# THERMOALKALINE PRETREATMENT INFLUENCE ON ANAEROBIC BIODEGRADABILITY OF FILTER CAKE FOR METHANE PRODUCTION

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Graphical Abstract
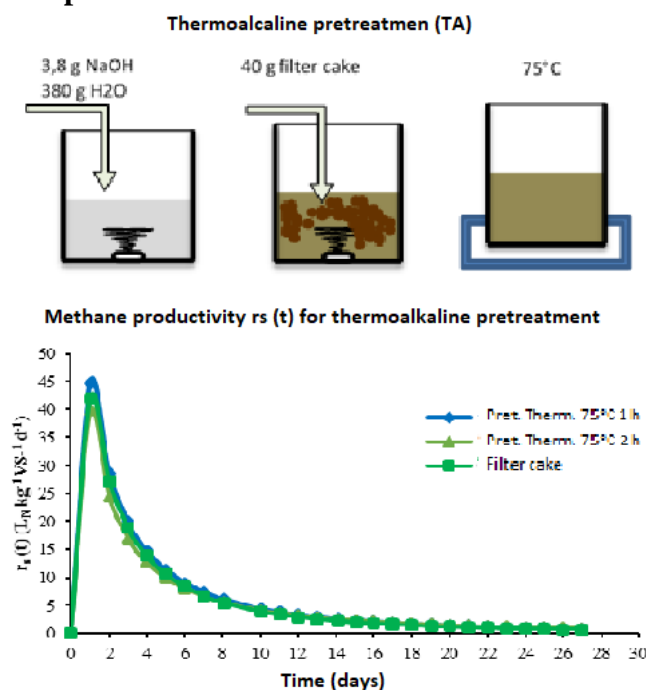
Abstract.

Currently millions of tons of solid waste are produced worldwide, receiving only a small part of some kind of treatment, the rest are used indiscriminately pollute the environment. Complexity of these wastes requires the study of alternative methods to help improve the efficiency of the stabilization process. Thermoalkaline pretreatment study was carried out taking into account the nature of filter cake from sugar manufacturing process. Sodium hydroxide NaOH was used as chemical agent and temperature conditions of 75 0C evaluated for different times. This research was conducted in order to determine the effect of pretreatment of filter cake to increase the yield of methane.

The physical-chemical characterization of filter cake from "Melanio Hernández" Sugar Mill (Sancti Spiritus, Cuba), it was carried out through analysis of total solids (ST), volatile solids (SV) and pH. Methane yield parameter for anaerobic digestion in mesophilic conditions (37 ± 1 C) was determined. It was demonstrated that filter cake is a solid residue of sugar industry in this sector with high energy potential due to its organic content for the production of methane. Pretreatment at 1 hour had greatest increase in methane potential with respect to the untreated filter cake. These results demonstrate the relevance of the thermoalkaline pretreatment severity in terms of time and sodium loading to obtain the optimum anaerobic biodegradability of this biomass.

Introduction

The world today faces an energy crisis due to the indiscriminate use of conventional fuels (oil, natural gas and coal); and becoming more serious by the non-renewable nature of these resources and its excessive use in different countries day ago. Within the ways that humanity has to alleviate energy and environmental problems, there is a greater use of renewable energy sources, among which the use of biomass stands out.

Power generation from biomass is a renewable source with the greatest potential in Cuba, from residual cattle and pigs, production of sugar, alcohol, coffee pulping and landfills, which are today, as a whole, a means of environmental pollution. [1] (Contreras Velásquez, 2006).

Filter cake is the main residue of the cane sugar industry, producing 30 to 50 kg per ton of processed raw material, which represents between 3 and 5% of the ground cane. This percentage and its composition vary with the agroecological characteristics of the area, with the crop harvested, factory efficiency, method of clarification used, among other factors [2] (Cárdenas, G.; S. Guzmán, 1983). This high content of insoluble organic matter 85% [3] (Sánchez et al., 2005), relatively low cost and large volumes generated make this biomass an attractive source for bioconversion processes.

Main uses are reported to filter cake have been as a soil in sugarcane agriculture, cattle feeding and extraction of waxes and oils . Even with the multiple uses that the filter cake has, large quantities of this waste remain unused, which leads to serious contamination problems in the areas destined for disposal and only a small part receives some type of treatment. An effective and practical method that is applied is to subject this residual to dehydration by heat, obtaining as a result a more stable and easy to use material called melote [4] (Sarria, P, Solano, A, Preston, TR, 1990).

In Cuba, the anaerobic decomposition of filter cake has been used as an alternative treatment [5] (Cruz, 1991, [6] González et al., 1995). For this, large volumes of water are used (volume ratio 1: 4, filter cake: water) in order to dilute the high content of suspended solids. Although there are advances in the study of solid waste treatment at the international level [7] (Zheng and Zhao et al., 2014), there are still aspects to be clarified about the possibility of a previous stage of treatment, which allows the final stabilization

of complex organic material. without the need for large dilutions. Moreover, when it is known the applicability of hydrolysis for various purposes in materials with a high carbohydrate content [8] (Rodríguez-Vázquez et al., 1992), which constitutes the limiting step in the anaerobic digestion process. Currentl y, there are different methods of pretreatment including mechanical, physical, thermal and chemical, as well as biological methods . In the thermoalkaline pretreatment several works confirm the aforementioned [9] (Teghammar et al., 2010). [10] Gossett et al. (1982) concluded that lignin pretreated by thermo-alkaline treatment at concentrations above one g L-1 had a greater inhibitory effect for methanogens.

In general, the selection of parameters during pretreatment is an important aspect for productivity and / or methane yield in all pretreatment methods addressed. In the case of the thermoalkaline pretreatment with NaOH, it could be thought of using the cleaning waters of the equipment containing soda to pretreat the filter cake and to reduce the pretreatment in terms of water and the purchase of this chemical for its subsequent conversion to bioethanol or biogas, which offer alternative solutions to use of economic and environmental potential of the biomass.

The objective of this investigation was to determine the effect of the thermoalkaline pretreatment with NaOH on the biodegradability of filter cake to increase the methane yield.

Materials and Methods

The filter cake used in the experiments was collected during the 2015 harvest in "Melanio Hernández" Sugar Mill, province of Sancti Spiritus, Cuba. The filter cake was air dried for 72 hours, and then stored at 4 °C in nylon bags.

- Analytical methods

Physical-chemical characterization of the filter cake consisted in the analysis of total solids (ST), volatile solids (SV) and pH, according to the standard methods [11] (APHA, 2012).

The pH was measured with a Crison 52-11 electrode, connected to a Crison GLP 22 pH / mV meter. The resolution of the reading is 0.01 pH units and the accuracy of $\pm$ 0.01. Calibration was performed with standard CRISON buffer solutions of pH 7.02 and 4.00 at 20 °C. The samples were mixed with water at a 1:10 ratio and stirred at 150 rpm for 20 minutes (VDI 4630 2005).

- Thermoalkaline pretreatment with sodium hydroxide (NaOH)

Thermoalkaline pretreatment with NaOH was carried out in two times, the first two repetitions in a time of 1 hour and the other two in 2 hours. To the mixture was added 3.8 g of sodium hydroxide, 40 g of filter cake and 380 g of water to keep the dilution of 10 parts thereof were hermetically sealed and covered with aluminum foil to prevent heat loss to the environment and placed in a thermoreactor, reaching the required temperature after 29 minutes of having put them in the equipment.

- Production and determination of methane potential.

Trials were carried out in batch, in triplicate, with the pretreated filter cake and without pretreatment in polyethylene reactors of 2 L capacity, at a constant temperature of 37 $\pm$ 1ºC. The reactors were placed in an incubator to keep the temperature constant.

For the test batch was used as an inoculum source one digestate plant family biogas hog manure substrate. The substrate mass was determined from equation 1.

$$p_i = \frac{m_i \cdot c_i}{m_s \cdot c_s} \qquad (1)$$

Where:

mi: inoculum mass (kg)

ms: substrate mass (kg)

ci: volatile solids concentration of inoculum (gkg-1)

cs: volatile solids concentration of substrate (gkg-1)

Volatile solids concentration of inoculum and of substrate were determined according to standard methods (APHA, 2012).

In the experiment, a control reactor was used (bottle with inoculum without substrate), with the objective of subtracting in the determination the methane formed from the organic matter contributed by the inoculum. All the bottles were shaken manually once a day to favor contact between the substrate and the microorganisms, re-suspend the sediments and break the layer of floating material.

The reactors were connected to graduated cylinders filled with 3% NaOH solution in order to dissolve the CO_2 content. Cumulative methane production was measured by liquid displacement. The gas pressure is calculated based on the height of liquid column and subtracted from atmospheric pressure before normalization (273 K and 101.29 kPa). The methane volume was standardized. The digestion process was stopped at 21 days when there was no more than 1% by volume of methane daily.

To refer to the volume of gas produced v1, measured at ambient temperature and pressure T1 and p1, at standard conditions T0 and p0 as standardized volume v0, equation 2 was applied according to manual VDI-4630 (2006). Before normalizing the volume of methane was subtracted the volume produced in control reactor (inoculum without substrate).

$$v_0 = v_1 \cdot \frac{(p_1 - p_w) \cdot T_0}{p_0 \cdot T_1} \qquad (2)$$

Where:

v0: Normalized methane volume (Nm3)

v1: Volume of ethane measured at temperature T1 and pressure p1 (m3)

p1: Pressure at which methane (mbar) was measured

pw: Vapor pressure of water at temperature T1 (mbar)

T1: Temperature at which methane was measured (K)

p0: Normal pressure (1013.25 mbar)

T0: Normal temperature (273.15 K)

Methane potential, defined as the amount of methane generated per amount of substrate was determined according to equation 3 (VDI-4630, 2006), during a time of digestion. The values obtained are represented in a cumulative biogas yield curve and B (mLNgSV-1) over time.

$$y_B = \frac{\sum_{t=0}^{t=21-29} V_B}{m_s} \qquad (3)$$

Where:

VB: Cumulative methane volume during the digestion time t (Nm3)

ms: Mass of substrate added to the reactor in terms of volatile solids (kgSV)

Another parameter of interest in the evaluation of the discontinuous anaerobic digestion process is the specific productivity of methane rs (t). His determination was performed using the Hill model [12] (Mahnert, 2007) according to (Equation 8).

$$r_{s(t)} = y'_{CH4(t)} = y_{CH4max} \cdot \frac{b.c^b.t^{b-1}}{(c^b + t^b)^2} \qquad (8)$$

Where:

y_{CH4} (t): Cumulative methane production (mLNg-1SV-1)

y_{CH4max}: Maximum methane yield (mLNg-1SV-1)

t: Digestion time (d)

b, c: Model coefficients

Results and Discussion

Filter cake used for biological pretreatment and anaerobic digestion is characterized in triplicate (Table 1). These results are similar to those reported by other authors (Sánchez et al., 2005; [13] Meunchang et al, 2005; [14] Baez-Smith, 2008; [15] Radjaram and Saravanane, 2011; [16] Lopez, 2013).

Table 1 shows the high content of organic matter, given by the values of volatile fractions, SV / ST and SV / MF of 80.38 and 76.32%, respectively.

The drawback inherent treatment of filter cake, is given by the intrinsic characteristics of the material, wherein the carbon source is largely insoluble form which hinders its metabolization. So that the microorganisms can assimilate the organic matter, this has to be in dissolved form, so that, if part of a complex waste, as it is this type of waste, it is necessary an initial stage of pre-treatment to help to the formation of simpler molecules that can be easily used by microorganisms in the subsequent biological treatment. This, together with the favorable conditions of pH and content of organic matter, will favor the final stabilization process.

Table 1. Chemical characterization of filter cake

Parameters	Unit	Filter cake	Values reported
pH		5.4±0.06	7,5[a], (4,5 - 5)[c], 7,7[d], 5,5[f]
ST	%MF	9.95 ±2.01	10[a], 9,09[b], 29[c], 20[e], 6,28[f]
SV	%ST	80.38±5.02	83,91[f]
SV	% MF	76.32 ±5.22	

Data are expressed as the mean value ± standard deviation. All percentages are on a dry basis, except for TS.

[a] Rouf et al., (2010); [b] López-González, 2013; [c] Radjaram y Saravanane (2011); [d] Meunchang et al., (2005); [e] Baez-Smith (2008); [f] Sánchez et al., (1996).

pH was 5.4, a value that is in the range reported by Meunchang et al., (2005), Radjaram and Saravanane (2011); Rouf et al., (2010); Sánchez et al., (1996). pH variation is due to the process of generation of filter cake, collection method, preservation and determination. Chemical composition of the filter cake

depends on a variety of factors including the variety of sugar cane, soil, nutrient, clarification process adopted, filtering operation, and other environmental factors (Velarde et al., 2004).

- Methane productivity

Specific productivity of methane behavior rs (t), according to model used by Mähnert 2007 is showing in figure. 1. The rs (t) increased the first days reaching the maximum value before day 2 with a maximum value of 44.73LN kg-1VS-1 d-1. Most of time the productivity of reactors was lower than that of untreated filter cake of 0-9 days, which indicates a longer delay phase.
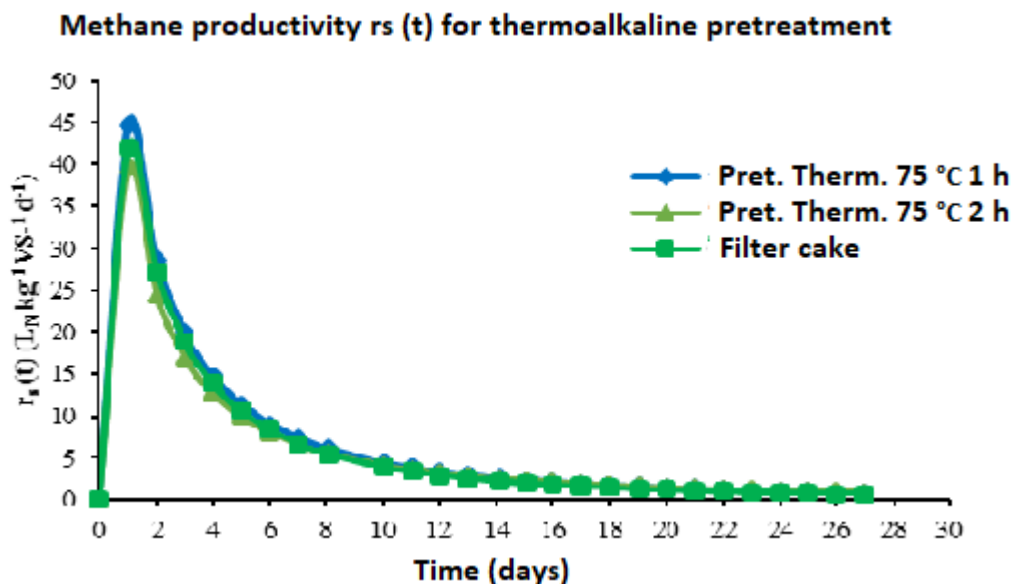

Figure 1 Specific Productivity of Methane rs (t) for pretreatment thermoalkaline

Conclusions
1. Filter cake is a solid residue of the sugar industry with high energy potential for the production of methane by its organic content.
2. The severity in the alkaline pretreatment in concentration and time drastically reduces the benefit of methane yield, which indicates the formation of unwanted byproducts.

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