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Achievements in recovery of bio-based natural resources and organic residuals to biogas

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Abstract. This paper aims to make visible some achievements currently developed by the institute ICPE-CA in the field of organic resources recovery. Innovative solutions for waste treatment to biogas and eco-fertilizers, but also experimental methods for extraction of valuable products from green biomass have been presented. Original research results were achieved for various anaerobic digestion tests under high hydrostatic pressures. Comparative analysis of the fermentative microbial activity for the selected work pressures, was proved to be of great importance in assessing the efficiency of the biogas reactors. Researches for identification of new biofuels to be used as renewable sources start from the oils-containing biomass, as well as tests for determining fat content in biomass have been pointed out. Finally, an innovative household biogas unit to treat a wide range of organic waste and wastewaters, designed to supply biogas for domestic usage simultaneously with lands sanitation, was briefly presented as well.

Keywords: waste, biogas, vegetal oils, fertilizers

1. Introduction

Organic waste and wastewaters generated as effluents in agriculture, in food-beverages processing industries and also municipal residuals are rich in organic compounds, being characterized by high biological oxygen demand and chemical oxygen demand along with fats, proteins, oil–grease, starch, sugars and many other recoverable nutrients like Nitrogen, Phosphorous and Potassium. They are also malodorous because of the decomposition of some of the contaminants causing discomfort to the surrounding population.

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On the other hand, the aquatic biodegradable waste such as algal biomass, mollusks or other dead marine organisms which are accumulated on the water surface, in the marshes and on the beaches at the seashore, represent an important cause of environmental pollution by gases generated during their biological decomposition, as well as by the bad odor and unpleasant view, while being a dangerous cause of infection, too. Dead algae and marine animals gathered on the beach have also a significant negative impact on the local tourism, and this further requires identify of some effective solutions for coastal sanitation, in order to increase the level of tourist attraction in seaside resorts and delta areas.

All such bio-based natural resources and biodegradable wastes could be a valuable renewable energy source to be used for biogas generation through anaerobic digestion, in proper reactors, under controlled process conditions. If this energy resource would be treated effectively, it could be a significant amount of biogas generated, given that algae do not contain lignin like other terrestrial plant material, so that the biogas conversion efficiency could be high.

In addition, fermentation residue could be used as a soil conditioner, thus reducing the need for chemical fertilizers and pesticides, contributing to increased competitiveness of agricultural products but also increase income and living standards of the population in the surrounding areas.

In this framework, finding new and efficient solutions for recovering of bio-based natural resources and organic waste has caught the attention and interest of researchers for many years. The importance and relevance of this research area is doubtless since a lot of problems could be solved, specifically to provide new sources of energy and reduce dependence on conventional fuels, improve the environment and living conditions of the inhabitants of isolated villages, developing of tourism in coastal and delta areas, promoting eco-fertilizing materials, development of specific technological industries through the transfer of research results to the producer of wastewater treatment plants and biogas facilities.

2. Material and methods

Anaerobic digestion to produce biogas and eco-fertilizers is a complex biochemical process which converts solid and liquid biomass wastes by using bacteria without the presence of oxygen, to produce biogas and a liquid effluent stream containing solids which can be used as a fertilizer. The stability of the anaerobic process is very fragile and the balance between several microbial populations must be controlled and maintained. It is well known that the methanogenic bacteria are temperature and pH sensitive [1].

In general, the optimum process parameters used for high biogas yield are pH 6.5-7.5 and mesophilic temperatures 35-37^{0}C. Despite a thermophilic system (50-55^{0}C) kills more pathogenic bacteria from biodegradable waste, such system has higher operating costs and it may be less stable. Since the mesophilic bacteria are also more tolerant to changes environmental conditions than thermophiles, mesophilic range is the proper option for the anaerobic digestion or organic waste. The feedstock material or biomass type differ from case to case (algae, other aquatic plants, dead marine organisms, organic waste etc.), however, the organic loading is the parameter which decides the quality and quantity of the biogas generated in biogas units [2].

The fundamental laboratory research, chemical and microbiological analyzes as well as study of fermentative processes has been carried out in scope of improving the biodegradability of organic materials and increase the yield of valuable biogas in technological processes. Laboratory experimentes for determination of biogas potential for algae or in mixture with other types of organic waste and high methane-content biogas have been achieved by the author under various national and international research projects for the past five years.

Lignin negatively affects the anaerobic bio-digestibility of lignocellulosic biomass in biogas systems. Lignin is a phenolic polymer having a very complex structure which forms a protective coating around cellulose and hemicelluloses, reducing the surface area available to enzymatic penetration and activity of fermentative microorganisms [3]. To achieve a high rate conversion of organic compounds to biogas, a pretreatment process is necessary for lignocellulosic materials in order to increase the solubilization of lignin and consequently the hydrolysis of carbohydrates. There many methods for acid treatment of biomass. Beckker et all proposed a biomass pretreatment with sulphuric acid (fed as concentrated H_2SO_4 min. 90 % to the reactor, or sulphuric acid formed in situ by adding SO_3 gas to the reactor, which forms sulphuric acid when dissolved in water [4].

Since it is proved that biodegradable residuals can be used successfully as feedstock for biogas facilities if mixed with straw, corn stover or other types of carbon-based hard biomass, the improving of their biodegradation represents an important target for many research studies.

In this scope, experimental research for enhancing the bio-digestibility of the soluble lignin by physical-chemical pretreatment of biomass, as well as the isolation and quantification of lignin contained in dry biomass, by using UV-VIS spectrometric techniques, has been carried out by the author of this paper.

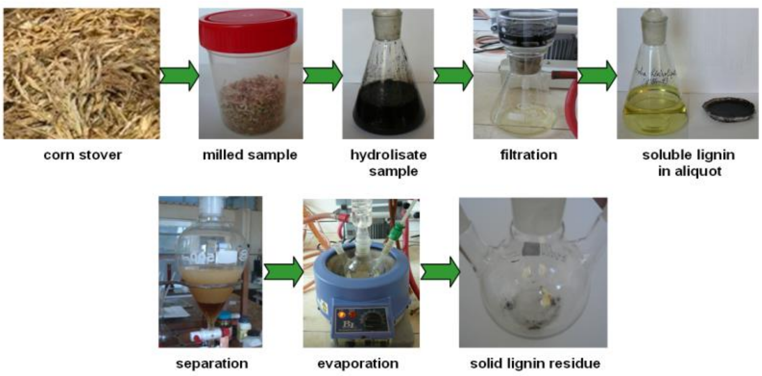

Fig. 1. Experimental steps for lignin extraction in biodegradability studies.

Lignin was extracted and isolated from acidic solution using methyl isobutyl ketone extraction. After solvent removing, the fraction was dried and the extracted lignin was dissolved in water to produce a set of lignin concentration standard and to obtain the lignin standard curve. The concentration of soluble lignin extracted from corn stover was measured by UV-VIS spectroscopy at a maximum wavelength of 320 nm [5]. These extraction and isolation experiments have been performed as a first step in a complex research aimed on assessment the soluble lignin degradation before and after applying some physical, chemical or physicochemical pretreatment methods in scope of enhance the bio-digestibility of corn residuals for biogas production.

The fat content in algal biomass and other types of organic waste is an important parameter to be considered in case of biomass recovery to vegetal oils and other related products. For assessing the fat content in algal biomass, serial of fat extraction experimentals have been performed for wet and dry biomass with the main purpose to identify new potential biofuels to be used as renewable sources.

For the quantitative determination of the fat content in biomass, a Gerhardt Soxtherm fat extractor has been used for the extraction in two steps followed by a subsequent gravimetric determination. Figure 2a and 2 b show the vegetal oil extracted from dry biomass in laboratry experiments by using a Gerhardt Soxtherm fat extractor.

Fig. 2, ***a*****.** Gerhardt Soxhlet fat extractor used for laboratory research.

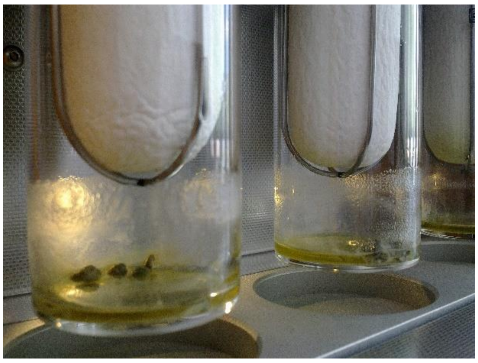

Fig. 2, *b*. Vegetail oils extracted from dry biomass.

Knowledge of the fundamental processes involved in the anaerobic digestion is very important for the design, construction and operation of the biogas plants. Theoretical studies have shown that, in ordinary cylinder-conical shaped vertical digesters, generating biogas practically occurs preponderantly in the upper layer of the organic slurry for a maximum depth of 4 m. The remaining volume of organic mass does not produce biogas since methanogenic microorganisms have been living latently in the lower layers of organic substrate. By homogenization, such inactive volumes will get lower pressure areas from the upper layers and the metabolic activity of methanogens will be resumed actively with biogas generation [6].

By fermentation of a large amount of biomass in tall fermentation tanks for producing biogas in industrial processes, an increased gas production could be provided if microbial activity was optimal, so that the biochemical processes to be carried out efficiently. It can be stated that fermentation in large reactors could be more economically advantageous compared to those processes that occur in small vessels. Studying the influence of pressure on biogas yield has been found of great interest for developers of anaerobic digesters [1].

Given the economical importance of these technological aspects, the influence of hydrostatic pressure on methanogens activity and consequently on biogas production in anaerobic digesters has been investigated by the author of this paper. The quality of biogas has been evaluated in terms of methane content in the gas resulting from fermentative processes in anoxic environments. The activity of methanogens was determined by instrumental chemical analysis, using a gas chromatograph fitted with a flame ionization detector. Biogas generated in fermentative processes has been periodically sampled and analyzed during the period of the highest microbial activity. Furthermore, the number of methanogens before anaerobic digestion and after conditioning under various pressures has been determined by using the most probable number analytical method.

The experiments of anaerobic digestion under conditions of high hydrostatic pressure were carried out in stainless steel laboratory vessels, each container having a capacity of 5 liters. The pressure vessels were manufactured by the German company Krautzberger and have been fitted with sealed removable lids which are able to keep tightly closed the air or various other inert gases such as argon, nitrogen used to pressurize the liquid or other materials with low viscosity. For the experiments of anaerobic digestion under high pressure conditions, there have been used a total of four such containers, which operated under the following conditions of pressure: 0 bar, 2 bar, 4 bar and 6 bar, respectively. For pressurization, Nitrogen type 5.0 of 9.999% purity has been used.

To create and maintain a constant temperature under a mesophylic temperature range, a 190 liter capacity temperature and climate test chamber type Vötsch Industrietechnik VC 4018, with digital control unit display of temperature and humidity, has been used for conditioning of the pressure vessels during the fermentative processes of the organic substrate with temperature deviation lower than ±0.5K.

In order to produce biogas, organic materials of various sources can be used. The most suitable substrates are mainly farm waste and wastewaters, vegetable waste, algae and aquatic waste, household leavings, residuals generated by food and beverages industries etc. For these experiments of anaerobic digestion to be performed in the four pressure vessels, an organic mixture of cattle manure and unfiltered whey which were diluted with water has been used.

Before starting the experiments of anaerobic digestion, the acidity of the organic slurry has been checked by using a Hanna Instruments pH-meter. The water content and respectively the total solid content of the biomass have also been determined after the pH adjustment. Achieving pressure conditions inside the vessels was done by introducing nitrogen until reaching the established pressure values indicated by the pressure gauge attached to the container. The influence of hydrostatic pressure on the bacterial activity in the organic slurry and implicitly on biogas production has been assessed by a qualitative analysis of the fermentative gases in terms of methane content, by using a gas chromatograph type Varian 450-GC.

3. Results and discussion

Lignin is very difficult to be decomposed in anaerobic conditions and possesses a barrier to biological degradation of cellulose and hemicelluloses. The composition and percentages of lignin, cellulose and hemicellulose in plants vary from one species to another, so it is difficult to generalize the structure and abundance of these polymers. Moreover, composition varies within a single plant (roots, stems, leaves), with age, stage of growth and with conditions under which the plant grows [7].

Preliminary experiments have been carried out to isolate and extract the lignin contained in corn leaves in order to develop some pretreatment methods to increase the bio-digestibility of biomass in anaerobic processes. The total mass of lignin isolated in the methyl isobutyl ketone was recorded and the solid residue was dissolved in ethanol for preparing of stock solution and making the dilutions for the standard curve. The concentration of soluble lignin extracted from corn leaves was measured by UV-VIS spectroscopy.

A set of aqueous standards was created using the stock solution and the absorbance was measured for different lignin concentrations in range of 0.002 mg/l to 0.5 mg/l. The absorbance of each standard was measured at wavelength in range of 200-400 nm using a UV-VIS spectrophotometer type Jasco V-570 and a curve of concentration versus UV-VIS absorption at 290 nm was created for soluble lignin extracted from corn biomass. The experimental results obtained in lignin decomposition tests proved an efficient lignin extraction after an acid pretreatment of the biomass sample. This experimental result shows that in case of ligno-cellulosic materials mixed with algal biomass, a pretreatment procedure prior to anaerobic digestion would increase the biogas quantity and quality.

Besides of biomass composition, there are many other physical, chemical and physiological factors that affect biodegradation of organic materials in anaerobic digesters and influence biogas generation. Thus, redox conditions, temperature, pH, hydraulic retention time, organic loading rate, mass mixing represents important factors to consider for a good conversion of organic waste to biogas in biogas systems [8].

In anaerobic digestion processes, the physiological and ecological investigation of methanogens has often involved monitoring of gases released under the complex metabolic processes. In general, the metabolism of the biological species producing biogas implies multiple biochemical reactions related to the oxidation of hydrogen, concomitantly with reduction of carbon dioxide.

Assessment of the microbial activity by means of the biogas production has been achieved by instrumental analysis for the experimental research carried out under hydrostatic pressure. The methane content in biogas was determined for all biomass samples corresponding to the four established conditioning pressures in range of 0 - 6 bar, based on the recorded chromatograms. Figure 3 indicates the graphic representation of variation of methane concentration in time, for the selected working pressures used in the four experiments [9].

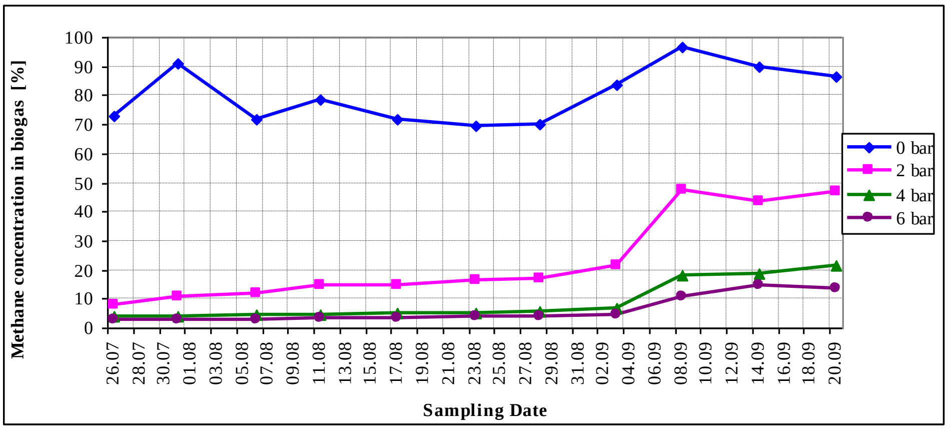

Fig. 3. Variation of methane content in biogas for different conditioning pressures [10].

Analyzing the data presented in Table 2, it can be remarked that the methane content in biogas is significantly superior for the biomass sample exposed for anaerobic digestion in standard pressure of 0 bar, compared to other biomass samples which have been fermented under various hydrostatic pressure up to 6 bar. It is clearly proved that the samples conditioned for fermentation at pressures of 2, 4 and 6 bars have produced a definitely lower quality biogas, which confirms the theory that the hydrostatic pressure has an adversely negative influence on methanogenesis.

As shown in the related experiments, the hydrostatic pressure has clearly an inhibitory effect on fermentative processes, so that the biochemical processes are much slowed. With the increasing pressure in the system, the microbial activity is clearly reduced, the level of decomposition of organic matter is significantly diminished and therefore the bacterial populations generate several specific metabolites (organic acids, methane, carbon dioxide, etc.) in much smaller quantities which make the oscillations in methane production be also reduced.

The secondary product in anaerobic digestion is the methanogenic digestate which has a fairly high content in nutrients such as nitrates and phosphates. Therefore, this by-product can provide nutrients for crop growth and can also be used to protect soils against erosion. Furthermore, it could reduce the need for synthetic fertilizers and soil conditioners which are produced by less sustainable methods, providing cost savings and environmental benefits. To be recycled as an eco-fertilizer, the digested residual must have a defined content of macronutrients. Its chemical quality should be considered in terms of heavy metals and other inorganic contaminant, persistent organic compounds and the content of macro-elements such as Nitrogen, Phosphorous and Potassium.

The applicative research carried out under national and bilateral cooperation projects has un essential role in the institute research framework. Thus, a biogas system intended to treat domestic waste has been designed and implemented in rural areas. The biogas unit is designed and built mainly for treatment and energy recovery of biodegradable waste generated in small farms but also for local municipalities to recovery various organic waste such as algae and other biodegradable waste generated in wetlands. Figure 4 shows the 4mc biogas unit built in Boteni, Argeş [11].

Fig. 4. Household biogas unit in operation in Boteni village, Argeş.

This biogas unit can bring multiple socio-economic benefits such as: generation of biogas as a valuable renewable energy source; treatment of domestic waste for prevention of soil and water pollution; production of ecological soil conditioners to be used in agriculture.

The development of such domestic-usage biogas technology, as well as of the facility for energy recovery and treatment of green algae and aquatic biodegradable waste, could lead to the development of particular small industries and thus create new jobs at businesses dealing with the civil construction and related activities, including land preparing, production and gas supply pipelines, systems and devices for gas distribution, biogas burners, gas cleaning systems and so on.

4. Conclusion

Various natural resources and organic waste represent a valuable renewable energy source to be used for biogas and other types of biofuels. In addition, the fermented slurry is a valuable by-product to be used as an ecological soil conditioner.

Fundamental and applicative research have been achieved by ICPE-CA for improving the biodegradability of biomass and increase the efficiency of bio-processes to be used for industrial applications. Thus, lignin decomposition tests shown a higher efficiency in energy recovery to biogas for ligno-cellulosic biomass. For the wet anaerobic digestion of such materials, a pre-treatment procedure is recommended to be applied prior to the biomass fermentation. The scope of these pretreatment methods is to enhance the enzymatic hydrolysis and to improve the conversion grade of lignocellulosic biomass to biogas in order to increase the effectiveness of the biogas plant.

Since hydrolysis of these complex organic matters is an important step for the high biodegradation of waste, several researches on improving the hydrolysis level of lignocellulosic biomass have been achieved.

Also, several laboratory experimentals of anaerobic digestion under hidrostatic pressure has proved to be of great importance for designers of biogas plants in terms of process efficiency. The assessment of biogas quality by instrumental analysis along with the determination of methanogens cell numbers per unit volume for the raw material and fermented slurry, has demonstrated a definitely higher efficiency of anaerobic digestion for the organic mixture exposed in anaerobic condition and lower hydrostatic pressure. These laboratory results lead to conclusion that efficiency of biogas production in vertical reactors is diminished with the height of the digester due to the negative influence of the hydrostatic pressure on the biogas producing microorganisms.

On the other side, the non-digested residuals generated as effluents in anaerobic process are rich in essential nutrients (N, P, K) and can be used as natural fertilizers. They can replace costly, fossil fuel-based fertilizers and are virtually odorless, pathogen-free, and most importantly, environmentally friendly.

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