PREVIEW OF A CONTROLLED BIODEGRADATION OF PRETREATED WASTES FROM AGRICULTURE AND FORESTRY

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Abstract

This work was based on the pretreatment of lingo-cellulosic wastes from agro – forestry organic wastes with samples being taken from stations of different sources. Between many of recommended and explained methods for pretreatment of the organic biomass we selected as the most effective, the way of acidic waste pretreatment and another scenario applying the alkaline method prior to the biodegradation through anaerobic bio-digestion for energy profit. For bio-methane profit process has been performed in a series of the experiments. From the various experiments we realized the great importance of the pre-treatment process for the biogas production.

Alkaline pretreatment (with NaOH) brought about a decay of lignin structure of biomass and increase access of enzymes in hemicellulose and cellulose. This method was more effective than acidic treatment due to the fact that was achieved more dissolved lignocellulose, which is indicated by the highest decrease of organic material in the treated samples.

To increase the acid concentration, it increases also the disintegration of lignocellulosic material. This is because with the increase of acid (H_2SO_4) concentration, enables separation of organic connections in walls of lignine, enabling easier attacking hemicellulose and cellulose.

We were focused more on the acidic and alkaline pretreatment and on the development of experiments, analysis of raw materials, taking samples before and after appropriate pretreatment. Surveillance and identification of changes occurring during pretreatment processes has been conducted for a certain period of time and the important conclusion has been taken.

Keywords: *biomass, organic waste, anaerobic digestion, alkaline and acidic pretreatment*

1. INTRODUCTION

Development of energy systems based on renewable biomass has been one of the global target for the studies recently. 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 main goal of pretreatment was to overcome this recalcitrance, to separate the cellulose from the matrix polymers, and to make it more accessible for enzymatic hydrolysis. And finally we analyzed the results achieved in performing experiments and discuss the possibilities existing for improving the biomass pretreatment process.

2. 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 as shown in Figure 1.

Fig. 1. Samples of all raw materials used for the experiments in raw: a) alfalfa, b) wheat straw, c) corn straw, d) corncob, e) a mixture of leaves and f) thin and dry wooden sticks.

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 as shown in Fig. 2.

Fig. 2. Photo of grinded samples stored in glass vessels

Determination of dry matter and moisture content, was calculated by sample weight loss at 105±2°C for a period of 24 h. Determination of organic matter and ash is done by using the muffle oven, at 450 ±20°C. The pH and the EC were measured from an aqueous extract using ph-meter and conductivity meter.

The organic nitrogen was evaluated using the Kjeldahl. Set of samples shown in table 1 has been pretreated according to the standard procedure in different condition varying from acid and alkaline added, followed by settling in 500 ml bottles for 40 days. 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.

Samples	Humidity (%)	Dry Mater (%)	pH	EC (µS/cm2)
Alfalfa	3.6	96.4	6.27	0.731
Wheat straw	3.5	96.5	6.35	2.80
Corn Straw	3.62	96.38	5.87	2.47
Corncob	3.45	96.55	6.28	3.85
Leafage+ branches	2.75	97.25	5.63	4.49

Table 1. Some properties of samples for pretreatment

Samples	Ash (%)	Organic Material (%)	Carbon (%)	Nitrogen (%)	C/N
Alfalfa	7.24	92.76	51.53	2.30	22.39
Wheat straw	6.69	93.30	51.84	1.78	29.12
Corn Straw	5.71	94.28	52.38	0.79	66.30
Corncob	7.48	92.52	51.40	0.36	142.78
Leafage+ branches	11.5	88.5	49.17	1.65	29.8

Table 2. 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.

Nr.	Alfalfa (g)	Wheat Straw (g)	Corn Straw(g)	H_2SO_4 (ml)	H_2O (ml)	NaOH (ml)
A	-	17.0	-	50 (95%)	1000	-
B	-	18.5	-	-	1000	60 (40%)
1	13.3	-	-	250 (20%)	250	-
2	13.3	-	-	250 (30%)	250	-
3	13.3	-	-	250 (40%)	250	-
4	-	-	13.3	250 (20%)	250	-
5	-	-	13.3	250 (30%)	250	-
6	-	-	13.3	250 (40%)	250	-
7	-	-	13.3	-	250	250 (10%)
8	-	-	13.3	-	250	250 (15%)
9	-	-	13.3	-	250	250 (20%)
10	13.3	-	-	-	250	250 (10%)

11	13.3	-	-	-	250	250 (15%)
12	13.3	-	-	-	250	250 (20%)

Table 3. Different composition and condition of samples for their pretreatment

A number of different tables 2, and 3 were constructed in such a way for expressing the results that we got during the experiments. In the figure 4, it is presented picture of samples taken from some organic wastes prior to pretreatment. The properties of samples taken from some organic wastes after their pretreatment process, are presented in figures 5 and 6.

3. RESULTS AND DISCUSSION

Impact of NaOH concentration on the parameter changes, and also deliberation time of organic matter from wheat straw during 24 hours of treatment are shown in figure 7.

Fig. 4. a) Setup of anaerobic digestion of pretreated samples, **b)** Experiments of biomass alkaline soaking

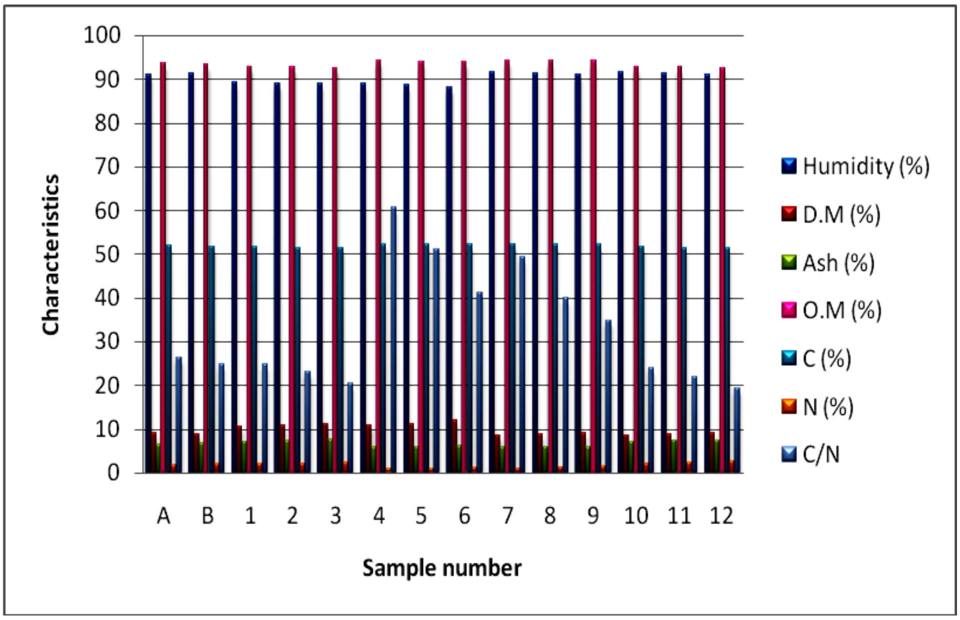

Fig. 5. Properties of samples taken of some organic wastes prior to pretreatment

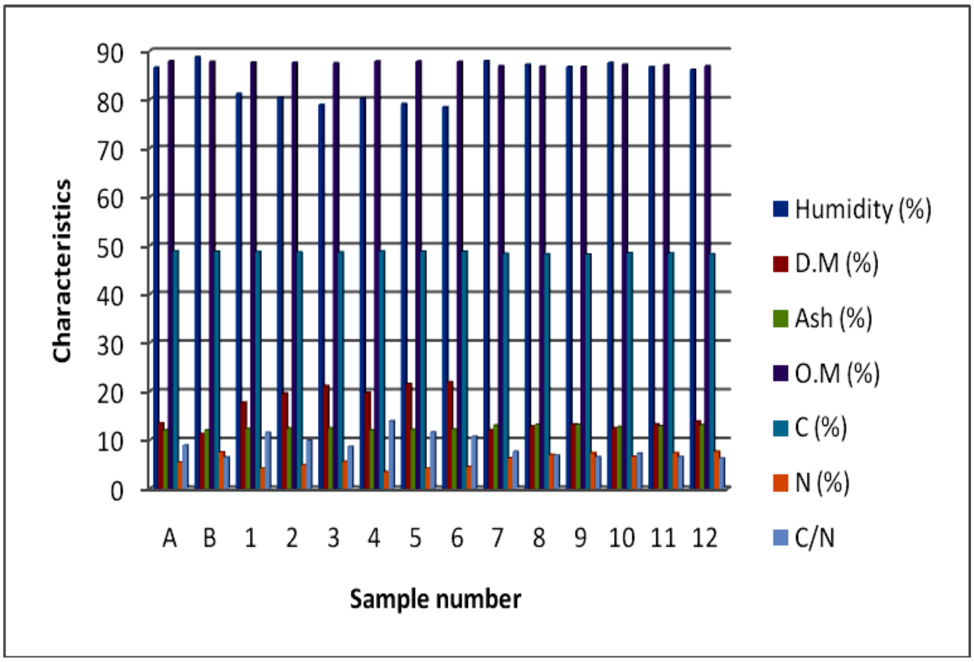

Fig. 6. Properties of samples taken of some organic wastes after pretreatment

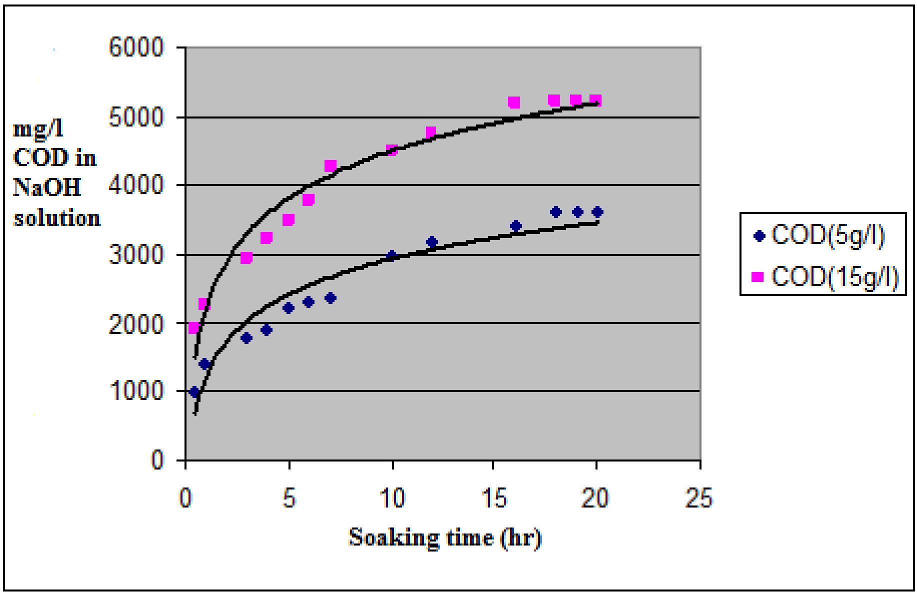

Fig. 7. Impact of NaOH concentration and deliberation time of organic matter from wheat straw during 24 hours of treatment

4. DISCUSSIONS

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 un 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 organic matter. 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 4.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 results shown in graph of figure 6.

5. CONCLUSIONS

From the development of various experiments realized 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. Without developed with precision all the pre-treatment steps can not obtain a certain residue, which will be ready for other stages of production of biogas.

- Alkaline pretreatment is one of the most effective treatments because enables the decay of lignin structure of biomass and increase access of enzymes of hemicellulose and cellulose.
- Alkaline pretreatment (with NaOH) is one of the pretreatments more effective than acid. Because during the pretreatment achieved more material dissolves lignocellulose, which is indicated by the highest decrease of organic material in the treated samples.
- In samples treated with acid (H_2SO_4), to increase the acid concentration increases and the disintegration of lignocellulosic material. This is because with the increase of acid concentration, enables separation of organic connections in walls of lignine, enabling easier attacking hemicellulose and cellulose.
- Termination of chemical bonds in the walls of lignine and hemicelluloze made easier by the combination of thermal pre-treatment with the basic.
- It should be emphasized that a great importance in the pre-treatment process has not only the choice of lignocellulose material to be treated, but the storage, drying and its fragmentation. 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 that will be pre-treated. In this way become possible attacks on faster lignocelulosic wall, biodegradable material growth and enable increasing the amount of biogas production.

REFERENCES

1. A. Demirbas, 2009 “Biofuels securing the planet’s future energy needs,” Energy Conversion and Management, vol. 50, no. 9, pp. 2239–2249.
2. S. T. Merino and J. Cherry, 2007 “Progress and challenges in enzyme development for biomass utilization,” Advances in Biochemical Engineering/Biotechnology, vol. 108, pp. 95–120.
3. M. E. Himmel, S.-Y. Ding, D. K. Johnson et al., 2007 “Biomass recalcitrance: engineering plants and enzymes for biofuels production,” Science, vol. 315, no. 5813, pp. 804–807.
4. H. Palonen, F. Tjerneld, G. Zacchi, and M. Tenkanen, 2004 “Adsorption of Trichoderma reesei CBH I and EG II and their catalytic domains on steam pretreated softwood and isolated lignin,” Journal of Biotechnology, vol. 107, no. 1, pp. 65–72.
5. N. Mosier, C. Wyman, B. Dale et al. 2005,“Features of promising technologies for pretreatment of lignocellulosic biomass,” Bioresource Technology, vol. 96, no. 6, pp. 673–686.

6. M. A. Patel, M. S. Ou, R. Harbrucker et al. 2006,"Isolation and characterization of acid-tolerant, thermophilic bacteria for effective fermentation of biomass-derived sugars to lactic acid,"Applied and Environmental Microbiology, vol.72, no.5, pp.3228–3235.
7. R. Kumar and C. E. Wyman, 2009 "Effects of cellulase and xylanase enzymes on the deconstruction of solids from pretreatment of poplar by leading technologies," Biotechnology Progress, vol. 25, no. 2, pp. 302–314