Biogas Production from Leather Industry Wastes

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Abstract

The main objective of the present study is to assess the potential of biogas production by various substrates containing collagen, including tannery wastes, in bench scale under controlled conditions. The collection of representative data about the biological degradation of leather industry waste through anaerobic pathway (in terms of generation capacity and gas composition) can be seen an important tool for the future development of technologies focused on maximum energy recovery from these wastes. The experiments started by the construction of sixteen bench bioreactors, with a volume of 300mL, containing gas sampling and gas volume measurement taps. In these bioreactors, the interesting substrates were isolated and inoculated with aerobic and anaerobic biological sludge from different wastewater treatment plants. The mole fractions of methane (CH_4), carbon dioxide (CO_2), nitrogen (N_2) and oxygen (O_2) in the generated gases inside the bioreactors were evaluated by gas chromatography, over a period of 20 and 120 days. The bench experiments show the previous adaptation of the *inocula* tested in the degradation of the collagen containing substrates. It was observed that the maximum rate of biogas generation occurs in periods less than 90 days reaching methane fraction (CH_4) higher than 90% by mass, and that an increase in chromium concentration in the substrate reduces the rate of biogas generation.

Keywords: leather waste, biogas, energy recovery; biodegradation of solid wastes.

1. Introduction

Environmental pollution is the main problem for the leather industry nowadays. The leather making process generates substantial quantities of solid and liquid wastes (hides and skins, fats, shavings and trimmings, buffing dust, process effluents, sludge). The most common way to manage solid wastes is by disposing of them on landfill sites (Yilmaz et al., 2007) where, according to Priebe *et al*. (2011), chrome shavings, wet-blue trimmings and sludge from tannery wastewater treatment plants can be degraded by microorganisms able to perform such degradation. Several analytical results of methane fractions observed in the exhausting gases were presented as evidence.

An alternative to landfilling is the controlled degradation of waste using microorganisms focused on the production of biogas. In the case of leather wastes, this is a not such a simple practice because these residues are essentially non-putrescible. Thus, prior practices, such as the preparation of the substrate and/or use of pre-adapted microorganisms (to leather

mineralization agents), must be studied. The use of these substrates, rich in carbonaceous matter, requires the establishment of efficient and economically viable biological degradation technologies. Zupancic and Jemec (2010) cited that the disposal of wastes generated in leather production is therefore a serious problem and the importance of technological measures to combat environmental challenges from leather processing is now increasingly recognized.

The study performed by Kolomaznik (2008) describes several developing technologies that aim to use and/or disposal of waste containing chromium. The difficulties associated with their processing are associated with the possibility of generating new waste containing Cr (VI). This contaminant has well-known systemic toxicity to the kidneys and when combined in the forms of calcium or magnesium chromate, it becomes a carcinogenic agent.

According to Dhayalan *et al*. (2007), it is important to set up a task force for developing a technology for the disposal of tanned leather solid waste. The current environmental regulations demand energy recovery from solid wastes, which consists of digesting solid wastes through anaerobic process to recover chemical energy and fuel energy. The two main advantages of this process are decontamination of waste by producing biogas and production of nutrient enriched effluents for agricultural purposes.

Gutterres *et al*. (2003) studied the various inputs employed by the leather industry during production processes. In terms of energy consumption in a finishing tannery, the total electrical and thermal portions, reveals a considerable demand for energy reaching values close to 0.37 $kW.m^{-2}.day^{-1}$.

Biogas is classified as a secondary energy source and defined as products that have been produced by transforming primary energy carriers into higher quality products by applying processes such as refining, fermentation, mechanical treatment, or burning in power stations. The medium characteristics of biogas are: 55 – 70% of methane (CH_4), 30 – 45% of carbon dioxide (CO_2) and traces of other gases. The energy content is 6.0 – 6.5 kWh m^{-3} and fuel equivalent 0.60 – 0.65 L $oil.m^{-3}$ of biogas (DEUBLEIN AND STEINHAUSER, 2008).

The analysis of such problems, from the environmental point of view (Priebe *et al*. 2012), is a reminder that the biogas is constituted by two of the main gaseous pollutants associated with the greenhouse effect. Methane is about twenty-one times more active in heat retention in comparison to carbon dioxide. Thus, the use of biogas energy proves energetically and environmentally interesting, both for power generation and reduction of environmental impact.

The mechanism of biogas formation occurs at four overlapping reaction stages named as hydrolysis, acidogenesis, acetogenesis and methanogenesis. According to Toerien (1970) and Chernicharo (1997), anaerobic degradation processes involve microbial communities from distinct physiological groups and characteristics that work as a consortia which are present in different groups of bacteria (facultative anaerobic, anaerobic and microaerophilic) and fungi. The major process and the last stage in biogas production through anaerobic decomposition of organic compounds is known as methanogenesis. There are two distinct routes whereby the methane is produced. These processes are determined by the type of methanogenic bacteria. Acetoclastic methanogenesis converts acetic acid to methane and carbon dioxide. This route accounts for approximately 60-70% of the methane formed during anaerobic degradation. The second route is the hydrogenotrophic methanogenesis that involves carbon dioxide and hydrogen to form methane and water.

Several studies were conducted aiming at the collection of data related to biodegradability of leather wastes and the potential for biogas generation by these materials. Such studies employ various sources of microorganisms, all of them using strictly anaerobic biota obtained from processes involving anaerobic treatment of tannery effluents or sewage. Cenni *et al*. (1982) made a short communication to draw attention to the potential for recovering energy from tannery wastes through anaerobic digestion; Lalitha *et al*. (1994) introduced the concept of interactive metabolic control in biomethanation of skin collagenous waste aiming the acceleration the maximal methane yield per gram of substrate; Covington and Yagoub (2006) studied the biodegradation of solid leather wastes comparing collagen tanned with chromium and mimosa extract in raw form and after heat denaturation; Dhayalan *et al*. (2007) presented a study in which biodegradability was explored by testing chrome tanned and vegetable tanned leather under anaerobic conditions. Two different sources of anaerobes were used and the effect of detanning was studied. Thangamani *et al*. (2010) conducted a study that proves that fleshing and primary sludge have a significant quantity of volatile solids capable of suffer biodegradation through anaerobic digestion; Zupancic and Jemec (2010) conducted tests of anaerobic digestion of fleshings , skin trimmings and wastewater in semi-continuous and sequencing batch reactors using mesophilic anaerobes from municipal sludge in the thermophilic zone; Kameswari *et al*. (2012) studied the co-digestion of leather wastes aiming to improve the processes of biogas generation by preparing the substrate with enzymes and optimization of the *inoculum*/substrate ratio. The maximum potential methane generation presented in the cited articles ranges between 41.25 and 648 mL of $CH4.g^{-1}$ crude waste.

The present study aims to present the results obtained in the test of different sources of microorganisms used *in natura*, i.e. without isolation, employed directly from the source. Tests were conducted with *microbiotas* (sludges) resulting from the anaerobic municipal sewage treatment plant (anaerobic digester), anaerobic wastewater treatment of a slaughterhouse (anaerobic pond) and the aerobic tannery treatment plant (activated sludge reactor). The performance evaluation of these *inocula* were based on pre-adaptation or ability of the microorganisms to digest/metabolize proteinaceous matter in the presence or absence of chromium.

The experiments aimed to evaluate the mixture of microorganisms originated from the aerobic sludge of a tannery treatment plant, which basically consists of a great number of aerobic bacteria, contains non-strict anaerobic microorganisms capable of generating methane. This choice is due to the lack of anaerobic wastewater treatment processes in southern Brazil (because it is difficult to maintain the temperature of the reactors especially in winter) that can provide microorganisms for the proposed tests. Furthermore, it can be a choice for implementing technologies for biogas generation in regions of low annual average temperature.

The evaluation was based on the volumes of biogas and the evolution of the concentration of methane in the biogas. The preliminary study of these behaviors is important for the future development of waste disposal technologies and treatment technologies for the leather chain as well to evaluate the possibility of energy recovery from these residues through cleaner technologies.

2. Material and Methods

2.1. Biogas Generation in Bench Scale Experiments

The evaluation of the potential for biogas generation by collagen materials, including chrome leather waste from tanneries, was conducted in three series of eight bench anaerobic bioreactors (hermetically sealed) with a useful volume of 350 mL. Such bioreactors were constructed in a cylindrical format so that they could be placed inside a thermostatic bath. These containers were made of glass; they contained one point for sampling the internal gases (septum) and a valve to perform the volume measurements of generated gases (Figure 1).

The experiments were conducted by filling the reactors with four different carbon sources: soybean meal, hydrolyzed collagen, Freiberg hide powder and wet-blue shavings (chrome shavings). These reactors were inoculated with the biological sludge and maintained in a thermostatic bath at 35ºC. The three biological sludges tested were collected in an anaerobic municipal sewage treatment plant (anaerobic digester), an anaerobic wastewater treatment of a slaughterhouse (anaerobic pond) and an aerobic tannery treatment plant (activated sludge reactor). The aerobic sludge was collected in a tannery that uses chromium salts as tanning agents. Table 1 presents the planning of these experiments using different carbon sources.

Table 1: Plan of experiments

Experiment Number (inoculum)	Carbon Source/Reactor				
	Blank	Soybean Meal	Hydrolyzed Collagen	Hide Powder	Chrome Shavings
Experiment 1 (activated sludge)	-	1 and 2	3 and 4	5 and 6	7 and 8
Experiment 2 (sewage sludge)	1 and 2	-	3 and 4	5 and 6	7 and 8
Experiment 3 (slaughterhouse sludge)	1 and 2	-	3 and 4	5 and 6	7 and 8

In order to ensure favorable conditions for the metabolism and growth of the microorganisms, a nutrient solution previously tested by Dettmer *et al*. (2012) was used. It consists of yeast extract, peptone, monobasic potassium phosphate and dibasic potassium phosphate.

All the experiments were performed as duplicates and daily measurements of produced biogas in each bioreactor were made until 30 days. After that, the measurements were performed at intervals of 3 to 4 days until generation ceased. The molar fractions of CH_4, CO_2, O_2 and N_2 were evaluated twice-weekly by gas chromatography. Table 3 lists the mass of each material added to the bioreactors.

The experiments employed four carbon sources as described above. Before starting the bench scale reactors, the weight of each carbon source were calculated using data from previous studies, as shown in Table 2. The materials employed - soybean meal, Freiberg hide powder (*Forschungsinstitut für Leder und Kunststoffbahnen gGmbh Freiberg - FILK*), hydrolyzed collagen (Protein Trading Co., Germany) and chrome shavings - were used and reported in other studies performed by Gutterres (2007, 2010) and Piccin *et al*. (2012).

Table 2. Characterization of the carbon sources employed in the experiments

Parameter	Soybean Meal*	Hydrolyzed Collagen**	Hide Powder***	Chrome Shavings****
Volatile Matter (%)	12.5	2 - 6	-	52.5
Protein Matter (%)	48	92 - 96	-	-
Total Ashes (%)	6	< 2.0	< 1.2	8.9

Source: *Brazilian Standard for Soybean Meal Type 1; **Gutterres, 2010; ***FILK; ****Piccin *et al*., 2012.

The concentrations in the nutrient solution were maintained constant and the mass of carbon sources was adjusted to keep protein concentration equal at all experiments based on Table 2. The mass of protein added was 5.3g.L^{-1} and the total organic load of the seeds (*inocula*) was 0.81, 1.05 and 1.67g for experiments I, II and III, respectively. The experiments were performed in dilute aqueous solution with a total volume of 275mL (250mL of nutrient solution and 25mL of *inoculum*).

Table 3: Components added to the bioreactors

Components	Blank		Soybean Meal		Hydrolyzed Collagen		Hide Powder		Chrome Shavings	
	Reactors									
	1*	2*	1**	2**	3	4	5	6	7	8
Carbon source (g)	0		3.5		1.7		1.63		1.7	
Sludge (*inoculum*) (mL)	25.0		25.0		25.0		25.0		25.0	
Yeast extract (g.L^{-1})	2.0		2.0		2.0		2.0		2.0	
Peptone (g.L^{-1})	1.0		1.0		1..0		1.0		1.0	
K_2HPO_4 (g.L^{-1})	7.0		7..0		7.0		7.0		7.0	
KH_2PO_4 (g.L^{-1})	3.0		3.0		3.0		3.0		3.0	

* Experiments II and III; Experiment I.

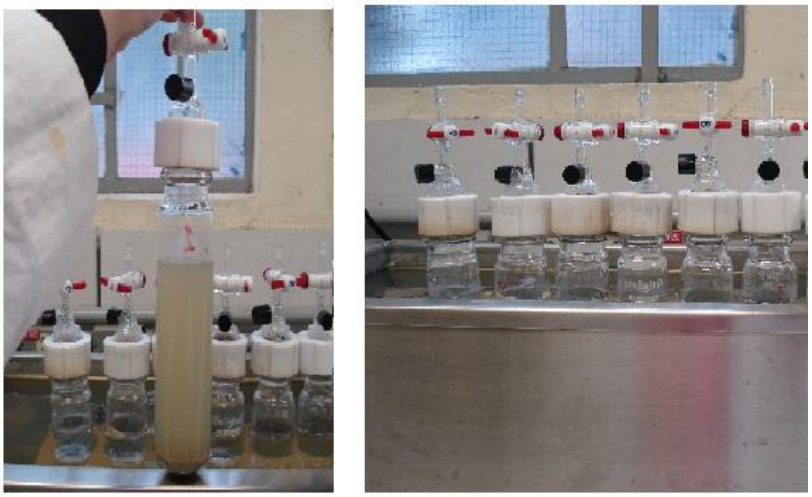

Figure 1: Bioreactor system

2.2. Volume Measures of Biogas

The volumes of biogas produced in the biological process were monitored by means of a water displacement method based on the Mariotte principle. The system constructed specifically for these purpose uses the volume of water displaced to quantify the volume of biogas generated. Figure 2 shows the equipment used in the volume measurements.

From the time of closing the reactors, the culture of microorganisms starts to consume the substrate producing gaseous products of its metabolism. This process increases the internal pressure of the reactors. When the reactor is connected to the Mariotte bottle, the overpressure is transferred to the Mariotte bottle and liquid contained within flask is displaced out. The measurement of the amount of fluid (mass) displaced allows us to calculate the volume of gases produced inside the reactors. To reduce the measurement error, the fluid consists of an aqueous solution with pH less than 3 so that the solubilization of biogas components (such as CO_2 and H_2S) is avoided. The gas volumes were determined from the mass of fluid displaced out using the specific gravity at room temperature.

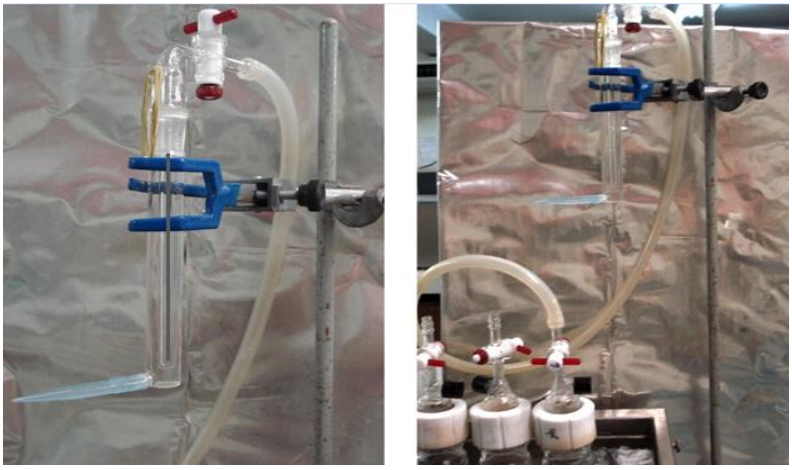

Figure 2. Bottle used in volume measurement of the generated biogas

2.3. Gas Chromatographic Analysis of Biogas

To determine air fraction (O2+N2), methane and carbon dioxide, the experiment used a gas chromatograph (GC) equipped with a thermal conductivity detector (TCD) and Porapak Q packed column (80-100 mesh). Helium was used as a carrier gas at 30 mL/min flow and the injector, oven and detector temperatures were held at 100, 60 and 100°C, respectively. To determine the proportions of oxygen and nitrogen in the air fraction (obtained in the Porapak Q column) a 13X Molecular Sieve (80-100mesh) packed column was employed, and the same detector (TCD) was used. Helium was used as the carrier gas at 20 mL/min flow and the injector, oven and detector temperatures were held at 80, 80 and 100°C. The equipment used was a gas chromatograph AutoSystem XL/GC, Perkin-Elmer, with interface command through the software Turbochrom 6.0. Development of the chromatographic conditions was based on the standard methods from ASTM and USEPA: ASTM D 1945-96, ASTM D 1946, USEPA Method 3A, Method 3C and Method 18.

The relative composition of gases present in the biogas samples was performed by area normalization and was expressed as molar fractions. Thermal response (TR) for gas

chromatographic analyses for each gas present in the biogas was obtained from the work performed by Dietz (1967) for thermal conductivity detectors (TCD). The areas obtained from the chromatograms in each column were divided by the thermal response to get the true areas of the interesting compounds. The true response values (true areas) give the mole percent of the components.

3. Results and Discussion

3.1. Characterization of Carbon Sources

The four carbon sources employed in the experiments of biological degradation intended for establishing the potential for biogas generation are listed in Table 4. These data were used to calculate the specific generation of biogas from each carbon source as described in Section 3.2. The samples were characterized by total ash content, volatile matter and protein matter and expressed on a wet basis.

Table 4. Analysis of the carbon sources employed in the experiments

Parameter	Soybean Meal	Hydrolyzed Collagen	Hide Powder	Chrome Shavings
Volatile Matter (%)	6.34	12.2	16.31	44.88
Total Ashes (%)	6.98	1.03	1.25	5.36
Organic Matter (%)	3.03	1.48	1.34	0.85

These results allow the establishment of the specific generation of biogas from each carbon source as described in Section 3.2. The deviations observed when comparing the results shown in Table 4 with those from Table 2, necessarily lead to use a different parameter to evaluate the biogas generation for each process condition. This parameter is the total amount of methane generated divided by the total organic mass of carbon source.

3.2. Biogas Generation by Different Materials

The first graph shows the results of daily readings of biogas generated in the experiment that aims to evaluate the performance of the aerobic sludge – Experiment I. The evaluation can be made in terms of the pre-adaptation to metabolize collagen substrates and the effect of chromium concentration over biogas production. Figure 3 shows the behavior curves of biogas production by plotting a graph of total accumulated volume *versus* time. The curves show the average volume produced by each pair of reactors that contains the same composition.

It can be observed that the three collagen substrates exhibited a very similar behavior. As expected, the hydrolyzed collagen led to the major production since the start of the experiment, followed by the other collagen materials. There is a clear decrease in total gas generation as a function of the presence and/or increase in chromium concentration. The smaller production observed for soybean meal substrate may be due to the fact that microorganisms are less adapted to metabolize vegetable proteins. Similarly, the major production associated with collagen protein may lie in the pre-adaptation of the *inoculum* to the substract (carbon source). Furthermore, hydrolyzed collagen presents the lowest chemical stability, leading to the best performance in terms of biogas generation between the collagen sources.

Another important observation is that the *inoculum* sampled in the tannery effluent treatment plant (activated sludge biological reactor) promotes the growth of facultative anaerobic microorganisms. This particular feature is due to dimensional characteristics of the equipment employed, which leads to longer periods of low oxygen concentration. These microorganisms are able to grow anaerobically, generating biogas with high methane fractions.

The production process of hide powder employs a minimum level of chromium in its chemical and biological stabilization. This characteristic makes it more chemically stable and not completely soluble, thus less degradable than hydrolyzed collagen, which explains the behavior observed. Chrome shavings showed the worst performance in terms of biogas generation, most likely associated with the stabilization degree as a result of the high concentration of chromium.

All the substrates presented the maximum rate of generation in periods of time less than 80 days, reaching percentages of methane in biogas over 80% molar. The volumes and times required for this *inoculum* to degrade collagen-containing substrates was positive. The behavior presented by soybean meal was somewhat unexpected because it was believed that this substrate must be fostered by its general characteristics of biodegradability.

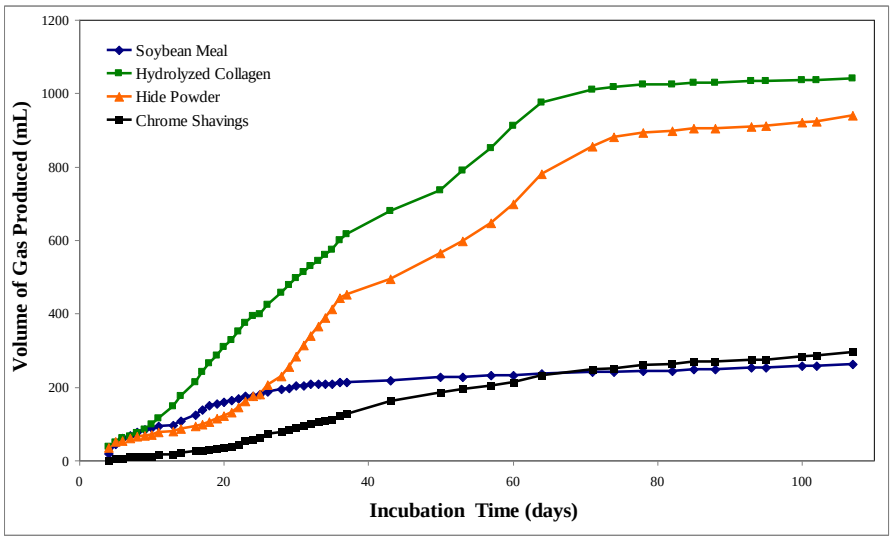

Figure 3. Characteristic curves of total gas production - Exp. I

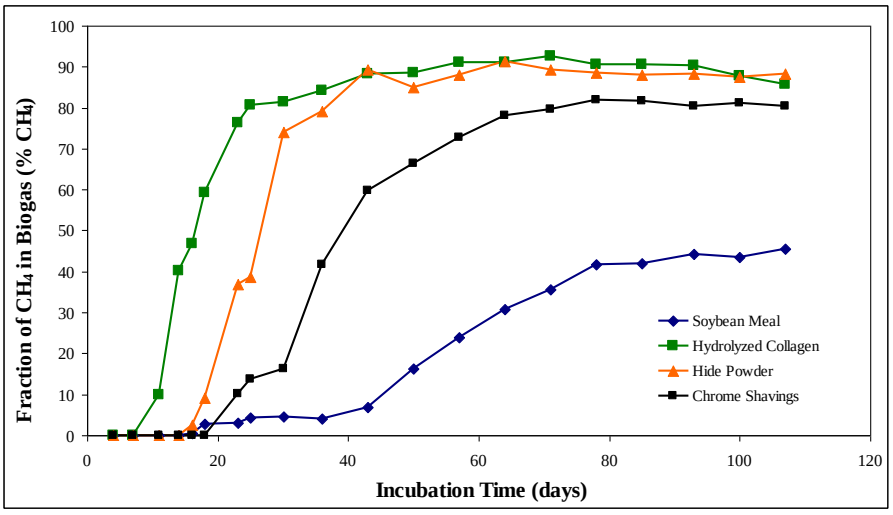

Figure 4. Evolution of methane fraction in biogas – Exp. I

Figures 5 and 6 show the generation profiles of biogas production in Experiment II, whose aim is to evaluate the performance of the slaughterhouse anaerobic sludge. This experiment reveals that the anaerobic microorganisms are able to metabolize the substrates much faster, reaching high volumes and methane fractions close to those observed in Experiment I.

As observed in Experiment I, the carbon sources containing chromium presented an inferior volume of generated biogas, probably caused by the increased stability of the carbon sources. Therefore, the increase of chromium concentration in the substrates reduced the production of biogas significantly.

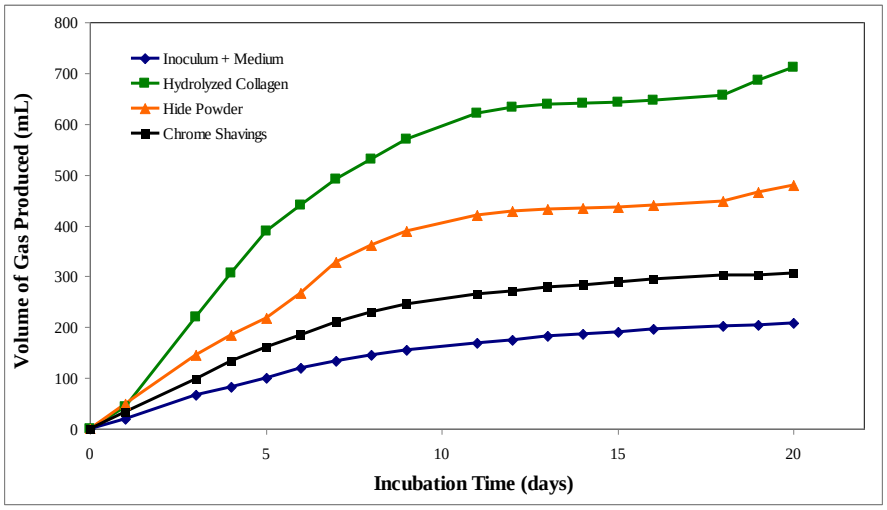

Figure 5. Characteristic curves of total gas production - Exp. II

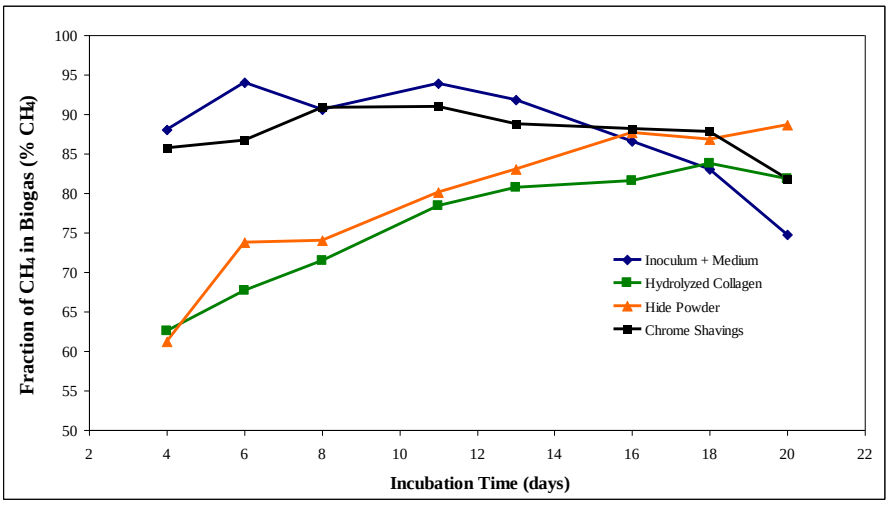

Figure 6. Evolution of methane fraction in biogas – Exp. II

The experiment, performed to evaluate the performance of the sewage anaerobic sludge (Experiment III), allows us to plot the graphs shown in Figures 7 and 8. This experiment presents generation profiles which reveal that these anaerobic microorganisms are fast as those found in slaughterhouse sludge, but their biogas generation was much lower. The generated volumes were near or below 20% of those observed in Experiment II, and the methane fractions in biogas were smaller than in the other two experiments. Again, the carbon sources containing chromium metal present an inferior volume of generated biogas. The small volumes of biogas generated in this experiment lead us to believe that the microorganisms lack pre-adaptation that enables them to metabolize collagen protein.

To compare the various degradation processes for each carbon source, the methane specific generation was calculated, as shown in Table 5. This parameter employs the total volume of methane produced as a function of the carbon source mass. The mass values relative to the culture medium and to the source of microorganisms (sludge) were not taken into consideration.

Table 5. Methane specific generation for each process condition

Carbon Source	Total Organic Mass (g)	Methane Specific Generation (mL CH_4/g)		
		Experiment I	Experiment II	Experiment III
Soybean Meal	3.03	1.72	-	-
Hydrolyzed Collagen	1.48	500.54	206.43	4.89
Hide Powder	1.34	488.33	117.15	3.29
Chrome Shavings	0.85	170.78	96.71	0.00

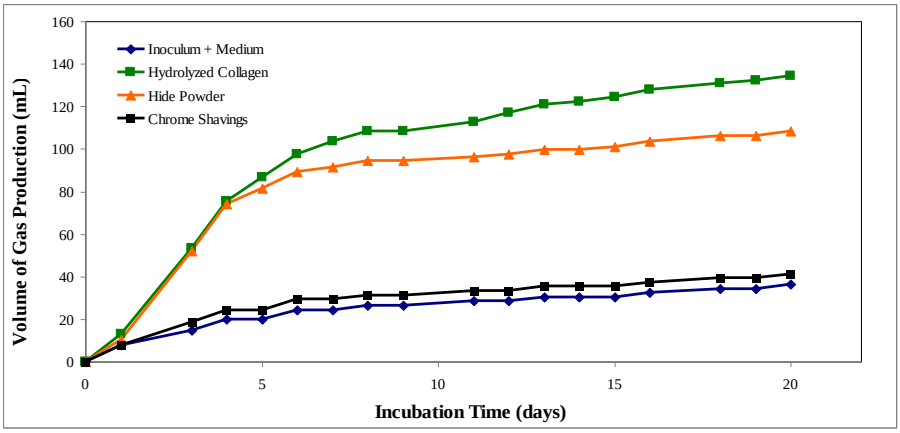

Figure 7. Characteristic curves of total gas production - Exp. III

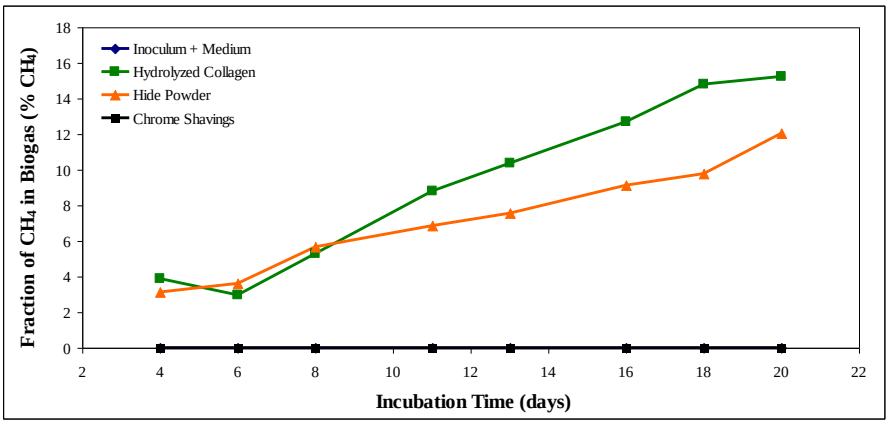

Figure 8. Evolution of methane fraction in biogas – Exp. III

The results found in Table 5 show that the microorganisms contained in the aerobic sludge (Experiment I) have greater ability to metabolize the substrates tested (except for soybean meal), followed by the anaerobic sludge collected in the slaughterhouse treatment plant (Experiment II). In these cases the biota was adapted to grow over substrates containing high fraction of collagenous protein. In the case of the microorganisms tested in Experiment III, the same is not true, as evidenced by the low production of biogas. Again, a direct relationship can be observed between chromium concentration and biogas production. This

negative influence is much worse in Experiment III, where methane production was null when chrome shavings were used as a carbon source.

Finally, it should be emphasized that the study involving a biota obtained from an aerobic process was necessary because of the technological state-of-the-art and the climatic characteristics of southern Brazil. The preliminary results point to the possibility of using non-strict anaerobic microorganisms to produce biogas. When pre-adapted, such organisms (although slower) may be an alternative for the biological degradation of leather wastes aiming at the production of biogas.

4. Conclusion

The results obtained and presented in this article show the performance of different cultures of microorganisms employed in biological degradation of leather wastes focused on biogas production. The results show the difficulty encountered by different biota to degrade chromium-containing wastes. It can be observed that some characteristics such as preadaptation to metabolize substrates containing collagen and to the presence of chromium must be taken into consideration when the focus is the optimization of biogas production.

Among the microorganism sources tested those sampled from effluent treatment processes containing protein materials showed larger capacities of biogas generation (all of them without prior isolation, used at raw state). The two different strict anaerobic biota tested were very efficient in terms of media adaptation and methane generation starting time but the volumes of generated methane were lower than expected.

The *inocula* tested which showed the best performance were sampled at the effluent treatment plant of the tannery and the slaughterhouse. They both showed typical features of the preadaptation to collagen-containing substrates. The tannery sludge studied proved to be better adapted to the presence of chromium.

5. Acknowledgements

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