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PRELIMINARY STUDIES CONCERNING THE USE OF POLIMER BASD MATERIALS FOR BIOGAS PRODUCTION AT SMALL SCALE

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Abstract: *Recently, renewable energy sources have garnered significant attention for their capacity to effectively handle and eliminate organic waste, including food waste, in an environmentally sustainable manner. Anaerobic digestion is a crucial technique used to manage and treat food waste and biomass waste. Biogas facilities function as a dual-purpose system, generating power and fertiliser, while also contributing to environmental conservation.*

1. INTRODUCTION

The primary challenge confronting mankind in the 21st century connected with energy and available resources. The phenomenon of energy-consuming industries is characterized by a simultaneous increase in their number and the depletion of fossil fuels, which are the primary energy sources used by these sectors. Concurrently, the pollution resulting from the use of these fuels has led to global issues, prompting international unions to enact legislation aimed at eradicating or reducing the use of these fuels in the next decades [1,2].

Hence, all developed, partially developed nations, and even most developing countries are endeavoring to devise a remedy to substitute these fuels and postpone the exhaustion of these fossil resources. An essential requirement for economic development and growth in modern civilizations is the presence of uninterrupted, sustainable, and cost-effective energy sources [3]. Post-industrial revolution, energy has progressively emerged as a crucial determinant in the national production and economic progress of industrialized nations, and subsequently by other developing countries. The present economy and society rely so heavily on energy that it is an inconceivable concept to envision existence without it, even for a brief period.

In the event of a disruption of its supply, the economic machinery would cease to function properly [4,5]. Hence, every nation is striving to achieve uninterrupted and enduring energy sources using any available means. Conversely, the global economic expansion and the rising energy demand have led to a rise in the prices of oil and gas, while the dependence on these resources for energy procurement has declined. Conventional and non-renewable fossil resources exert a significant influence on energy security. This issue has piqued the interest of numerous governments worldwide in the matter of energy supply security and has prompted intense focus on substantial transformations in their energy economy [6–9]. In this context, technological advancements offer potential answers for the generation of energy required by humanity. By finding these novel techniques, a significant advancement has been made in the domain of restructuring energy generation in infrastructure. Utilizing inexhaustible reservoirs of renewable energy has significant implications in this context [10,11]. The dispersion and allocation of these elements

in the natural environment have led to the shift of energy generation systems towards localized systems, thereby enabling the utilization of novel energy sources for this specific objective.

Presently, different research worldwide is being focused on topics such as energy, the

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environment, the reduction or neutralization of hazardous waste materials, the depletion of fossil resources, and the continuous rise in energy consumption due to demographic reasons [12–14]. Indeed, these concerns unequivocally demonstrate that it is untenable to depend on the current energy sources [15]. The significant research undertaken in recent decades to explore novel and beneficial sources can be regarded as a clear demonstration of the significance of these principles and the associated scientific fields [16]. Presently, most nations worldwide have refined their programs to enhance the longevity of their fossil resources by optimizing their utilization. Simultaneously, they are implementing solutions dedicated to decreasing the proportion of fossil resource consumption by adopting renewable energy technology [17]. In the same time, one important factor is the allocate the available resources to the task of prolonging the lifespan of fossil resources and identifying compatible alternatives. There is ample evidence indicating that global energy policies that encourage the optimal utilization of fossil fuels and energy are not ecologically feasible due to their significant contribution to environmental degradation at local, regional, and global scales.

Numerous studies have demonstrated that the incorporation of renewable energy sources into the total energy composition can effectively mitigate or even eliminate each of these adverse environmental consequences [18–20]. Undoubtedly, in this century, fossil fuels will progressively be replaced by renewable energies such as solar, wind, hydroelectric, biomass, geothermal, and others.

Of particular significance among these energy sources is biogas derived from biomass. Currently, biogas holds significant relevance and position because of its advantages in terms of environmental sustainability, energy generation, production of high-quality fertilizer, and its feasibility for production near human settlements. Despite the long-standing acknowledgment of biogas worldwide, its widespread and prevalent application has mostly emerged in the past century, particularly in the last thirty years. Biogas, derived from biomass, is an excellent option for selecting alternative energy sources for communities due to its cost-effectiveness and local origin in terms of production [21–23]. Furthermore, it serves as a valuable energy resource for several purposes, including but not limited to heating, lighting, and producing small-scale electrical power. Moreover, biogas not only generates energy but also yields agricultural fertilizer and enhances the overall public health and illness management in society.

As an energy carrier, it is an appropriate remedy for the management of solid waste. Effluent and solid waste materials generated by industries and communities contribute significantly to environmental degradation. However, the application of biogas technology can significantly mitigate this issue. Additionally, the energy and fertilizer generated from biogas can be repurposed. Biogas extraction can be achieved from different sources, like anaerobic wastewater treatment operations (UASB) or landfills, therefore partially offsetting the consumption expenses associated with this infrastructure [27–29]. Biogas systems offer substantial environmental advantages that surpass those of traditional purifying methods employed thus far. Furthermore, these advantages encompass odor management, enhancement of air and water quality, augmentation of the nutritional content of the generated fertilizer, mitigation of greenhouse gas emissions, and acquisition of biogas as an energy source. It is worth noting that the generated biogas has the capability to generate both electrical and thermal energy simultaneously. Biogenic gas production is a well-established method for generating renewable energy and decomposing organic waste.

Microbial species employ several metabolic routes to decompose organic substances in an anaerobic digestion process, resulting in the production of biogas [30]. For millennia, this process has been used to produce heat and power in private houses. The biogas sector is currently experiencing rapid growth, and recent achievements are generating the necessary foundation for the development of biogas facilities as state-of-the-art bioenergy production facilities. Biogas installations serve as the basis for circular economy, which focuses on nutrient recycling, reduction of greenhouse gas emissions, and bioremediation.

2. METHOD

To generate biogas, the findings from prior studies were examined, and bioreactors fabricated from PLA, PET-G, and recycled PLA, using 3D printers, were employed. The outcomes vary depending on the specific recipes which have been investigated.

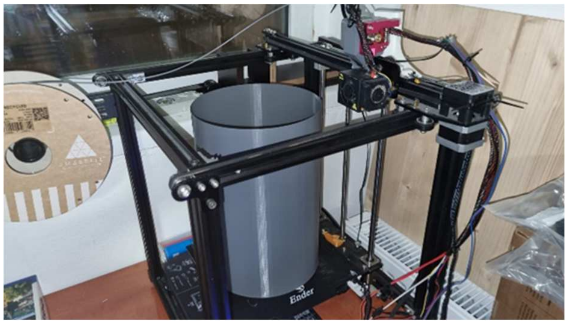

Fig. 1 The construction of bioreactors using 3D printing

Different types of polymers are used specifically to test their utility and durability. This approach is of interest, especially in small scale, because this direction has not been approached in general literature so far.

The reactors are composed by 2 parts, body and lid. The lid has incorporated two orifices that are used as follows:

The first route (orifice – with a bigger diameter) involves connecting a material sample element (a syringe) to a pipe within the reactor.

Route 2 (the orifice with a smaller diameter) establishes a connection between the upper part of the reactor and a receptacle responsible for the storage of the generated biogas.

Fig. 2 Stainless steel-back and polymer-front bioreactors

The main advantage for these reactors involves lower construction costs and requires simpler construction conditions. The experiment took place without the use of agitation devices and the used heating device was a thermostatic bath to maintain a stable temperature regime.

The tests took place at two temperature regimes (38 °C and 42 °C), the substrate used for testing was a mixture of cow manure and corn silage from an installation located in Timis County and the experiment took place until no biogas was longer produced, for an estimate of 20 days. The temperature control average was between 0.5 °C and 1 °C and the pH did not necessitate to be corrected during the process.

3. RESULTS

The amount of biogas produced during the first set of experiments, which were carried out in PLA and PET G bioreactors, is shown in the following figure.

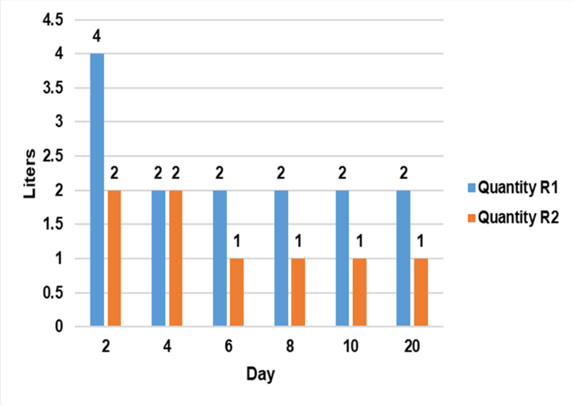

Fig. 3. Batch 1. Biogas quantity

The tested material was a mixture of corn silage, cow manure, and chicken manure, in varying proportions.

The first tank was PET G and the second was PLA. It can be observed that in the reservoir made of PET G, the production of biogas is higher, most likely because the bacteria were not affected by the source of the material used. It is evident that there is not a single cause, but most likely, the substrate used was not contaminated and the process took place under good conditions.

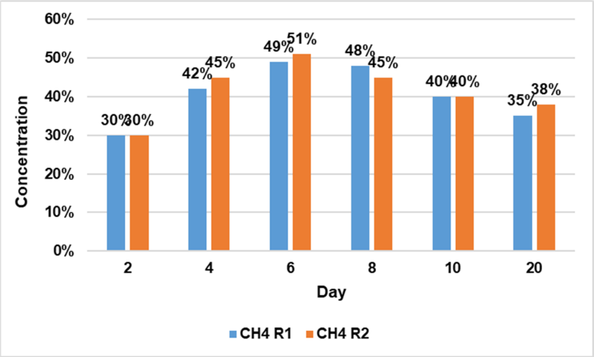

Fig.4 Batch 1. CH4 quantity

In terms of concentration from the total volume, it can be observed that the biogas production was similar, with a maximum of about 50% for both types of bioreactors, which indicates that the two materials used are suitable for this process.

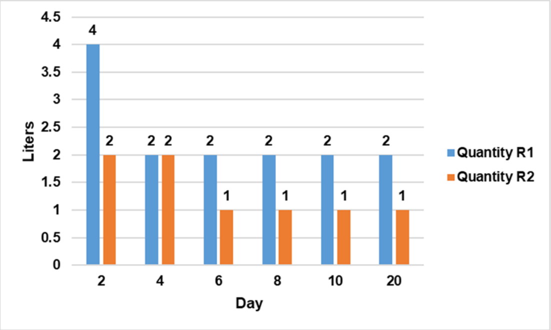

Fig. 5 Batch 2. Biogas quantity

A second set of experimental determinations was carried out, using the same substrate and the same materials for the bioreactors, and a similar behavior was observed, while varying the process temperature from 38 ˚C to 42 ˚C. It is once again observed that the PET G bioreactor has a higher biogas production than the one made of PLA.

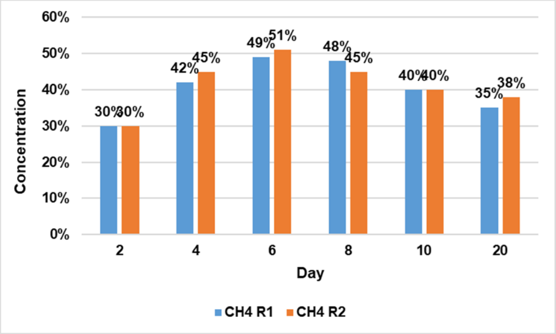

Fig.6 Batch 2. CH4 quantity

From the figure above, it can be observed that for this test batch, the concentration of methane in the produced biogas does not exceed 55% volumetric participation, which needs to be optimized for the upcoming test sets.

Based on the obtained data from the experimental phase, the next step was to approximate the calorific value of the produced biogas, based on the methane content of the gaseous mixture. It was taken into consideration a percentage of 50% methane by volume and the calculation considered further similar data, obtained using the calorimetric approach.

The ambient temperature and pressure was measured by means of a thermal hygrometer and a barometer, while the input value of the gas pressure was approximated from previous experimental determinations.

The main mathematical equations used are [31]:

$$H_S \cdot V_0 = m \cdot c \cdot (t_2 - t_1) \qquad (1)$$

Where:

H_S – superior calorific value [J/m^{3}N];

m – water capacity measured in calorimeter [kg];

c – mass heat capacity of water [J / kg*K];

t_1, t_2 – water temperatures at the inlet and outlet of the calorimeter [°C];

V_0 – the volume of gas burned relative to the normal state [m^{3}N].

$$V_0 = V\frac{T_0}{T}\frac{p}{p_0} \ [\mathrm{m^3N}] \qquad (2)$$

Where:

V – volume of gas burned for m kg of water [m^{3}N];

T, p – state parameters of fuel gas read from the devices on the meter;

T_0, p_0 – state parameters at normal physical conditions.

$$H_i = H_S - \frac{r \cdot w}{V_o} \ [\mathrm{kJ/m^3N}] \qquad (3)$$

Where:

Hi – inferior calorific value [J/m^{3}N];

r – 2260 kJ / kg – heat of vaporization of water at atmospheric pressure;

w – the amount of condensate from the combustion gases [kg].

The data considered for the calculus were as follows:

tgas = 25°C

measured amount of water = 2 kg
patm = 1007 mbar – atmospheric pressure
overpressure = 2 mbar
p = 1009 mbar
p_0 = 1013 mbar- normal atmospheric pressure
$V = 2 * 10^{-3}$ m^3
t_1 = 23°C
t_2 = 27°C
c = 4182 J/Kg*K
The amount of condensate obtained was
$w = 3 * 10^{-3}$ kg
From equation (2) it results that
$Vo = 1.82 * 10^{-3}$ m^3N
From equation (1), one can deduce that the superior calorific value, Hs is:
Hs = 18382 KJ / m^3N
From equation (3), it results that the inferior calorific value, Hi is:
Hi = 14597 KJ/m^3N

This value correlates with a low calorific value, which can be still suitable for firing applications, but the best scenarios is represented by a biogas with more than 60% methane content, that has a calorific value of more that 20000 KJ/m^3N.

The next part considered an approximate analysis of the process's efficiency regarding CO_2 retention and was conducted, estimating the amount of 6 kg of biodegradable material (waste). From the waste analysis, it results that it contains [32]:
- 0.0065 x 6 = 0.39 kg of sulfur (S);
- 0.2738 x 6 = 1,6428 kg carbon (C);
Considering an average composition of biogas of 74% and CO2 of 26% converted to mg/m^3 results in:
The production of 0.055 m^3 of biogas means:
biogas 0.74 x 0.055 = 0.0407 m^3 CH_4, resulting in 0.0407 x 5 = 0.2035 m^3 of combustion gases to which CO_2 is also added:
0.26 x 0.055 = 0.0143 m^3 CO_2, considered unprocessed, results in:
0.2035 + 0.0143 = 0.03465 m^3 of combustion gases.
Regarding the carbon from waste used in biogas production it results:
For CH_4: 0.0407 m^3 contains:
- 1 mole of CH_4 which contains 12 g of C (at 55 l); for estimated 1 m^3 it will contain 1,000: 1 x 55 x 12 = 660 g of C.
- The methane production which has been consumed:
600 x 0.0407 = 26862 g C = 0.026862 kg Carbon
The produced carbon dioxide, 0.0143 m^3 contains: 44: 55 = 0.8 g; 12 : 44 = 0.272% C/mol gCO_2
1 m^3 CO2 contains:
1000 : 55 x 12 = 218.18 g C; reporting:
0.0143 x 218.18 = 3,119 g C = 0.003kg C

Considering the carbon content in the used material for biogas production and the carbon in the resulting biogas, it results the folowing:
1,6428 – 0,026862 – 0,003 = 1,37118 kg of carbon in the remaining residue.
Considering that after the biogas processing of the waste, a residue of approximately 4 kg dry with a carbon content of 1,37118 kg remained, it results in:
1,37118: 4 = 0.342795, which means 35% carbon. The residue with a carbon concentration of 35% has a calorific value of approximately 2,000 kcal/kg. This residue can then be used for burning or as fertilizer.
The retention of CO_2 of about 5% means, compared to an initial average of 31%:
5 : 31 = 0.16, which is 16%
Considering the amount of biodegradable waste used for a biogas production "batch" of 6 kg with an average calorific value of 3,000 kcal/kg, it results, theoretically, in 1,8 Gcal upon combustion.
Taking into account the losses due to ash residues, heat losses through the conversion system, and gases released into the chimney, it would mean an average of 1 Gcal of usable thermal energy.
At a price of 989,36 ron/Gcal for Gcal at COLTERM, the result is: - current price per ton
1 x 989,36 = 989,36 ron
From 6 kg of waste, approximately 0.0407 m^3 of methane were produced.(CH_4).
With a calorific value of 8,500 kcal/m^3, the biogas produced in a batch would mean, through

combustion:
8,500 x 0.0407 = 399.5 Gcal.
At a price of 989,36 ron/Gcal at COLTERM, the result is:
399,5 x 989,36 = 395,24 ron
When burning the waste resulting from the biogas plant (approximately 4 kg), considered at a calorific power of 2,000 kcal/kg, the result is:
4 x 2,000 = 0,8 Gcal
Practically, the usable energy produced will be around 0,8 Gcal.
0,8 x 989,36 = 791,4 ron
The value resulting from the sum of thermal energy produced from biogas and from the incineration of the waste used is
395,24 + 791,4 = 1186,7 ron
When used for electricity production in a generator, it would theoretically mean an electrical equivalent of 861 kcal/kW, but the efficiency when used in the generator is a maximum of 50%:
399,5 : 861 x 0.5 = 0,231 kWel
The price of 1 MWel at COLTERM is 382 ron
Therefore, from the electricity, a value of:
0,231 x 382 = 88,24 ron
Considering the use of biogas for electricity production and the incineration of the resulting waste means:
791,4 + 88,24 = 879,64 ron
To this value, the equivalent of 0.5 Gcal of residual thermal energy recovered from electricity production can be added:
879,64 + 0.5 x 989,36 = 1,374 ron
Comparing the results and not taking into account the possible use as fertilizer of the waste/residue obtained after biogas production means that the direct burning or burning with the addition of another supporting fuel of biodegradable waste brings superior benefits.

4. CONCLUSIONS AND RECOMMENDATIONS

The present study was focused to determine the potential to use different types of materials for creation of polimer based reactors for biogas production using anaerobic digestion.

The tests were conducted in similar conditions using different polimer materials, PLA and PET G to determine if those materials are suitable to sustain this type of process and to produce biogas, in comparison with an initial model created from stainless steel.

The preliminary results indicate that the produced biogas reached a maximum concentration of methane in the order of 50% which indicates that the used materials are suitable for other studies in terms of process optimization for obtaining better methane yields and obtained biogas quantities.

Estimated calorific value obtained for the produced biogas underlines the need for optimization for the energy carrier to be suitable for further firing processes.

Further studies are under way to determine how to maximize the potential of this type of reactors for better process conditions and comparative measurements for different temperature regimes.

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STUDII PRELIMINARE PRIVIND UTILIZAREA MATERIALELOR PE BAZĂ DE POLIMERI PENTRU PRODUCȚIA DE BIOGAZ LA SCARĂ REDUSĂ

Rezumat: Recent, sursele regenerabile de energie au atras o atenție semnificativă pentru capacitatea lor de a gestiona și elimina eficient deşeurile organice, inclusiv deşeurile alimentare, într-o manieră durabilă din punct de vedere ecologic. Digestia anaerobă este o tehnică crucială utilizată pentru gestionarea și tratarea deşeurilor alimentare și a deşeurilor de biomasă. Instalațiile de biogaz funcționează ca un sistem cu dublu scop, generând energie și îngrăşăminte, contribuind în acelaşi timp la conservarea mediului.

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