

EXPERIMENTAL APPROACH FOR CATALYTIC COMBUSTION OF BIOGAS Preliminary Research

by

**Stefan IZVOREAN^a, Adrian Eugen CIOABLA^a, Timotei Bogdan BACOS^{a*},
Andrei Tiberiu BORBOREAN^a, Srbislav B. GENIĆ^b, Dorin LELEA^a,
Francisc POPESCU^a, and Maja S. TRUMIĆ^c**

^a Faculty of Mechanical Engineering, University Politehnica Timisoara, Timisoara, Romania

^b Faculty of Mechanical Engineering, University of Belgrade, Belgrade, Serbia

^c Technical Faculty in Bor, University of Belgrade, Bor, Serbia

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Nowadays, the use for renewable resources comes as a necessity to stringent energetic consumption issues that are related to both economic and energy autonomy (if possible) by using alternative sources of energy. In this context, one possible solution could be the application of anaerobic digestion processes, with a main energy carrier as result in the production of biogas. The focus for the present paper is to analyze the possibility to obtain biogas through anaerobic digestion of solid agricultural wastes (degraded corn and wheat) in municipal waste-waters substrate. The biogas production was tested on a self-sustained double biogas reactors and CH₄ production obtained presented. Combustion of biogas-like syngas simulating produced biogas was performed in the presence of ZnAl₂O₄ and CoAl₂O₄ catalyst, in an experimental combustor. Experiments conducted showed that both corn and wheat blended with municipal waste-water produce biogas with up to 80% CH₄ concentration and that combustion behavior of biogas is improved in presence of CoAl₂O₄ catalyst.

Key words: biogas, anaerobic digestion, catalytic combustion

Introduction

The use of biofuels represents one of the current trends in the modern society, due to its possible impact on energy autonomy and using alternative energy carriers from local sources.

Of course, there are a lot of possibilities and alternatives but the overall purpose it's to implement new ideas or concepts in modern life for energy capitalization and usage. Also this approach decreases the carbon footprint with impact on reducing pollution and local greenhouse effect. In this context, there exists a Circular Economy Action Plan that involves using resources like biomass, raw materials, biodegradable waste and biological materials, that otherwise remain untapped as a source of energy [1].

In this context, anaerobic fermentation processes are one of the used methods of conversion, used for biogas production as a renewable energy carrier for firing applications [2].

Relative to the impact on different resources from industry, for example, for the beer industry in Europe in the year 2013 the EU, namely EU-28 produced an equivalent of 383553000 hl [3].

* Corresponding author, e-mail: bacost@yahoo.com

As food waste, the Waste and Resources Action Programme (WRAP) highlighted around 9.5 millionnns of food wastes was generated in the UK during 2018, valued at £19 billion, and is associated with 25 millionnns of GHG emissions [4].

The anaerobic digestion technology has witnessed a constantly rising deployment also in agricultural farms, municipal waste treatment plants, and agricultural farms [5].

Biogas, as a direct energy carrier from anaerobic digestion, contains around 60-70 vol.% methane [5], which can be used for producing biomethane which can be further used as a biofuel with domestic cooking applications, and supplying to the centralized gas grids to reduce GHG emissions. However, the remaining fraction of the biogas contains about 30-40 vol.% CO₂ which is undesirable for the applications of biomethane.

For example, as per the current government norms, the purity of CH₄ to be injected into the gas grid needs to be greater than 95 vol.% [6], implying that biogas upgrading stage is needed for the use of anaerobic digestion derived biomethane as a displacement of natural gas in the grid.

As described in literature, the full process of anaerobic digestion could be divided into four different phases. The first one is hydrolysis, in which the complex organic matter (mainly composed by proteins, carbohydrates and lipids) is attacked by the hydrolytic bacteria and degraded into monomers and oligomers. The second step consists in acidogenesis. During this phase the previously produced soluble monomers are transformed into volatile fatty acids, alcohols and ketones. The acetogens bacteria react with these new substances previously produced and, in the Acetogenesis phase, CH₃COOH, CO₂, and H₂ are obtained. The last phase of this conversion process is methanogenesis and consists of production of CH₄ by uptake of acetic acid and H₂ [1].

A possibility to optimize the firing process is given by the use catalysts in order to influence the quality of the flame and the reduction of pollutants in flue gases.

Research in use of metal oxides catalysts in biogas applied technologies varies from improvements in biogas residue bottom ash incineration [7] with the advantage of producing biogas residue biochar, to contribution complete combustion of biogas in catalytic heat generators [8, 9] and biogas catalytic reforming into syngas. Biogas reforming catalysts range from noble metals (Rh, Ru, Pt, Pd, Ir) [10-13] to base metals (Ni, Co) supported over metal oxides, mixed oxides and perovskites [14-16]. Particular attention is devoted to the development of non-noble metal catalysts, due to high cost and limited availability of noble metals.

Also combustion within porous inert media (PIM) shows distinctive difference from open flame burning systems. The first important factor influencing combustion within PIM, is high area/volume ratio implying high efficiency in heat transfer between flue gas and porous media [17].

In this context, the current paper is a study upon producing biogas from different alternative residual and the potential effect on using porous media combustion in conjuncture with catalysts that are not noble metals based in biogas like mixtures with impact on firing parameters and process optimization at laboratory scale.

Methodology

The biogas was obtained by using a pilot installation located at the Faculty of mechanical engineering, University politehnica Timisoara. Relative to the practical approach (experimental part), the chosen substrates are going to be mixtures of cereal degraded material (corn and wheat) and waste-water from local sources (e.g. treatment plant). The pilot installation was built in this purpose, namely to obtain biogas using different types of biomass in liquid formulas. The general schematics of the pilot installation are presented in fig. 1 and the general description is given.

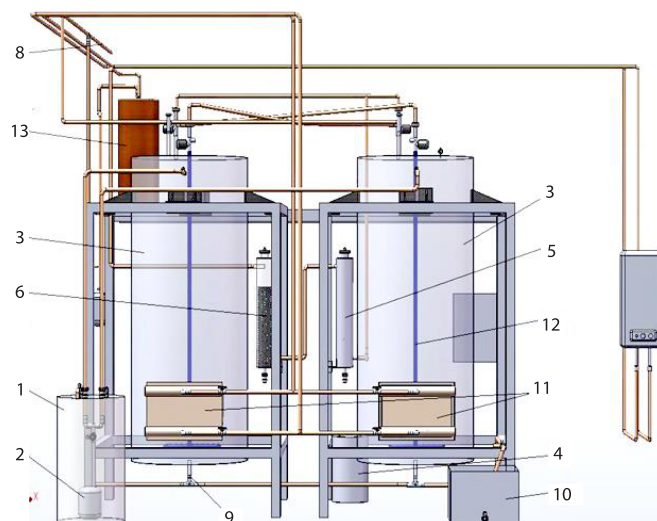


Figure 1. Schematic view of the pilot installation used for obtaining biogas from biomass; 1 – biomass/water mixture vessel, 2 – biomass transport pump, 3 – fermentation reactors, 4 – pH correction agent vessel, 5 – H_2S capture system, 6 – CO_2 capture system, 7 – CO_2 compression and storage, 8 – purified biogas outlet, 9 – biomass residue discharge, 10 – biomass residue storage, 11 – fermentation reactors heaters, 12 – cross reactors bubbling system, and 13 – biogas sampling vessel

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. The biomass suspension is transported by the pump and introduced into the fermentation reactors. 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 retaining the H_2S and after that, through a system used for retaining CO_2 , 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. The used material is discharged through the means of a gravimetric system, 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 and sent to the sewerage network, or is transported by the re-circulation pump from the suspension preparation tank. The fermentation reactors are thermostat heated with the system. For the homogenization of the suspension is used a bubbling system 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 positioned at the top of the reservoirs.

The raw materials used for the experimental part were preliminary analyzed in terms of their general properties, data being presented in tabs. 1 and 2.

The substrate raw materials composition was analyzed in accordance with European biomass standards:

- The EN ISO 18134 – Solid biofuels – Determination of moisture content – Oven dry Method 3.
- The EN ISO 18122 – Solid biofuels – Determination of ash content.
- The EN 14918 – Solid biofuels – Determination of calorific value.

Table 1. Overall properties for tested substrate materials (Part 1)

Material	Moisture content (db) [%]	Ash content (db) [%]	Gross calorific value (db) [Jg ⁻¹]	Net calorific value (db) [Jg ⁻¹]	Carbon content [%]
Corn	10	1.55	18400	16800	40.3
Wheat	9.65	5.55	19000	17500	41.1
Waste-water treatment plant	5.8	36	15000	14100	32.1

Table 2. Overall properties for tested substrate materials (Part 2)

Material	Nitrogen content [%]	Volatile matter content (db) [%]	Sulphur content (db) [%]	Hydrogen content [%]	Chlorine content (db) [%]
Corn	1.3	85.7	0.103	6.6	0.034
Wheat	2.1	78.5	0.149	6.1	0.042
Waste-water treatment plant	5.1	37.7	0.51	5.1	0.11

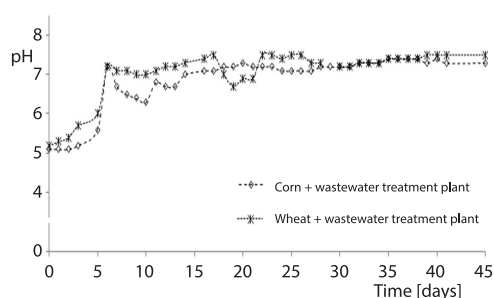
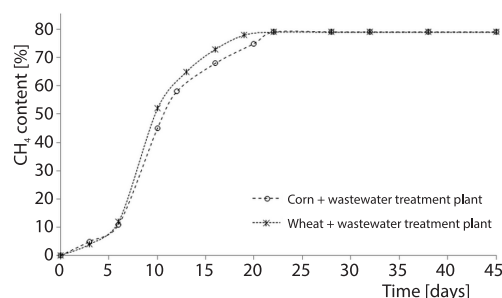
- The EN ISO 16948 – Solid biofuels – Determination of total content of carbon, hydrogen and nitrogen.
- The EN ISO 16994 – Solid biofuels – Determination of total content of sulfur and chlorine.
- The EN ISO 18123 – Solid biofuels – Determination of the content of volatile matter.

Experiment approach and discussions

Experimental biogas production

The laboratory determinations were made, as previously mentioned, by using the pilot installation in regard to determining the best material from the chosen ones in terms of quality and quantity for the produced biogas. Raw waste agricultural residues used as substrate for biogas production thru anaerobic digestion have the main advantage of producing similar CH₄/CO₂ ration with organic (animal) waste or landfill biogas, in addition much lower H₂S and NH₃ content [17].

The determinations were made in parallel, having as base material corn and wheat in mixture with waste-water from treatment plant – this was the first batch of material. From the fig. 2, it can be observed that the initial values were about 5-5.2 and after initial pH corrections, between days 5-8 the pH was risen to values in the range 6.5-7.5. Until the end of the process the pH remains in this domain. The temperature of the process was established between 34-36 °C.

**Figure 2. The pH variation vs. reaction time****Figure 3. The CH₄ evolution in reaction time**

From fig. 3 it can be observed that from the first 5 days the base materials produced methane in low concentrations, reaching a maximum value of 74-75% after about 20 days and staying high until the end of the determination. This shows great potential for both recipes.

The CO₂ decreased according to the methane increase in percentage, showing a minimum value of about 20-25 % at the end of the determination, fig. 4.

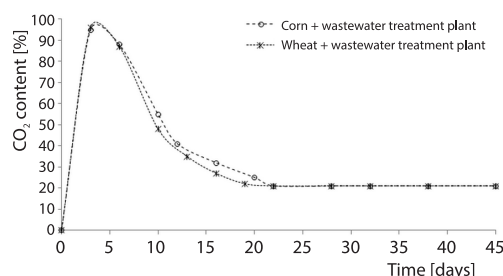


Figure 4. The CO₂ evolution in reaction time

Experimental catalytic combustion of biogas-like mixtures

Due to the preliminary good results obtained in laboratory, the next step was to try and apply the main biogas composition of about 80% CH₄ and about 20% CO₂ for further testing, as a syngas testing recipe, emulating the initial composition of biogas obtained during experiments, using a separate facility and controlled conditions, whilst using different types of catalysts made using the knowledge of the team involved in the testing creation and development. The pilot installation is built at the University of Belgrade, Mechanical engineering faculty, Serbia.

The initial steps relative to the experimental part involved documentation over experiments previously made on the installation and general data of the used test rig.

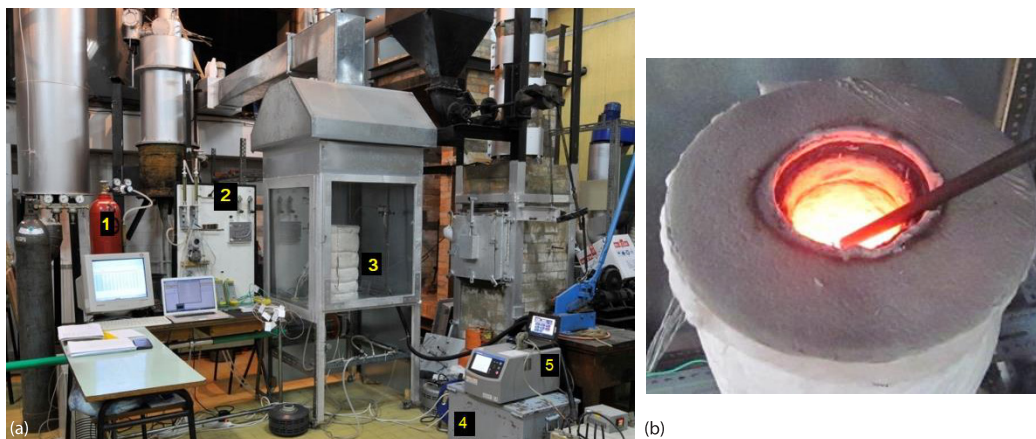


Figure 5. Test rig [1]; (a) overall view and (b) combustor view

From the figure 5(a) one can observe the overall test rig. The porous burner is designed as a cylinder of internal diameter of 70 mm and height of 512 mm. The wall of cylindrical chamber is made of three layers (insulating ceramic blanket of 42.5 mm, refractory concrete of 20 mm and ceramic fibers of 17.5 mm). Porous bed is made up of tabular alumina spheres of diameter 13 mm, forming a bed porosity of 0.45. The height of porous bed is 253 mm. At inlet of the burner there is a flashback arrestor consisting of porous plate and layer of packed ceramic spheres of small diameter of 6 mm. The premixed fuel-air mixture enters the burner through mixing chamber with excess air equal to $\lambda = (1.1-2.0)$, at initial atmospheric temperature [18].

After the initial testing of all the components of the test rig, the initial tests started, using one of the catalysts produced inside University Politehnica Timisoara and destined to be used for this type of determinations, using as base fuel a gas mixture composed of 80% CH₄ and 20% CO₂, which represents the most representative value for the produced biogas during the experimental testing inside the Multifunctional Laboratory located at the Faculty of mechanical engineering, University politehnica Timisoara. The initial step for determinations was to first try a gas made from the gas mixture without any catalyst in order to observe the temperature profile during firing. The catalysts used were ZnAl₂O₄ and CoAl₂O₄, in pebble shape.

Figure 6. Temperature profiles; test without catalyst – excess air ratio $\lambda = 1.6$ (a) and position of thermocouples (b) (for color image see journal web site)

During the initial test, it was determined the position of the flame inside the burner, relative to the value t_1 measured with the help of the positioned thermocouple on the burner and the data acquisition system.

From tab. 3 one can observe the general characteristics of the flue gas measured in real time inside the burner, the overall data is in the range of excess air $\lambda = 1.6$. For safety reasons and also in order to determine if the overall process is suitable for further determinations, there was made another test with excess air $\lambda = 2$. In the fig. 7 is presented the overall graphic for temperature variation during the firing process. Position of temperature sensors in combustion chamber is given in fig. 6(b).

The flame got a lower position inside the burner which was directly influenced by the increased air excess – characteristic for this type of process.

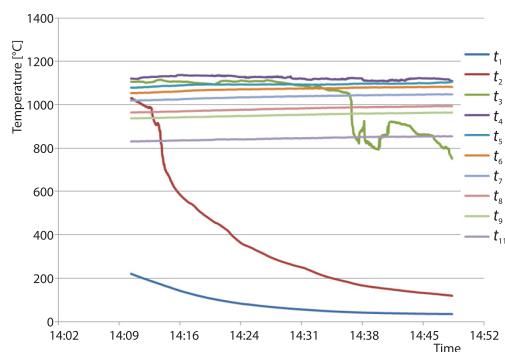


Figure 7. Test without catalyst – excess air ratio $\lambda = 2.0$ (for color image see journal web site)

Table 3. Flue gas analysis of catalytic combustion rig stack, air excess $\lambda = 1.6$

O ₂ [%]	CO ₂ [%]	NO _x [ppm]	CO [ppm]
8.78	8.12	4	442

Table 4. Flue gas analysis of catalytic combustion rig stack, air excess $\lambda = 2.0$

O ₂ [%]	CO ₂ [%]	NO _x [ppm]	CO [ppm]
11.10	6.63	1	28

Making a comparison between tabs. 3 and 4 one can observe easily that the increased air excess affects the overall composition for the obtained flue gas, by modifying the obtained composition both in terms of O₂ and CO₂.

Because the flame attained a lower position, the gas had the possibility to be better burnt, thus the lower concentration of CO – which represents in fact a good aspect for this measurement. After determining the initial temperature profile for the gas mixture, the burner was prepared in order to test the catalysts inside of it.

The tests were carried out on two catalysts as it can be seen in the fig. 8, and the testing was performed at different air excess ratios but the most relevant results were obtained for air ratio of 1.8. Depending on conditions of combustion (mainly of gaseous fuel composition, fuel-air ratio and power rate of the burner) it can be observed different types of temperature profiles in axial direction of the ceramic burner. If the flame is located in lowest part of the burner ($z_m = 0$), at the surface of separation the two zones of different porosities – between flame arrestor and main part of packed bed of pebbles/spheres, it is possible to conclude that the combustion is stable. Marginal position of

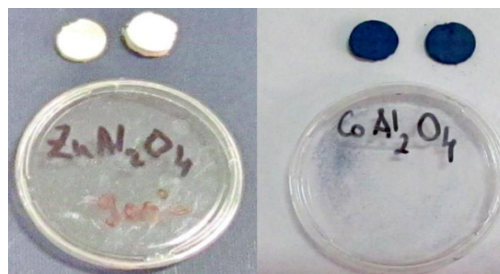


Figure 8. The ZnAl₂O₄ catalyst (a) and CoAl₂O₄ (b) catalyst's before the process

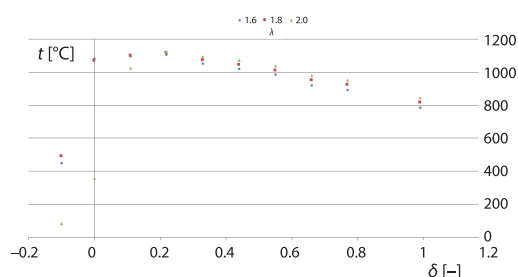


Figure 9. Temperature distribution in axial direction for different air-fuel ratio (1.6-2.0)

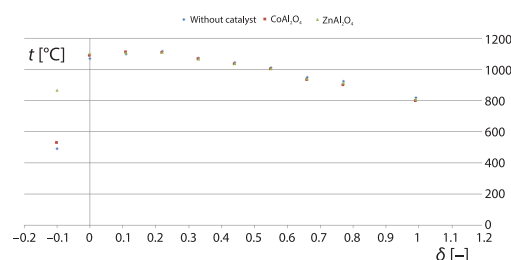


Figure 10. Comparative temperature distribution along the axis of the porous burner – without and with two different types of the catalyst (CoAl_2O_4 and ZnAl_2O_4) (for color image see journal web site)

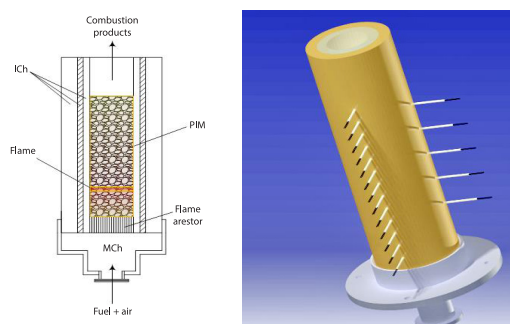


Figure 11. Porous ceramic burner with a packed bed of uniform alumina spheres with thermocouples; schematics (a) and CAD design (b)

along the burner axis are measured in experiments without catalyst. A possible influence of the catalyst could be lowering the activation energy, thus decreasing the temperature of the flame and consequently decreasing the temperature of flue gases along the axes of the porous backed bed of the ceramic burner.

Conclusions

The initial point of study related to using different types of materials tested initially inside a pilot installation, and the overall conclusion of the initial testing implies the fact that both tested recipes can be further used with success for high quality biogas (from the point of view of methane concentration) in terms of laboratory applications.

the flame that indices stable operating regime of porous burner is $z_m < 55.7$ mm (axial co-ordinate of packed bed of spheres), measured from the upper surface of flame arrestor. If the flame passes z_m , it can be concluded that the flame will be eventually pushed out the porous packed bed and the flame will be extinguished.

A non-dimensional ratio factor, δ , between the position of a thermocouple and the total height of the burner bed was defined. If the thermocouple is mounted at the end of the bed, the $\delta = 1$. Small spheres of Al_2O_3 (11 mm in diameter) were added to the combustion chamber bed to function as flame arrestor. Negative δ shows the position of a thermocouple mounted inside the flame arrestor.

The highest temperatures show where the flame is stabilized inside the porous bed. For $\lambda = 1.6$ flame is located at relative position $\delta = 0$. Increasing the λ to 1.8 and 2.0, flame moves toward exit. For $\lambda = 2.0$ flame is located at $\delta = 0.22$ ($\delta = L/z$ relative co-ordinate in axial direction, position of the thermocouple along the burner axis, where L is total height of porous bed of the burner), fig. 9.

The catalyst was positioned at the boundary between a packed bed and flame arrestor – position 0 shown in fig. 11, that presents the longitudinal section of the burner and the thermocouples' position along the burner's axis.

The position of the flame is settled at the boundary between the packed bed and flame arrestor (where we measured maximum temperature). Figure 10 shows minor temperature differences, where the highest temperatures

The obtained configuration was then translated into a biogas-like mixture, used for the study of catalytic firing. For the proposed study, two types of catalyst were investigated: 4.28 grams of ZnAl_2O_4 catalyst and 3.975 grams of CoAl_2O_4 catalyst.

According to presented data of experimental research of influence different catalyst on stabilization of combustion it is possible to conclude are as follows.

- There is slight difference in temperature profiles for combustion of gaseous fuel ($\text{CH}_4 = 80.6 \text{ vol.}\%$, $\text{CO}_2 = 19.4 \text{ vol.}\%$) within porous inert media without catalyst and using different type of catalyst.
- For presented regime it was obtained different temperature profiles in axial direction of the porous inert media of ceramic burner.
- Possible influence on stabilization of the flame using catalyst is observed by the position of the flame.

Lower the flame within porous inert media, more stable combustion is the experimental research can be expanded, as further applications, in order to:

- Simulate more different regimes, as well as to investigate influence of catalyst at higher working temperatures.
- Simulate influence of quantity of catalyst on combustion stabilization.
- Produce different shapes and porosity of catalyst and investigate the influence of specific area of contact between reactants.
- Investigate influence and efficiency of commercial catalyst on combustion stability within porous inert media.

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