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Evaluation of the Biochemical Methane Potential of Pig Manure, Organic Fraction of Municipal Solid Waste and Cocoa Industry Residues in Colombia

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Colombia is a country with national policies, in order to manage, direct and guide necessary actions to treat solid waste and reduce the negative environmental impacts that these generated after their disposition. These policies are consistent with international guidelines, and it is from them that efforts are made to reduce world consumption of primary energy, thus generating interest in the potential use of biomass as a source alternative energy. The biochemical methane potential (BMP) is a test used to characterize the raw materials in trials related to the optimization of anaerobic digestion and co-digestion; it allows to find the type of substrate and co-substrate with the greatest methane potential production. This study focuses on the evaluation of the production of methane through the anaerobic process of digestion and co-digestion using three different available substrates in Colombia, of which there is very few information on the methane production potential (cocoa shell and pods), along with other common waste (organic fraction of municipal solid waste and pig manure). This evaluation was realized applying the BMP test to each individual substrate and six mixtures of these substrates; anaerobic processes of digestion and co-digestion were carried out, by testing with batch reactors of 250 mL, in mesophilic conditions (32ºC - 36ºC), obtaining the BMP of each substrate and of the mixtures. To these residues, a physical-chemical characterization was realized prior the BMP test, which was determined: values of solid volatile, total solids, organic matter and nitrogen Kjeldahl. With the obtained characterization six mixtures were prepared to evaluate: three with carbon/nitrogen (C/N) relation of 25 and three with C/N relation equal to 35. Methanation potential was also evaluated in three levels of volatile solids grams (gVs): 0.5, 1 and 2. The three residues evaluated (pig manure, cocoa shell and pods, and organic fraction of municipal solid waste) have the ability to be used for the production of methane. In the trial of BMP, the pig manure was the higher methane production with 437.33 mL CH4/gVs, followed by organic fraction of municipal solid waste with a generation of 377.25 mL CH4/gVs. The test results of anaerobic co-digestion indicate that the best mix in terms of biogas production is the Mixture1, with 25 C/N relation and 0.5 gVs, which allows inferring optimal condition at the start of the experiment. This mixture reports a production of methane 2,485.91 mL CH4/gVs. The results obtained in the different tests allow visualizing that the application of this methodology serves as a valuation of the solid residues that cause a negative impact on the environment.

1. Introduction

Currently, large amounts of waste from the agricultural activity are generated, in the case of countries such as China these waste amounted to 600 million tons per year in 2013 (Zhang et al., 2016) a fairly representative figure that generates environmental problems. On the other hand, countries like Mexico generate 76 million

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tons of organic residues from fruits and vegetables that are generated by the food industry, agroindustrial and domestic sector (González et al., 2015). In the case of Colombia, municipal solid waste (MSW), as well as those from livestock and agro-industrial processes, are the most prominent, it is so for the year 2007 approximately 120.210 tons/year of RSU were generated in the main cities of the country, the above mentioned waste were originated only from centers of market (UPME, 2011), therefore, it is necessary to work on alternatives that allow an adequate management of this waste, as well as its use.

Anaerobic co-digestion is a process that offers different advantages to the problematic that has been mentioned previously among which are: The reduction of greenhouse gases, the minimization of the consumption of fossil fuels (Cabeza et al., 2016), the reduction of deforestation, the reduction of emissions from waste such as pig manure, among others (Thien, C. et al., 2012). As for the process, this presents benefits as dilution of toxic compounds, a better balance of nutrients, synergistic effects of the micro-organisms, as well as an increase in the load of biodegradable organic matter, and in general a better production yield of biogas (Gottardo, M et al., 2015). It also allows the use of nutrients from different wastes and balances the bacterial community in order to optimize the performance of the process (Zhang et al., 2016). It is important to note that biogas allows diversifying the sources of energy that are currently (Kheiredine B. et al., 2014). Additional to the advantages that it represents for the environment, biogas can be used for the generation of electricity or heating, thus contributing to minimizing the current dependence on fossil fuels (Li Y et al., 2016).

The present study was realized by applying the BMP test which is an index of anaerobic biodegradability of organic waste and determines the experimental value of maximum methane production that generates a known amount of organic waste (González et al., 2015). The BMP is used to optimize the anaerobic digestion which allows finding which substrate has the greatest potential and of this way determine the methane production of different mixtures. The probability and rate of degradation of the substrate depend on the rate of the concentration of microorganisms during the test, the pH and the temperature of the inoculum and the samples (Cabeza et al., 2016). This project focuses primarily on evaluating methane production through the process of anaerobic co-digestion using some of the different substrates available in Colombia and on which it exists little information about the performance of methane (cocoa), as well as other residues of common origin (organic fraction of municipal solid waste and pig manure). This was carried out by applying the BPM test for the different types of waste and their corresponding mixtures. It is a preliminary study that allows clarifying the potential of valorization of the residues that have been evaluated by means of anaerobic co-digestion.

2. Materials and Methods

In this study the anaerobic co-digestion process was carried out using batch reactors of 250 mL, in mesophilic conditions of 32°C, realizing an analysis of the biochemical methane potential (BPM) of three substrates: municipal solid waste (MSW), cocoa industry residues (CIR) and pig manure (PM), which previously were characterized physicochemical evaluating them volatile solid, total solid, organic matter, nitrogen Kjeldahl and chemical oxygen demand (COD). Each substrate was evaluated under static condition tests.

Inoculum: The inoculum that was used for all tests was a sludge from a biodigestor located at the sewage plant of Alpina S.A., in Sopo, Cundinamarca (Colombia). This sludge was selected because coming from a stabilized running system it gave us assurance of obtaining biogas production.

Substrates and co-substrates: The substrates used for testing were the cocoa industry residues (CIR), pig manure (PM) and organic fraction of municipal solid waste (MSW). The substrates were previously placed in a freezer at -4ºC, in order to avoid the change in the physiochemical characteristics.

The cocoa industry residues were simulated in the laboratory based on different references found of this industry (Federación Nacional de Cacaoteros, 2013). Cocoa shells and pods were used and obtained from a private farm located in the department of Santander – Colombia. The cocoa species worked for the trial was Trinitarian; this species is caused by the crossing of other two cocoas (Federación Nacional de Cacaoteros, 2013) and is characterized by a wide variability of shapes, sizes, and behavior, being nowadays the cocoa type that prevails in Colombia (Federación Nacional de Cacaoteros, 2013). These waste went through a process of downsizing where they were cut and then liquefied. Pig manure was obtained in Marengo Agricultural Research Center (C.A.M) belonging to the National University located in the municipality of Mosquera (Cundinamarca). The residues come from animals fed on commercial concentrate. Of the total composition of municipal solid waste in the city of Bogota, 65% are potentially useful organic solid waste (UAESP, 2011), Which are constituted by food waste (fruits, vegetables, processed food and unprocessed, meat, between others) belonging to the domestic sector, market square, and restaurants. The sample used for the experimentation came from two typical households in the city of Bogota; in this, only the organic fraction composed of vegetables, fruits, and processed food was taken. These waste also went through a process of downsizing and liquefied.

The BPM methodology used in this study is based on the principles described by Owen et al (1979) and Angelidaki et al (2009). The tests were carried out in 250 mL bottles by triplicate, with a working volume of 80%. The mixing ratio of the volatile solids of the substrate and inoculum in the individual tests (S/X) was of 1.5432 to minimize the inhibition by acidification or ammonium toxicity. Meanwhile, in the six mixtures of the substrates evaluated an S/X ratio of 3 was set. The total volume of work mentioned above was completed with distilled water. Then the bottles were closed with plastic lids and sealed with silicone, but not before having measured the corresponding pH of the contents of each one of them, which should be in a range of 6,3-7,8, with an ideal pH of 7 (Kondusamy et al., 2014). Once sealed, the bottles were placed in a thermostatic bath with an automatic controller without agitation at a temperature mesophilic constant of 32°C for 20 days (during the period of the test none of the reactors was fed). Methane production was monitored daily by volume displacement, wherein the carbon dioxide present in the biogas was retained by the bubbling of the biogas in a solution of NaOH with alkaline pH, pH>9 (Cendales Ladino, 2011). The anaerobic co-digestion test in discontinuous regime was carried out monitoring six mixtures. Three of them had C/N 25 and differed between them by the content of grams of volatile solids (gVs); mixtures were tested with 0.5 gVs, 1 gVs and 2 gVs. The other three mixtures evaluated were set a C/N relation of 35 and the gVs content was varied at the same three levels (see Table 1).

Table 1: Description of mixtures used in co-digestion tests

	C/N	gVs
Mix 1	25	0.5
Mix 2	25	1
Mix 3	25	2
Mix 4	35	0.5
Mix 5	35	1
Mix 6	35	2

The relation of substrates was established in such a way that the C/N relation was reached and the amount of gVs were fixed taking into account the physicochemical characterization of the substrates used. The parameters analyzed for the substrates were the following: Total Solids (ST) according to 2540B from the Standard Methods (APHA), Volatile Solids (SV) according to D3174 from the American Society for Testing and Materials (ASTM), Chemical Oxygen Demand (COD) according to D1252 - 06 from the American Society for Testing and Materials (ASTM), And Kjeldahl Nitrogen (NTK) according to D1426-15 from the American Society for Testing and Materials (ASTM).

3. Results and Analysis of Results

Table 2 presents the main characteristics of the substrates, which facilitated the determination of the amounts of the same that were used on each individual and co-digestion test. The volatile solids and total solids allow to determine the amount of organic matter (OM) in the substrate since this is greater than 70%, it is possible to infer that there will be a good biological digestion in the initial stage of each test. Regarding nitrogen, it can be observed that most substrates have a low content of this, which in principle will benefit the system, since not having high concentrations of nitrogen this will not allow the process to be inhibited in the beginning due to the generation of free ammonia derived from the degradation of proteins (Fierro Fernández, 2014). The lowest concentration of this parameter is presented by the residues of the cocoa industry, and it could be thought that this would affect the balance and requirements of microorganisms during the digestion.

Table 2: Physicochemical characteristics of substrates

SUBSTRATES	PARAMETERS				
	TS (%)[b]	**VS (%)[b]**	**DQO (g/L) [a]**	**NTK (%)[a]**	**OM (%)**
Pig Manure	31.47	24.31	25.71	1.88	77.24
Cocoa Industry Residues	15.94	14.96	10.46	0.99	93.85
Municipal Solid Waste	22.76	21.24	13.73	1.56	93.32

a. Sample on dry basis / b. Sample on wet basis

The BPM for each substrate during the test is presented in Table 3. The pig manure presents the highest production of methane with 437.33 mL CH_4/gVs followed by the municipal solid waste whose production was 377.25 mL CH_4/gVs and finally the cocoa industry residues with a generation of 200.42 mL CH_4/gVs. The above mentioned residues possess different relations C/N being the highest one corresponding to the cocoa industry residues with 55, what implies that this one is rich in carbon and poor in nitrogen, which causes that the decomposition of materials occurs more slowly and therefore the multiplication and the development of bacteria is low by the lack of nitrogen, and this would prevent a rapid fermentation of the organic material and in turn, can present losses of carbon in the form of carbon dioxide (CO_2), for anaerobic digestion the bacteria use 25 to 35 times more carbon than nitrogen and the ratio of carbon to nitrogen should be 25-30:1 (Kondusamy et al., 2014), according to the above the substrate that has the closest proximity to this optimal relation is the pig manure with a C/N of 23.8, the excess of nitrogen can also cause problems due to the ammonium formation which affects the anaerobic process for residues with a high C/N proportion (Kondusamy et al., 2014).

Table 3: Methane production of the different substrates used in the test

SUBSTRATES	mL CH_4/gVs	C/N
Pig manure	437.33	23.8
Municipal solid waste	377.25	34.7
Cocoa industry residues	200.42	55

An important factor to take into account regarding the process of methane generation is the pretreatment that is done in the different substrates, in this investigation the reduction of the size of each residue was carried out, in some residues a reduction of the particle has been realized by low sizes to 5mm (Li et al., 2014), and in some cases only the reduction of the particle has been realized (Qiao W., 2011) without specifying the size that is reached with the reduction of the particle. A decrease in the particle will allow the large organic polymers (hydrocarbons, lipids, proteins) of the substrate to be easier to biodegrade by the microorganisms in the different stages of the anaerobic digestion especially in the hydrolytic stage because it is the one that limits the global speed of the process (Veeken et al., 1999). The treatment of the substrate by mechanical disintegration has positive effects on the anaerobic biodegradability of the substrate, the reason is the increase of the specific surface available in the medium (Kondusamy et al., 2014). As for municipal solid waste, these present during the test a production similar to that reported in the literature found for that residue, since the methane generation for the test was 377.25 mL CH_4/gVs, while the one consulted is around the 323 mL CH_4/gVs (Nielfa et al., 2015) and 343.7 mL CH_4/gVs (Browne J et al.,2014) respectively. As for the mixtures, there were evaluated 6 mixtures which show themselves in table 4.

Table 4: Methane production of the different mixtures evaluated in the test

MIXTURES	gVs	C/N	mL CH_4/gVs
Mix 1	0.5	25	2485.91
Mix 2	1	25	941.91
Mix 3	2	25	600.99
Mix 4	0.5	35	2189.24
Mix 5	1	35	1100.74
Mix 6	2	35	421.99

Each of the mixtures consists of inoculum, pig manure, municipal solid waste and cocoa industry residues. Regarding volatile solids, some studies indicate that the adequate proportion for optimum results is between 0.23 and 2.09 gVs (Nielfa A et al. 2014), in some cases, this value has been fixed in 2 gVs (Tuesorn S et al. 2013). As for the anaerobic digestion and specifically respect to C/N relation, the addition of a carbon-rich co-substrate to the sewage sludge which has a low C/N allows an optimal C/N (Wickham R et al.2016), the importance of an optimal C/N is that a low C/N relation generates toxicity problems in reactors (Fierro Fernández et al., 2014).

Figure 1, shows the methane production corresponding to each of the mixtures mentioned above being mixture 1 which present the best performance followed by the mixture 4, both mixtures correspond to 0.5 gVs with the difference that mixture 1 corresponds to C/N 25 and mixture 4 to C/N 35, the above demonstrates that as it was mentioned at the beginning an optimum C/N is one that is in the range of 20 to 30 for anaerobic systems. Additionally, the co-digestion process verifies that it is possible to reduce the deviation that is generated in the biogas production for each mixture compared to the yields of the individual substrates. This is related to the use of sewage sludge from a biodigestor as a support substrate and the continuous availability of metabolites that maintain the activity of the consortium.

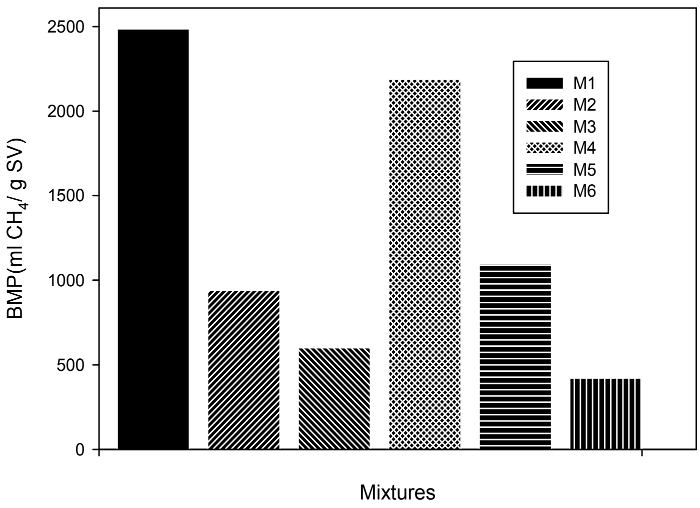

Figure 1: Biological potential of methane production of the six mixtures evaluated

Figure 2 compares the performance of mix 1 which has a BPM of 2485.91 mL CH_4/gVs which compared to the substrate of better performance which is the pig manure represents a performance 5.7 times greater, while the performance of mix 1 respect with the substrate of lower performance is 12.5 times greater, this increase in methane production suggests a better interaction between the mixture of the substrates, and can be explained by the macro and micronutrient content of pig manure and the municipal solid waste that support the process, including the damping system.

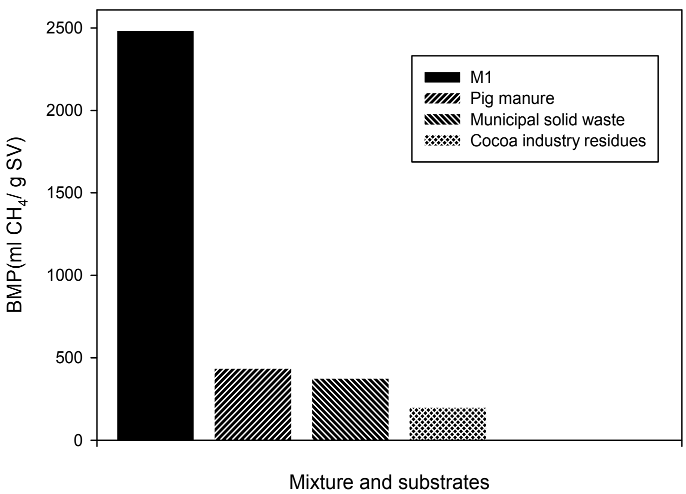

Figure 2: Biological potential of methane production of mixture 1 with respect to individual substrates.

4. Conclusions

The three residues evaluated (pig manure, cocoa industry residues and organic fraction of municipal solid waste) have the capacity to be used for the production of methane. In the BPM test, pig manure presented the highest methane production with 437.33 mL CH_4/gVs, followed by municipal solid waste with a generation of 377.25 mL CH_4/gVs. A pre-treatment to the anaerobic digestion benefits the system because it facilitates the degradation of macromolecules and increases the speed of the hydrolysis phase. The results of the anaerobic co-digestion test show that the best blend in terms of biogas production is mixture 1 with a C/N 25 relation and 0.5 gVs establishing an optimum performance condition. Mixture 1 had a methane production of 2485.91 mL CH_4/gVs. The results obtained in the different tests indicate that the application of this methodology allows the valuation of solid waste that is currently causing a negative environmental impact. The biogas potential found for the individual substrates and their corresponding mixtures is the first phase for the creation of empirical y models that facilitate the optimization of the anaerobic co-digestion process.

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