both processes, while the lowest values were registered for the barley batch.

From the point of view of the obtained biogas quantities in the same period of time, the highest values were registered for two row barley while for the barley batch there was the lowest quantity produced (about 13.5 m^3); the wheat and wheat bran batch produced the same biogas quantity – 17 m^3.

According to the net calorific values of the digestates investigated, the barley digestate has the highest value, even after 65 days of anaerobic digestion which makes it suitable for future use in energy field. On the other hand, barley digestate has the low content in Cr and Pb and it can be recommended for further use in agriculture as nutrient fertilizer or organic amendments.

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