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Case Studies in Biogas Production from Different Substrates

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Abstract

The present paper involves applicative research in the field of biogas production with the accent on small laboratory scale installations built for biogas production, preliminary testing of substrate for biogas production and combustion applications for biogas-like mixtures. The interconnected aspect of the presented material involves cumulative expertise in multidisciplinary fields of interest and continuous development of possibilities to determine the energetic potential of substrates subjected to biodegradable fermentation conversion for further applications. The research analyzed the combustion behavior of biogas with different methane/carbon dioxide ratio without and in the presence of specific catalysts. Also, laboratory analysis on biomass substrates for determining their physical and chemical potential for different applications was performed. The main conclusions are drawn revolve around the untapped potential of the different types of biomasses that are not commonly used in the production of renewable energy carriers, like biogas, and also the potential use of residual biomass in combustion processes for an enclosed life cycle from cradle to the grave. The study involving the use of catalysts in biogas combustion processes present possible solutions which can be developed and implemented for increasing the combustion quality by using relatively cost-effective materials for the production of catalytic materials.

Keywords: biomass, biogas, anaerobic digestion, renewable energy, combustion

1. Introduction

Renewable energy sources have become a milestone of the next decades for European Union member states, due to tough deadline targets to reduce their energy production dependency on fossil fuels. In June 2021, thru its new European Climate Law, the EU targets a reduction of greenhouse gases emission of at least 55% by 2030, compared to the 1990 level, and a net-zero greenhouse gas emissions in the EU by 2050. On top of this ambitious target, the EU is pushing its member states to complete climate neutrality by 2050. In this frame, the new 2030 greenhouse gases emission reduction target for Romania is 12.5% (in respect to 2005 inventory), a target that Romania has already passed in several chapters, with a total reduction in 2019 of 65% compared to 1990 emissions inventory, being the member state that achieved the highest greenhouse gases emissions reduction in the EU, along with Lithuania. However, for a specific chapter, the “transportation, buildings and agriculture sector” Romania has a new reduction target of 12.7% by 2030 (compared to 2005 national GHG inventory) [1].

Having in mind that for Romania most of the industrial sectors have or are close to reach their targets for 2030 and the main 2 sectors that still must reduce with 12.7% of their greenhouse gases emissions by 2030 are transportation and agriculture are clear that the focus should be on developing the renewable sources that can have a significant impact on both sectors. The renewable energy sector had a fast development in the past 2 decades, however, the energy production from biomass/biogas did not increase as other sources. For example, in 2019 in Romania the installed renewable energy installed capacities from biomass/biogas was of 124.16 MW while the photovoltaic installed capacities were 1358.43 MW and wind farms at 2960.64 MW. With this data on mind it becomes quite clear that Romania's focus in the next period should be on biomass/biogas production facilities development as not only will reduce dependency on methane imports but will contribute to reaching greenhouse gasses emissions from the agriculture sector.

The production of biogas from biomass substrates thru anaerobic digestion is well known since antiquity, the technology being constantly developed but due to environmental impact thru pollutants developed (solid, gas and liquids) faces continuous challenges, with continuous scientific efforts in research for innovative materials to be used in biogas production from biomass and urban waste waters [2].

In the Romanian case and any other country with significant agricultural areas and also a large number of urban agglomerations, the potential sources for biogas production thru anaerobe digestion can be classified in four main groups:

- Organic wastes from agricultural/zootechnie – with all potential biodegradable materials;
- Agriculture and food waste, such as manure and wastes from treatment plants in form of organic-rich sludge;
- Municipal wastes in form of fermentable fractions;
- Sludge from municipal wastewater treatment plants [3].

In terms of biogas production from any of the sources classified above, the most critical parameter in obtaining the best CH_4/CO_2 ratio after anaerobic digestion is the substrate composition, as today's substrates are mostly formed for co-digestion of a minimum two waste materials. Depending on the substrate composition the anaerobic reaction temperature will have a different effect on variation of pH, volatile fatty acids, total solid degradation and ammonia/nitrogen ratio that would affect the stability of the digestion process [4].

In the EU country, all biofuels (solid, liquid or gaseous) have a subsidy from EU public budgets and accordingly the production of biofuels is subject to sustainability criteria under the Renewable Energy Directive [5]. The Directive introduces significant restrains in the production of raw agricultural materials for energy use, mainly to protect primary forests and biodiversity. In respect of the Directive, the Romanian focus for developing a sustainable biofuel (with emphasis on biogas production for energy purposes) industry should be on agricultural and urban wastes.

2. Applied research on case study

Currently, the focus is to work on small-scale installations for testing in a controlled environment the potential for different materials and the possibility to develop new bioreactors for further use in anaerobic fermentation processes.

The present chapter will highlight a part of the research conducted so far, covering three main parts:

- Testing in firing processes of biogas and biogas – like mixtures – for this study, the used biogas recipe contained methane and carbon dioxide in known volume participation, initial tests were performed without catalysts and further determinations were carried on using different types of laboratories determined catalysts to determine their potential influence during the combustion process;
- Laboratory analysis on biomass substrates for determining their physical and chemical potential for different applications – the analysis for chosen biomass was performed by the European Standards for solid biofuels (EN ISO 18134 – Solid biofuels – Determination of moisture content – Oven dry method (3), EN ISO 18122 – Solid biofuels – Determination of ash content; EN 14918 – Solid biofuels – Determination of calorific value; EN ISO 16948 – Solid biofuels – Determination of total content of carbon, hydrogen and nitrogen; EN ISO 16994 – Solid biofuels – Determination of total content of sulfur and chlorine; EN ISO 18123 – Solid biofuels – Determination of the content of volatile matter; CEN/TS 15370 – Determination of ash melting behavior);
- Laboratory studies for biogas production and system development in terms of parameter monitoring and initial inputs for new different materials used for anaerobic digestion processes – the test rigs for laboratory determinations were developed in house and the main testing conditions involved using a known temperature regime (mesophilic or thermophilic), the existence or absence for materials homogenization, and continuous measuring of pH, and volume participation of methane, carbon dioxide and hydrogen sulphide in the produced biogas.

2.1 Testing in combustion processes of biogas: like mixtures

Biogas like mixtures represent, in our case, mixtures containing 70–75% methane and around 25–30% carbon dioxide, concentrations by volume, to assess the energetic potential for this type of materials, by comparison with real biogas testing, which contains also other elements, like hydrogen sulfide (the main corrosive and toxic component in biogas), ammonia, water and other impurities from the process of anaerobic digestion.

First, we will present in short, some determinations relative to biogas determinations. Those determinations were made for determining the biogas potential in firing processes and were carried out in situ, by using pilot patented installations, but for our discussions, the test rigs will not be presented, only the part needed for the firing testing.

The tests were carried out at a location for an industrial partner for Politehnica University, and the produced biogas came from anaerobic digestion of municipal residues.

The figure below presents the test rig developed for firing tests (**Figure 1**).

As it can be observed above, from left to right there are the following components: biogas pipe, connected with the system for pressure control and measuring, the burner (in yellow) and the entrance to the firing chamber, where the tests were carried out. At the end of the chamber, there were measured the flue gas and the temperatures were determined at specific points on the outside wall of the testing chamber. The next images will present some results for the measurements of the flue gas. The equipment used in this regard was TESTO 350XL and DELTA 1600 S IV gas analyzers.



Figure 1.
Elements of the test rig.

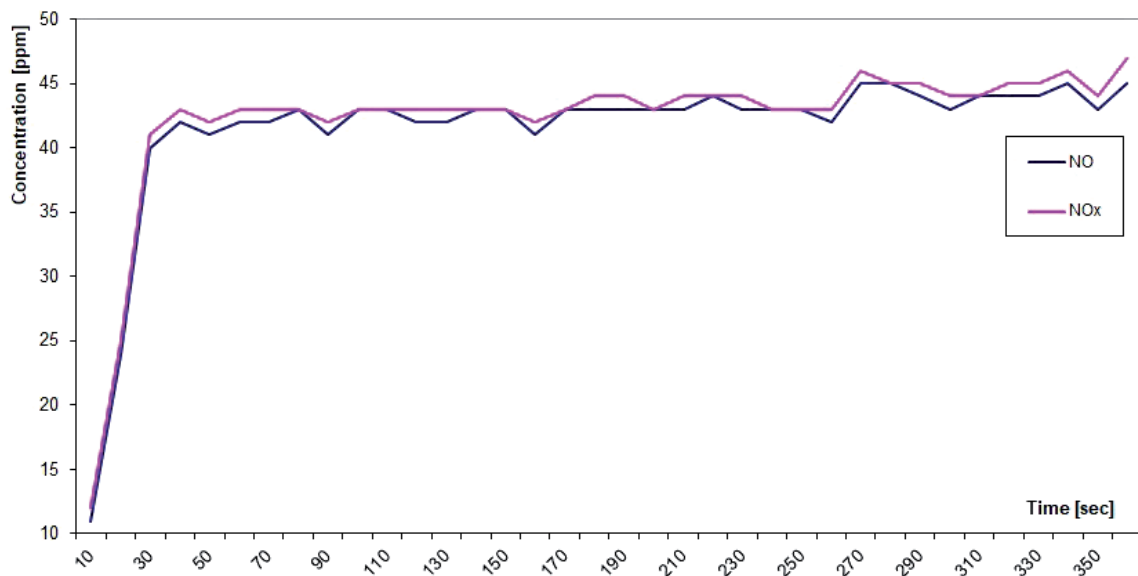


Figure 2.
NO, NOx concentration evolution in time.

Figure 2 presents the time variation of NO and NOx during the combustion process of biogas containing around 75% methane and 24% carbon dioxide. The produced biogas was without a filtering system. From the presented graphic, it can be determined that the nitrogen oxides concentration is very low (ppm values), at around 40–43 ppm, which represents very good results in this context.

The used burner had a constructive air-cooled system of the flue gas and by this method, combined with a relatively high rate of combustion, the resulting NOx emission was very low, which represents a positive aspect in this context (**Figure 3**).

Carbon monoxide is one of the most dangerous flue gasses in high quantities and it needs relatively high temperatures and safe firing conditions to be present in low concentrations. The maximum values for CO concentration during the process are also very low, at around 35 ppm, a very good indicator for a relatively complete

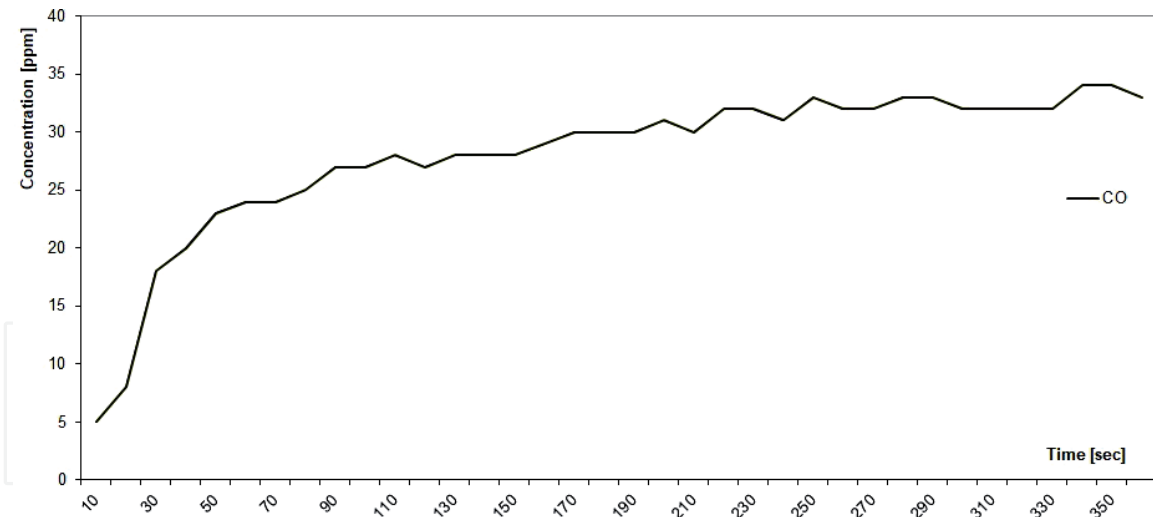


Figure 3.
CO concentration evolution in time.

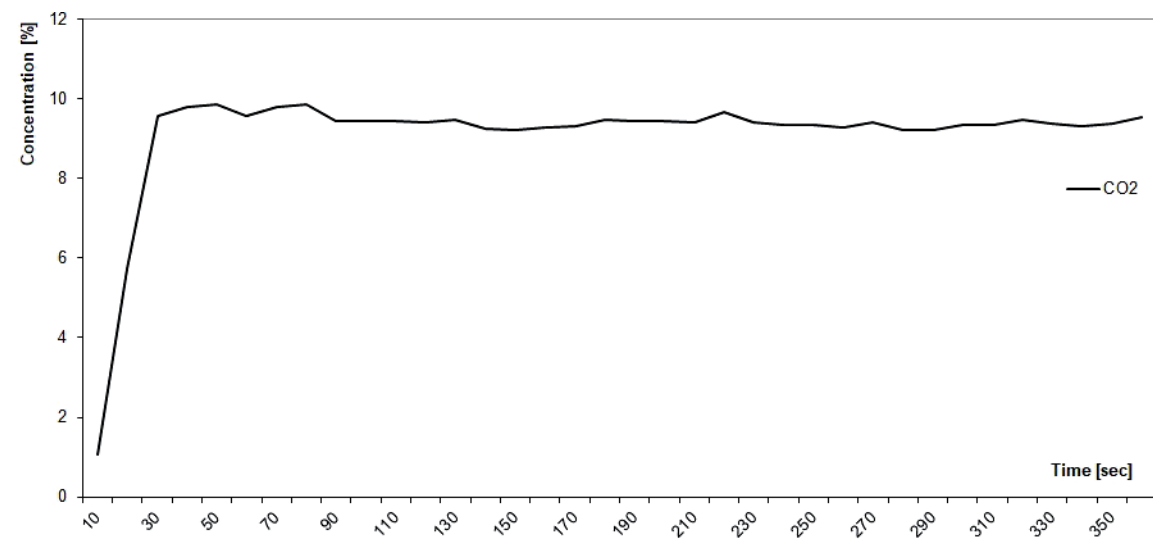


Figure 4.
CO₂ concentration evolution in time.

firing process. The obtained values used by parallel measurement with all the other existent flue gas, indicated the low volume presence of CO which is a positive argument for a very safe firing process.

As observed in **Figure 4**, CO₂ concentration maximum values were at around 9–10%. It is important to have in mind the fact that those values started at around 25–30% by volume before the firing process, which indicates also that the firing parameters were efficient, even if the overall CO₂ did not burn (because of its inert nature to firing reaction). Next, there are going to be presented tests made together with collaborators from Serbia, the Mechanical Engineering Faculty in Belgrade.

The tests were carried out in the presence and absence of catalysts to observe their influence over the firing parameters and also the flue gas was analyzed with the help of a Horiba gas analyzer coupled with a special developed system used for data collection and registration, containing temperature and pressure sensors, and data control and storage equipment (**Figure 5**).

The used catalysts were ZnAl₂O₄, CoAl₂O₄ and ZnCr₂O₄. The obtained pellets were inserted in a metal matrix for protection purposes and the firing chamber was prepared for preliminary tests.

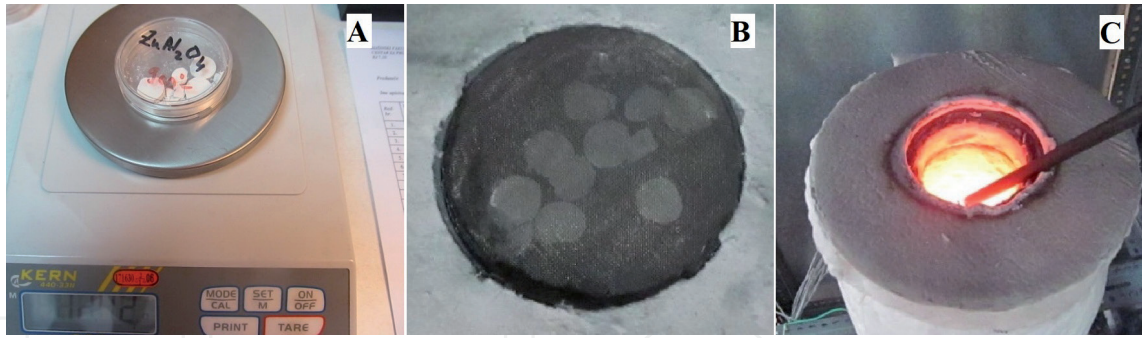


Figure 5. Preparation of $ZnAl_2O_4$ catalysts: A – Weighting; B – Insertion in the metal matrix; C – Initial testing with and without catalysts.

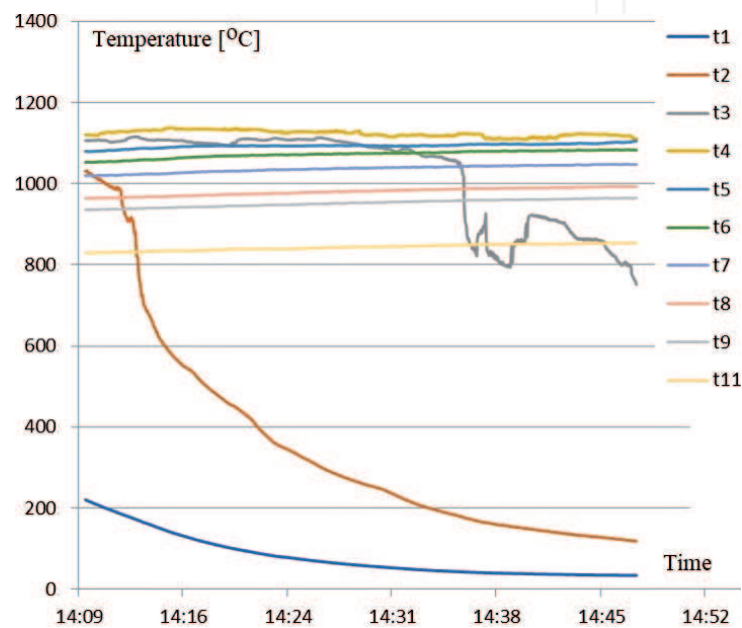


Figure 6. Temperature values inside the combustion chamber, without catalyst presence.

Before recorded measurements, there were made some preliminary trials to calibrate all the necessary equipment and sensors on the used firing chamber. The next part will present in summary just a small part of the determinations performed inside the firing chamber, with and without the existence of catalysts (**Figure 6** and **Table 1**).

From the gathered data, it was determined that at the base of the reactor, the maximum temperature reached was around 1058°C , with very low gaseous emissions (**Figure 7** and **Table 2**).

By comparison with the first scenario, it can be observed that the maximum temperature reached at the solid phase (the base of the reactor) is around 1097°C , slightly higher than for the process without catalyst, but it was observed an increase of CO concentration, which indicated an incomplete combustion process. The main indicator of an increased CO is usually the area with high temperatures. This aspect combined with an ineffective air/fuel ratio can have as a main result the higher CO concentration, at least this is the author's present explication to this phenomenon.

The only catalyst presented in this study was $ZnCr_2O_4$, because for the other used catalysts, there was no visible influence over the firing parameters overall, this meaning they had a very limited impact in this testing scenario. Of course, further testing is to be made available to determine possible applications for the used catalysts and to test new ones for better results over impact during combustion processes.

Excess air				[-]	2.0					
Burner power				kW	1.5					
Fuel ratio CH ₄ :CO ₂				[-]	80.4:19.6					
Fuel lower heating value				[kJ/m ³]	28847.52					
Fuel consumption				[m ³ /h]	0.1872					
Air consumption				[kg/h]	3.7041					
Burner pebble bed diameter				[mm]	13					
Burner pebble bed height				[mm]	253					
Burner pebble bed porosity				[-]	44.94					
Flame arrestor bed diameter				[mm]	6					
Flame arrestor bed height				[mm]	107.5					
Temperature distribution within the porous burner – gaseous phase										
-0.1	0	0.11	0.22	0.33	0.44	0.55	0.66	0.77	0.99	
t ₁	t ₂	t ₃	t ₄	t ₅	t ₆	t ₇	t ₈	t ₉	t ₁₁	
80.5	354	1022.3	1123.8	1093.5	1072.5	1036.5	980.4	951.9	843.2	
Temperature distribution within the porous burner – solid phase										
0		0.44			0.66			0.88		
t _{s1}		t _{s3}			t _{s4}			t _{s5}		
784.3		1058.2			1012.6			943.0		
Flue gas analysis at the exit of the burner										
O ₂ [%]		CO ₂ [%]			NOx [ppm]			CO [ppm]		
11.10		6.63			1			28		

Table 1.
 Testing without catalyst.

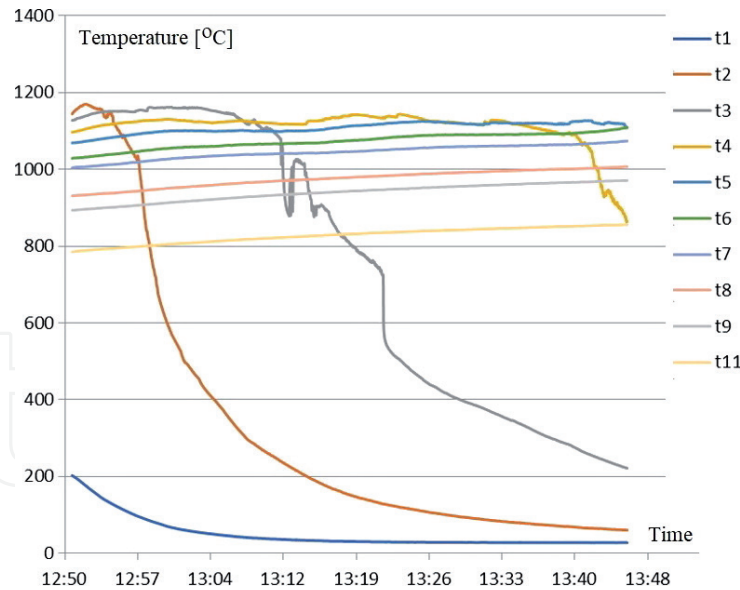


Figure 7.
Temperature values inside the combustion chamber, with $ZnCr_2O_4$ catalyst presence.

Overall, the started research is to be continued and further tests need to be done for simulating more different regimes, as well as to investigate the influence of catalysts at higher working temperatures.

2.2 Laboratory analysis on biomass substrates for determining their physical and chemical potential for different applications

This part of the present material will underline a part of the experimental determinations for different types of biomasses to determine their potential for anaerobic digestion or firing (co-firing) processes.

The used standards for laboratory determinations were:

- EN ISO 18134 – Solid biofuels. Determination of moisture content. Oven dry method;
- EN ISO 18122 – Solid biofuels. Determination of ash content;
- EN 14918 – Solid biofuels. Determination of calorific value;
- EN ISO 16948 – Solid biofuels. Determination of total content of carbon, hydrogen and nitrogen;
- EN ISO 16994 – Solid biofuels. Determination of total content of sulfur and chlorine;
- EN ISO 18123 – Solid biofuels. Determination of the content of volatile matter;
- CEN/TS 15370 – Determination of ash melting behavior.

The next table presents a small part of the determinations made for different types of biomasses (**Table 3**).

The chosen materials came from a very large selection, which stands as a base material for a database created by the first author of this chapter, database that is continuously under development and contains materials from agricultural, forestry,

Excess air				[-]	2.0					
Burner power				kW	1.5					
Fuel ratio CH ₄ :CO ₂				[-]	80.4:19.6					
Fuel lower heating value				[kJ/m ³]	28847.52					
Fuel consumption				[m ³ /h]	0.1872					
Air consumption				[kg/h]	3.7041					
Burner pebble bed diameter				[mm]	13					
Burner pebble bed height				[mm]	253					
Burner pebble bed porosity				[-]	44.94					
Flame arrestor bed diameter				[mm]	6					
Flame arrestor bed height				[mm]	1075					
Temperature distribution within the porous burner – gaseous phase										
-0.1	0	0.11	0.22	0.33	0.44	0.55	0.66	0.77	0.99	
t ₁	t ₂	t ₃	t ₄	t ₅	t ₆	t ₇	t ₈	t ₉	t ₁₁	
49.4	322	747	1108.7	1107.7	1073.2	1044.7	975.2	938.8	827.3	
Temperature distribution within the porous burner – solid phase										
0		0.44			0.66			0.88		
t _{s1}		t _{s3}			t _{s4}			t _{s5}		
531.3		1065.2			1011.2			930.7		
Flue gas analysis at the exit of the burner										
O ₂ [%]		CO ₂ [%]			NOx [ppm]			CO [ppm]		
11.7		6.30			2			248		

Table 2.
 Testing ZnCr₂O₄ catalyst.

Material	Observations	Source
Paulownia (<i>Paulownia tomentosa</i>)	pre-dried sawdust	entire plant
White poplar (<i>Populus alba</i>)	pre-dried sawdust	entire plant
Elephant grass (<i>Pennisetum purpureum</i>)	pre-dried sawdust	entire plant
Hemp (<i>Cannabis sativa</i>)	pre-dried sawdust	entire plant
Sunroot (<i>Helianthus tuberosus</i>)	pre-dried sawdust	entire plant

Table 3.
Types of analyzed biomass.

household, municipal, and industrial fields of application for all that involves biodegradable or partially degradable materials.

The next tables are going to present some general aspects concerning the properties of the studied materials and the potential application for energetic conversion (**Table 4**).

The moisture of the presented materials is considered for already pre-dried materials. From an ash content, the white poplar and sunroot have the largest values, making them not the first choice for firing processes, due to their high residue and ash content.

The calorific value is high for all the studied materials, and a very interesting aspect is the fact that the arborescent samples have net calorific values close to plant biomass, making them suitable for both energy conversion processes.

The carbon content and nitrogen are very specific for biomass, while the hydrogen content is close in value from one species to another, except hemp. There are no exceptional or different values than the ones expected for this type of material. Relative to C/N ratio, the best suitable biomass would be Sunroot, with a ratio of around 31. According to existing literature, the optimum domain for C/N ratio should be between 20 and 30, but from experience some materials do not meet these criteria and can be used for anaerobic digestion (**Table 5**).

The four specific points are very important to determine the specific temperatures at which the materials are starting to transform and reach a flowing point.

Material	Moisture content [%]	Ash content [%]	C [%]	H [%]	N [%]	Volatile content [%]	Gross calorific value [J/g]	Net calorific value [J/g]
Paulownia (<i>Paulownia tomentosa</i>)	10.04	1.12	45.6	6.44	0.329	84.16	20,218	18,659
White poplar (<i>Populus alba</i>)	10.7	5.93	43.6	6.4	0.92	76.8	19,350	17,764
Elephant grass (<i>Pennisetum purpureum</i>)	12.7	1.86	42.6	6.3	0.09	83.9	19,234	17,651
Hemp (<i>Cannabis sativa</i>)	15.5	2.87	48.3	5.4	0.45	79.1	19,334	17,940
Sunroot (<i>Helianthus tuberosus</i>)	11.3	5.94	45.3	5.59	1.46	74.3	18,277	16,903

Table 4.
Material energy properties, analysis on a dry basis.

Material	Shrinking temperature [°C]	Deformation temperature [°C]	Hemisphere temperature [°C]	Flow temperature [°C]
Paulownia (Paulownia tomentosa)	1080	1280	1370	1400
White poplar (Populus alba)	1010	1540	> 1540	> 1540
Elephant grass (Pennisetum purpureum)	730	1010	1250	1280
Hemp (Cannabis sativa)	960	1240	1300	1320
Sunroot (Helianthus tuberosus)	610	1280	1490	> 1540

Table 5.
 Material chemical properties, analysis on dry basis.

In this regard, combined with the energetic values and the ash content, it can be determined a good behavior of materials from a firing process point of view.

The sunroot material presented an unexpected high value for flowing temperature, while the rest of the materials presented expected values. The bark in white poplar made that the specific flowing point to be of a high value, as estimated.

In the context of the presented materials, the bark is to be excluded from analyzed samples, and the high ash content is a parameter that determines if the materials are suitable for combustion, co-combustion or other processes.

Of course, there are other parameters to be considered, like chlorine, sulfur or heavy metals, when taking into consideration all the variables to the energetic conversion, but this is just a partial analysis and the conclusions are traced accordingly.

The main applications for the study was to determine the energetic potential of biomass types not usually applied for firing or anaerobe digestion processes and to study their potential application in those two directions. The materials were chosen because there is not enough literature to discuss different potential applications for Elephant grass, hemp or sunroot in anaerobic digestion or combustion, while Paulownia and White poplar were chosen as comparative used materials, especially for firing applications. Present studies are made for anaerobic digestion of a part of the studied materials, but the work is still in progress.

2.3 Laboratory studies for biogas production and system development in terms of parameter monitoring and initial inputs for new different materials used for anaerobic digestion processes

This last part represents the focus of the research developed so far by the chapter authors. First, there will be depicted some of the small-scale test rigs developed so far, starting with commercial ideas, but less expensive and with good capability in terms of process control and results.

The next two figures present small-scale test rigs designed for preliminary testing of biogas production from different substrates (**Figure 8**).

The components found in the figure are:

1. Thermostatic bath with 6–8 places for heating the used materials for the anaerobic fermentation process (the temperature is controlled with the help of a thermostat and can be checked with the help of a thermometer inserted into the bath);

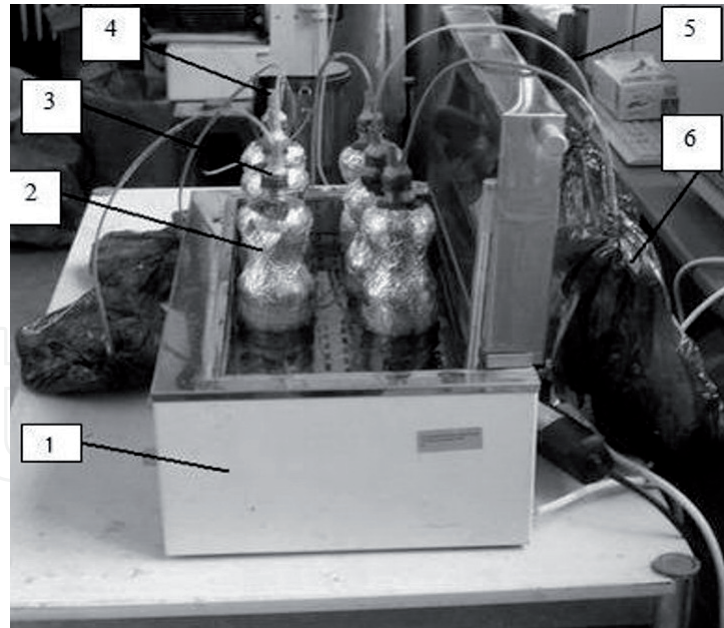


Figure 8.
Small scale test bench.

2. plastic bottles with a total volume of 1 (or 2) L, depending on the testing setup, filled up to about 0.8 (or 1.5) L with the materials used for determinations;
3. the corks of the plastic bottles were modified to allow both samplings for pH checking, homogenization using plastic syringes, and gas transfer from the bottles into the gas bags. Also, because of the light sensibility of the anaerobic bacteria, the bottles were covered with aluminum foil;
4. hose orifice for syringe insertion, used for sampling and homogenization;
5. connection (small diameter hose) between the plastic bottle and the gas bag for biogas storage;
6. gas bag for biogas storage.

The second small-scale test rig is dedicated to processes at ~4 L and allows better control for substrate agitation, while offering different levels for temperature (**Figures 9 and 10**).

Each part is a separate module composed of the reactor with lid, syringe for sampling and pH control and control panel for controlling temperature and agitation inside each reactor. In **Figure 11** there can be observed 4 modules that work independently from one to another. Both test rigs were used to determine biogas potential in terms of quantity and methane, carbon dioxide, hydrogen sulfide and dissolved oxygen for different recipes/substrates. The next part presents preliminary results for different experiments.

2.4 Laboratory production of biogas from waste waters, on 2 L scale test bench

The experiments were conducted in two batches. For the first batch, the used substrate materials were: waste water from urban treatment plant (M1), waste water from brew factory (M2), 95% waste water from treatment plant and 5% beet molasses (MM1), 95% waste water from brew factory and 5% beet molasses (MM2), 95% waste water from treatment plant and 5% cow whey (ZM1) and 95%



Figure 9.
Small scale modules.

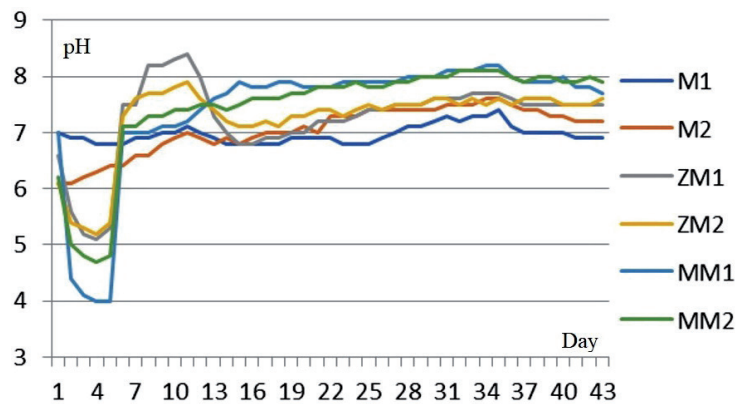


Figure 10.
Substrate pH variation in time, first batch.

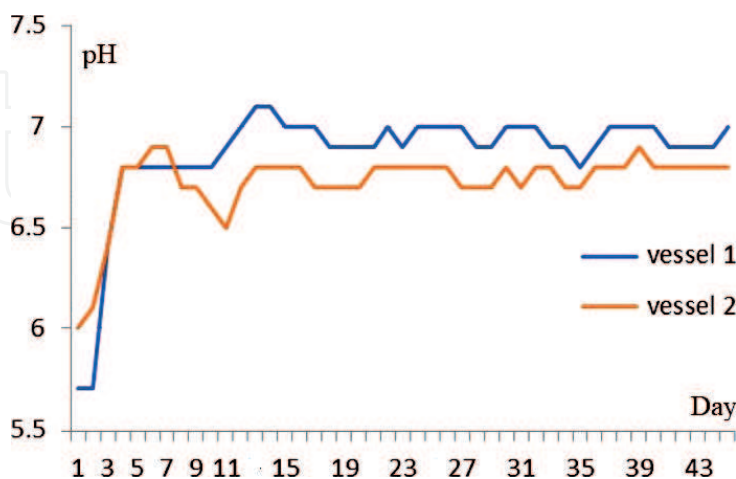


Figure 11.
Substrate pH variation in time, second batch.

waste water from brew factory and 5% cow whey (ZM2). The temperature regime was held at 36–37°C and the process parameters which were controlled consisted in pH, biogas partial composition and obtained quantities. The pH time variation for the material batches is presented in **Figure 12**.

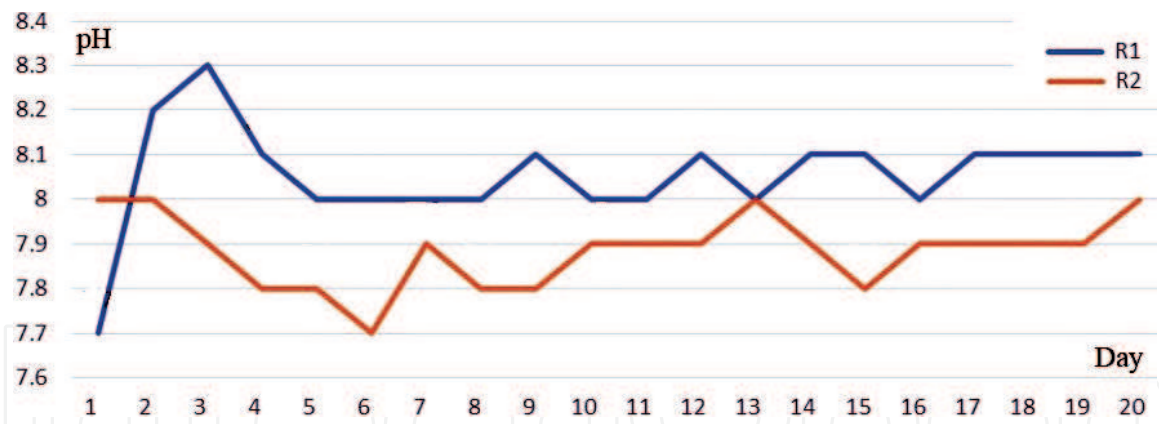


Figure 12.
Substrate pH variation in time, first batch on 4 L reactors.

From the pH variation, it can be observed that the co-fermented batches containing molasses for both residual sludges had the lowest pH, which increased after many corrections, which inhibited the fermentation process.

The pH for M1 and M2 was in the correct range and needed small interventions in terms of correction, the batch failed to produce a cumulative quantity of biogas that could be properly analyzed.

The most notable biogas quantities were produced by the MM1 (6 L) and ZM1 (4.5 L) batches. The maximum composition obtained after analyzing the produced biogas was for MM1, with 75% CH₄ and 10% CO₂.

On the second batch, the experiments were conducted in parallel, the second batch material used was formed as follows: 91% residual water from the treatment plant, 4% dehydrated sludge from the treatment plant and 5% cow whey for the first vessel and 91% residual water from the beer factory, 4% dehydrated sludge from treatment plant and 5% cow whey for the second glass vessel. The pH of the suspension was corrected with a solution of NH₃ 20% concentration and the temperature regime was held inside the domain of 36–37°C.

It can be observed that during the process, the batches presented a relatively high pH value which made the use of the NH₃ suspension to be made just at the beginning of the process when the starting pH wasn't neutral.

Even if both batches produced biogas, the main composition of the produced gas until the end of the process was about 60 ÷ 61% CH₄ and 38 ÷ 40% CO₂ for both batches of material.

The produced quantities were about 4 L of gas for the mixture with residual water from the treatment plant, 4% dehydrated sludge from the treatment plant and 5% cow whey and about 5 L for the batch composed by residual water from the beer factory, and 4% dehydrated sludge from treatment plant and 5% cow whey.

2.5 Laboratory production of biogas from waste waters, on 4 L scale reactors

These experiments were also conducted in two batches. For the first batch, two reactors were used which had a total volume of 5 L each, of which 4 L was the useful volume. The temperature of reactor 1 (TR1) was 37°C and the temperature of reactor 2 (TR2) was 42°C. Reactor 1 (R1) had a 3.5 L suspension consisting of a specific mixture of biogas with corn silage and wet fraction plus 100 g of degraded maize grains. Reactor 2 (R2) had a 3.5 L suspension consisting of a specific mixture of biogas with corn silage and wet fraction plus 100 g of potato peel.

The figure above shows the pH levels for the two reactors used within 20 days of the experiments. It can be observed that in the first phase (the first 7 days the

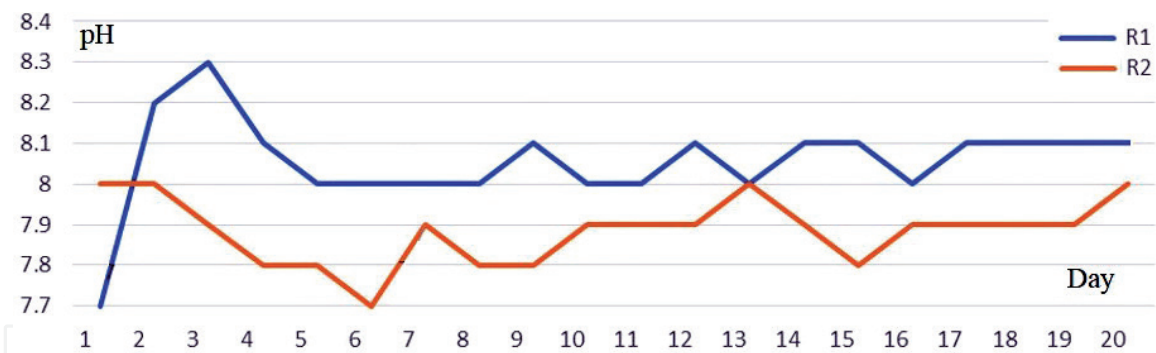


Figure 13.
Substrate pH variation in time, second batch on 4 L reactors.

pH has a slightly decreasing tendency varying between 7.8 and 8.3, in this sense, it is observed that the substrate used is very stable over time even in the initial phase which has as specific a relatively acidic pH (below 6).

Throughout the process, the pH remains slightly alkaline for both reactors, being a good indicator for optimal development of the anaerobic fermentation process.

The first reactor was heated in mesophilic mode, and reactor number 2 in thermophilic mode (in its lower range), and in correlation with the pH identified during the experiment the elements of influence are favorable to produce a quantity optimal biogas with a relatively high methane concentration.

The cumulative amounts of biogas for the two reactors identify a value of about 14 L of biogas for reactor number 1 and about 8 L of biogas for reactor number 2. The difference in quantity between the two reactors can be explained by the temperature regime applied to each reactor in part (the thermophilic regime has as specific a higher production in the time of biogas) and the slightly different composition because the potato peel has a high starch content, an aspect that can be beneficial but also inhibitory, by the appearance of the foaming phenomenon, depending on the behavior of each load separately.

On the second batch, two reactors were used which had a total volume of 5 L each, of which 3.5 L was the useful volume. The temperature of reactor 1 (TR1) was 37°C and the temperature of reactor 2 (TR2) was 42°C. Reactor 1 (R1) had a 3.5 L suspension consisting of a specific mixture of biogas with maize silage and wet fraction of animal biomass plus 100 g of degraded maize grains. Reactor 2 (R2) had a 3.5 L suspension consisting of a specific mixture of biogas with corn silage and the wet fraction of animal biomass plus 100 g of potato peel (**Figure 13**).

For batch number 2, a similar pH behavior is observed for the two reactors with maximum values of about 8.3 for R1 and 7.9 for R2. Under certain conditions, pH values above 8 can slightly inhibit the biogas production process, but some substrates react positively to slightly higher pH values (between 7.5 and 8).

The temperature regime chosen is similar to that of the first batch, again noting that the heating system ensures a relatively constant temperature throughout the process for both reactors, with a difference of up to one degree compared to the desired operating temperature. Reactor number 1 produced about 14 L of biogas while reactor number 2 produced about 8 L of biogas, in this case, both the higher pH values and the slightly higher temperature range high being a negative influencing factor on the anaerobic fermentation process.

The concentration of methane for reactor number 1 is about 49% while for reactor number 2 it is about 51%, values which again are an indicator of a low potential for the use of independent in combustion processes.

3. Conclusion

Relative to the presented material, the further conclusions can be traced:

- The most important catalyst with positive results in terms of the combustion process is $ZnCr_2O_4$ and further determinations must be made to determine if other catalysts can be used with better results than the existing ones.
- The analyzed materials have good energetic potential which can be further studied in terms of firing or co-combustion processes and anaerobe digestion for biogas production – chemical analysis is the most important one to determine further process influence in this regard.
- Small-scale bioreactors were developed in-house after ideas collected from literature and existing experience in practical determinations at the laboratory level.
- During testing, temperature and pH proved to be very important to maintain a live microbiota and increase the anaerobic digestion process speed in time, with good indicators relative to biogas quantity and volume participation of methane (over 50% allows firing process).

All the presented elements, even if presented separately, are interconnected to add plus value to a known conversion process to further bring new perspectives in terms of used substrates, increased quality for the produced biogas in terms of methane concentration and further applications in firing processes to maximize the energetic output conversion to heat or electric energy.

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Conflict of interest

The authors declare no conflict of interest.

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