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Experiments on the First Selected Pretreatment Method of Bio-Wastes for the Albanian Conditions

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ABSTRACT

During our study we examined different resources of organic biomass in actual reality for Albania and we tried to find a suitable utilization process in the energy sector for heat (energy) production. Emphasis has been given to the agricultural and forestry wastes as well as animal organic wastes, aimed to proceed some tendency reaching a suitable status of a mixture prepared from these organic wastes, in order to get as much as possible biogas (Methane).

Different alternative methods of degradation or disintegration of waste such as: composting or burning does not resolve permanently the accumulation of waste, since that they themselves leave a certain residue. On the other hand we have performed different pretreatment methods for bio-wastes and their combinations, leading to an easier process for anaerobic bio digestion which may be engineering considered as a process in which operating a present number of organisms can produce a mixture of gases (Biogas composed of 60% methane and 40% carbon dioxide) and a mixture of liquid which held a high value of mineral nutrient elements like nitrogen, phosphorus, etc.

We have already studied also the possibility of bioethanol obtaining using organic residuals and some preliminary results have been reported in this paper.

Keywords: *Bio-resources, agro wastes, biomass, bio-energy, biogas, bioethanol.*

INTRODUCTION

Pretreatment of lignocellulosic biomass was seen as a key step in the production of bioenergy[1]. Lignocellulosic biomass contains polymers of cellulose, hemicellulose, and lignin, bound together in a complex structure[2,3]. Liquid biofuels, such as ethanol, can be made from biomass via fermentation of sugars derived from the cellulose and hemicellulose within lignocellulosic materials, but the biomass must be subjected to pretreatment processes to liberate the sugars needed for fermentation[4,5]. This article will focus on the overall analysis of the organic raw materials, which will be used for the development of experiments. The intention was to analyze the physical - chemical properties of the samples, which will be used as raw material for the pre-treatment process for biogas production[6,7]. It has been determined characteristics such as: humidity, dry matter, ash, the carbon to nitrogen, ratio, pH value, electrical conductivity and biological oxygen demand (BOD). Raw materials to be analyzed were: alfalfa, wheat straw, corn straw, corncob and a mixture of leaves and thin and dry wooden sticks, all taken from a field area in suburban of Tirana.

In this work we have explained the priorities of pre-treatment methods, advantages and disadvantages of all pretreatment methods. Also we analyzed combinations of different pretreatments, to highlight the advantages of each combination.

The pretreatment process helps to make it more easier the enzymatic hydrolysis. And finally we analyzed the results achieved in performing experiments and discuss the possibilities existing for improving the biomass pretreatment process.

Alternative methods of treatment of waste such as: composting or burning does not resolve permanently the accumulation of waste, since that they themselves leave a certain residue[8].

MATERIALS AND METHODS

Different raw materials can produce different amounts of biogas depending on their content of carbohydrates, fats and proteins. Theoretically, all biodegradable materials with reasonable lignin content are suitable as raw materials for biogas processes. For the calculation basis we have taken into consideration some organic waste coming from land located in Tirana region of Albania. We have evaluated analysis for organic fraction, ash, carbon content, nitrogen content, pH value, and electric conductance. Raw organic materials that have been selected were; alfalfa (lentil), wheat straw, corn straw, corncob and a mixture of leaves and thin sticks.

EXPERIMENTAL RESULTS

The following chemical and physical properties were determined: pH value, conductivity, moisture, ash and total concentrations of N, P, K. The moisture was calculated by sample weight loss at 105 °C for a period of 24 h, and stored in a glass bottles. Set of samples shown in figure 1 and 2 has been pretreated according to standard procedure in different condition varying from acid and alkaline added rested in 500 ml bottles for 40 days.

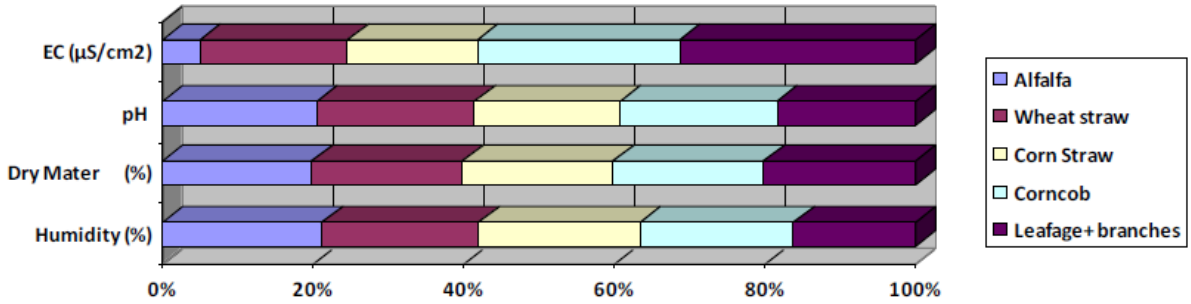
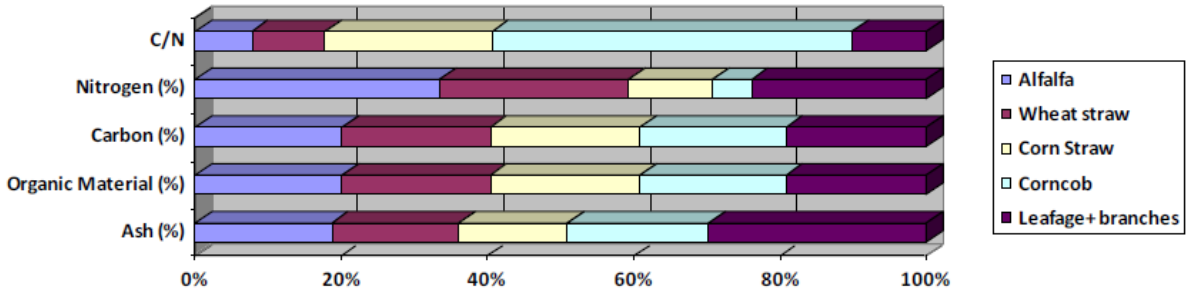


Figure1. *some properties of samples for pretreatment*



Then were performed tests for aerobic digestion for 14 days at 70°C. Then sample bottles were kept at 40 °C for other 26 days. Results of some properties of row materials combination as in *Figure 2. Other properties: Ash, organic materials and carbon content of samples for treatment* Organic samples have been comprised of lignin, cellulose and hemicelluloses and are strongly depended from geographical position and climate at the site. Higher value of C/N was at corn straw which has also higher value of Carbon content. On a dry basis, biomass is constituted from 88% to 99.9% of organic compounds. The average composition based on dry weight for wood is: cellulose 40-45%; lignin 17-35%; hemicellulose 20%-35%; and 25-35% lignin while extractives vary from 1 to more than 10% [9]. As a matter of fact, wastes from degradable forest material contains less inorganic matter than straw and cereals. Different composition and condition of samples for their pretreatment have been previewed for the experimental work and was realized with corrected recipes according to the recommendations of the other works[11].

Pretreatment of Agro-Bio-Wastes

Through carrying out some experiments for anaerobic digestion of these bio-organic wastes, have been resulted that there is actually an alternative methodology for further treatment. So, it was showed a clear advantage such as having low nutrient requirements, there is some energy savings and generation of low quantities of sludge, also can d\be mentioned an excellent waste stabilization, and which is more important, the production of bio-methane happened without requiring residue special pretreatment. Anaerobic digestion can be tested also for higher temperature ranges including mesophilic temperatures of approximately

35^0C and thermophilic temperatures ranging from 55 to 60^0C. we were focused in a classical process applying mesophylic temperatures.

However, the thermophilic temperature range are to be considered as alternative because it makes faster reactions, is characterized by higher gas production, than does the mesophilic temperature range. The bio-waste disposal is always a matter of great concern since they are considered as a quite dangerous source of environmental pollution.

It has been under our focus the possibility of producing biogas from anaerobic disintegration of biomass discharge. Other advantages of this technology are potential improvement of biomethane yield due to the supply of additional nutrients from the co-digestates and more efficient use of equipment and cost-sharing by processing multiple waste streams in a single facility, while at the same time it may secure a much more stable year round operation. It was also examined, in lab scale experimental set-up, the capability of a centrally located anaerobic digestion facility for managing different wastewater streams in order to secure a stable operation. We have also calculated the amount of the biomethane that can be produced from co-treatment of different wastes. As it can be seen the bigger contribution to the biomethane produced rate was in case of cereal straws, due to the fact that polymeric Carbon rows can be broken easier into smaller molecules which fasten the degradation process. Meanwhile other two types of wastes contribute in stabilizing the nitrogen content for the microorganisms attack, keeping the optimal value of the C/N ratio during degradation. All necessary experiments and tests have been performed in a laboratory set up equipment as shown in figure 3, a and b:

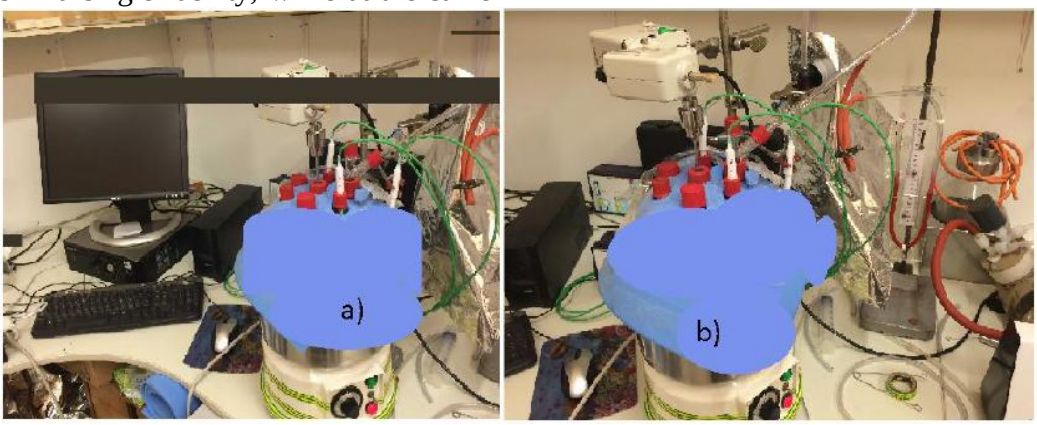


Figure3. *Laboratory set up for the biogas producing from organic wastes in their mixing according to the scenarios: a) before hydrolysis, b) after biodegradation*

Discussion of the Results

Impact of NaOH concentration and deliberation time of organic matter from wheat straw during 24 hours of treatment are shown in constantly changing during the reaction time, and considerable changes has happened in samples characteristics during and after agro-wastes pretreatment.

Modeling Process of Pretreatment

Process modeling and simulation was performed using two specialized engineering software like Super Pro Designer, SimSci Suite 2014 ®, and ASPEN PRO v8.6® being bought from the original companies from USA, thanks to the support offered from the National Program, and has been quite effective and helpful for carrying out the process of anaerobic degradation.Considering all reaction kinetics of first order, and applying all databanks data from the satellite, reaching the right acido-basic equilibriums, we have performed regular modeling procedure and computer simulation for the process with our data.

As shown above, it was drawn a suitable process flow diagram presented in figure 4, using the engineering software so called Super Pro Designer which has been also installed into our server.

We have also performed the computer simulation procedure aiming to have the optimal value for the biogas (methane) cost, and optimal expenditures during production.

We have used also the ASPEN PLUS vs 8.7 for the process scaling up and anaerobic reactor design and was designed the flow sheet of the same process by this software.

We have also used the computer procedure for the process optimization addressing sensitivity analysis as the most important indicator for the performance of the process.

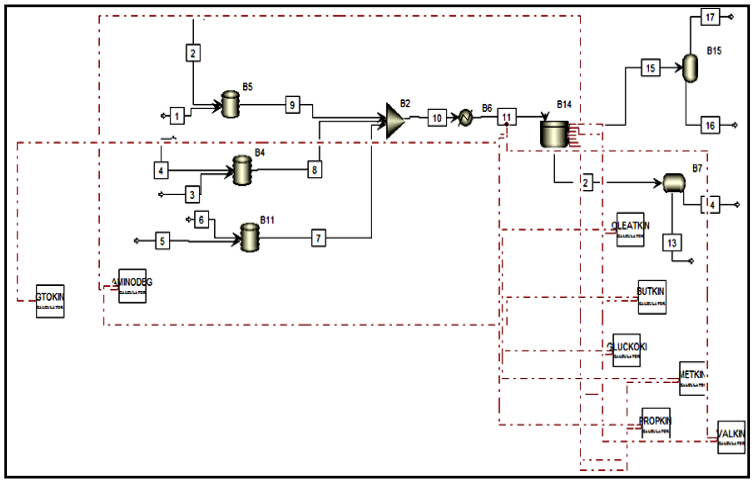


Figure 4. *Process flow sheet and simulative boxes for the biodegradation of agri-organic wastes*

As it can be seen, there are some changes in values of the properties of the materials before their treatment. And further organic material content is higher in samples treated with sulphuric acid than in samples with base treated. Of course this is strongly depended of the acid concentration or alkali concentration in the media treated. On the other hand, there was no changes of that in alfalfa case, it was higher when it was base treated, than when acid treated, while Carbon content was slightly higher during alkaline treated. The carbon content of the samples was in depended of pretreatment method. It can be clearly seen that the organic matter was consumed in a great portion of it from the beginning till end of experiments, which is caused by the degradation of it from the hydrolysis during pretreatment. Further one can see that during basic pretreatment we got a smaller decrease of organic matter, than during acidic treatment. Also ash content was decreased during pretreatment, due to the decrease of O.M. On the other hand the Nitrogen content was increased during pretreatment, due to the fact of mineralization of Nitrogen into the form of ammonia, nitrates, nitrites etc.

Consequently, the ratio C/N was decreased accordingly, but slower in basic treatment. Alkaline pretreatment of wheat straw by soaking in condition of a mean value of 13.7 g VS/l solution, in bottles shown in figure 3.b, using working solution of 5 g/l and 15 g/l and the process is ended in 18 hours, after which we have the respective results.

We have also used model so called ADM1 for verification of calculation values, preferable for the type of microbial kinetics of the involving reactions. For the design procedure we have chosen a batch type reactor with a total volume of 29.23 m³ and a working volume of 23.38 m³. Process has been selected to be performed under mesofillic conditions at 35 up to 37°C. Heating agent is working through a stainless steel coil type heat exchanger and optimal thickness of the thermo isolation was calculated to keep heat loss in the levels of less than 3%. Reactor is working periodically each 25 days a cycle, i.e. 13 cycles yearly for a total working hours 7800 h/y.

For the analysis and evaluation of technologies available internationally as well as for the process development and the optimization of procedures, we were studying all possibilities existing from the best practice. We wanted to find and determine the potential the biogas yields of these materials on the basis of continuous and continuous fermentation tests.

CONCLUSIONS

From the various experiments realized it was shown the great importance of the pre-treatment process in other stages of the production of biogas. Pretreatment is one of the main stages of the biogas production.

- Alkaline pretreatment (with NaOH) was a pretreatment method more effective than the acid type treatment, because during the pretreatment achieved more material dissolves lignocellulose, which is indicated by the highest decrease of organic material in the treated samples.
- When treated with acid (H_2SO_4), increasing the acid concentration, increases also the disintegration of lignocellulosic material caused by the increase of acid

concentration, enables separation of organic connections in walls of lignine, enabling easier attacking hemicellulose and cellulose.

- To have a pre-treatment as well, and a performance in the production of biogas must not only make a combination of pretreatment methods but also the raw material used;
- The possibility of bio-ethanol production in organic farming was studied by choosing and estimating the potential of raw materials (maize).
- The experiments proved that maize is a suitable medium for ethanol production and successfully could be used in the on the farm bio refinery concept.
- Bioethanol produced by maize, which is a neutral carbon fuel that reduces CO_2 emissions, is a very good alternative solution to fulfill nowadays world energetically needs.

RECOMMENDATIONS

- The design of the specific plant for the treatment of agricultural and forestry wastes needs to be done specifically related to their characteristics and infrastructure facilities. With the support of the international agencies and experts in the field of organic waste management needs to be considering all existing situations and experience within the country;
- As a final result is to be build a national strategy for the agro-forestry wastes management and real time monitoring system that will ensure reliable information on the status of the biomass and biogas production capacity throughout Albania.

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