Steam explosion utilization as pre-treatment of chrome leather waste in order to produce biogas

Laís Bavaresco[1], Daniele Perondi[2], Aline Dettmer[3]

[1]Energy and Bioprocess Laboratory, University of Caxias do Sul, Francisco Getúlio Vargas Street, 1130, Petrópolis, Caxias do Sul, RS, Brasil, ZIP CODE 95070-560, phone: +55 54 9144-2089, e-mail: lbavaresco@ucs.br

[2]Energy and Bioprocess Laboratory, University of Caxias do Sul, Francisco Getúlio Vargas Street, 1130, Petrópolis, Caxias do Sul, RS, Brasil, ZIP CODE 95070-560, phone: +55 54 9989-5200, e-mail: dani.perondi@gmail.com

[3]Energy and Bioprocess Laboratory, University of Caxias do Sul, Francisco Getúlio Vargas Street, 1130, Petrópolis, Caxias do Sul, RS, Brasil, ZIP CODE 95070560, phone: +55 54 9956-3724, e-mail: adettmer@ucs.br

Abstract

The leather processing generates considerable amounts of solid and liquid wastes. In the Brazilian leather industry, most of the chromium solid wastes (mainly consisting of pieces of chromed leather) are sent to landfills for hazardous industrial waste. Anaerobic digestion can be an alternative for managing these wastes. The main product of this process is biogas, a primary energy source. The use of pre-treatments, such as steam explosion, aims to disrupt the binding between the protein and the tanning agent. Combined with other pretreatments, such as chromium precipitation, is possible improve leather biodegradation. In this paper, chromium-tanned leather shavings underwent a steam explosion process. Different conditions of time and temperature for the pretreatment were evaluated by processing 200 g of the waste. The material obtained was subjected to anaerobic biodegradation with microorganisms for five weeks. During this period, the gases generated in the biodegradation were identified and quantified. By linking parameters such as organic carbon, chromium, total and volatile solids it was possible to identify the best pretreatment condition for a higher biogas production.

Keywords: leather, anaerobic digestion, biogas, steam explosion.

Introduction

Nowadays it is extremely relevant to establish sustainable conditions for industrial processes. Industry continuous growth has been generating an increased amount of wastes, which cause considerable environmental impacts. In terms of leather production, Brazilian industries have a large global market share; especially the ones in the state of Rio Grande do Sul, where tanneries and industries that employ leather as raw material are particularly important for the local economy.

Animal skin processing generates a great amount of liquid and solid waste. Solid waste management, especially management of chromium-tanned leather wastes, is a challenging problem faced by industries. The high amounts of solid wastes generated in leather industries do not usually result from the process inefficiency. They are a result of the inescapable need to remove constituents of the skin, which by its characteristics or defects cannot be part of the final product (Dhayalan et al. 2007; Figueiredo 2000).

In Brazil, most solid wastes containing chromium are sent to landfills for hazardous wastes. However, this solid waste management system becomes highly inactive, due to the non-biodegradability of tanned leather. There is still no effective way to use these materials so that they return to the manufacturing process, thereby generating a production cycle (Vaz et al. 2009). However, some studies report possible reuse of these materials (Dettmer et al 2010; Piccin et al 2013). Therefore, researches for treatment solutions for this waste are economically and environmentally important.

Approximately 90% of tanneries worldwide use chromium salts as tanning agent. The use of other tanning agents have not produced leather with the same good characteristics that chromium confers to the final product (smoothness, filling, strength, flexibility). Anaerobic digestion is an alternative for the management of chromium-tanned leather wastes. It is a natural process that occurs in the absence of molecular oxygen, where the bacterial populations interact closely to promote stable and self- regulated fermentation of organic matter (Christy, Gopinath, Divya 2014).

The biogas, a primary energy source, is formed from the degradation of organic matter and typically consists of 60% of methane, 35% of carbon dioxide and 5% of a mixture of gases such as hydrogen, nitrogen, hydrogen sulfide, carbon monoxide, ammonia, oxygen and volatile amines (Figueiredo 2011; Kipper 2013).

In order to increase the residue degradability, a pre-treatment process is necessary. Chromium-tanned leather waste is highly stable and a pre-treatment makes it more susceptible to degradation by microorganisms. The use of pre-treatments aims to solubilize and hydrolyze the material so that its degradability in the biological reactors is higher (Siddique, Munaim, Zularisam 2014). The pretreatment applied to leather wastes intended to achieve destabilization of the bonds between the tanning agent and the protein. It is believed that steam explosion reverses the tanning reaction and thus facilitates the degradation of the resulting proteins and/or amino acids.

Material and Methods

2.1. Materials used

For the experiments, it was used chromium-tanned leather shavings and hide powder as substrates. The first was provided by a local tannery and the latter was provided by the Laboratory for Leather and Environment (LACOURO, Porto Alegre, Brazil). The sludge from effluent treatment station (ETE) of the University of Caxias do Sul (UCS) was used as inoculum

2.2. Methods

2.2.1. Biogas Production

Leather wastes were subjected to pretreatment by steam explosion. The process was performed with about 200 g of leather waste at two different temperatures, 130 and 150°C, and two different retention times, 10 and 20 min, in duplicates. A new steam explosion was carried out on the same sample condition that generated more biogas. In this sample, chromium was precipitated. Precipitation was carried out first with concentrated sulfuric acid and then with the addition of sodium hydroxide 12 mol/L.

In order to evaluate biogas production, the samples were placed in glass vials. The inoculum was added to the samples in five additions of 2 mL each, containing microorganisms previously isolated (Silva, 2015). While the first addition was performed 24 h after the beginning of the test, the other additions were made every seven days. The vials were placed in a thermostatic bath at 35°C. Tests were performed in duplicate. Table 1 presents the list of samples used in the tests.

The determination of the test time was made through measurement of the gas generated, so when there was no more generation of gas, the samples were removed from the thermostatic bath. The volume of biogas produced was determined through the displacement of a water column.

Table 1- Testing biogas generation

Sample	Composition	Volumeofwaste
AA	Leather waste (pretreatment: 150°C/20 minutes)	50 mL of leather + 20 mL of sludge
AB	Leather waste(pretreatment: 130°C/20 minutes)	50 mL of leather + 20 mL of sludge
AC	Leather waste(pretreatment: 150°C/10 minutes)	50 mL of leather + 20 mL of sludge
AD	Leather waste(pretreatment: 130°C/10 minutes)	50 mL of leather + 20 mL of sludge
AP	Leather hide poder	3 grams hide powder + 20 mL of sludge
AL	Sludge UCS	20 mL of sludge
AE	Leather waste (pretreatment: 150°C/20minutes + chrome precipitation)	50 mL of leather + 20 mL of sludge

The analysis of the molar fraction of gas generated in the anaerobic digestion was conducted with a gas chromatograph (DaniGC). Nitrogen was chosen as carrier gas due to the analytes to be measured. A Thermal Conductivity Detector (TCD) and a capillary column Supelco CarboxenTM 1006 (30m × 0,53mm) were also employed for the tests. The compounds analyzed were carbon dioxide, methane and hydrogen. The molar concentration of the compounds in the sample was determined using response factors (DIETZ 1967).

1.1.1. Characterization of samples

Leather wastes were characterized before and after the steam explosion. The samples obtained after the anaerobic digestion process were also characterized. Total dissolved solids, fixed dissolved and volatile dissolved solids were determined according to NBR 14550, ABNT (2000). Carbon or organic matter present in a sample can be determined by gravimetric method or mass loss on ignition. The determination of humidity percentage for leather waste followed an adapted method based on standard D3790-79, American Society for Testing and Materials (ASTM 2012). The determination of chromium oxide in leather was based on the standard ASTM D2807-93 (2009) using the perchloric acid method.

2 – Results and discussion

2.1. Characterization of the materials used

Table 2 presents the results obtained for humidity, total, fixed and volatile solids and total chromium. Some differences are found when comparing literature results for raw material characterization and the ones obtained in this study. This can be explained by the different ways of processing hides, different types of chemicals and their respective concentrations and different steps of processing in which the material was collected.

Table 2 – Characterization of leather, hide powder and sludge used in this work.

Parameter	Leather	Hide powder	Sludge1	Sludge2
Humidity (%)	45,48	16,76	-	-
Total solids (%)	54,52	83,24	1,84	2,39
Fixed solids(%)	3,97	0,62	0,80	1,06
Volatile solids (%)	50,55	82,62	1,04	1,33
Total chromium*(%)	4,02	0,53	-	-

*Results reported on a dry basis.

1.1. Measured gas volume

The volume of biogas was measured daily to obtain a total volume of accumulated biogas per gram of solid (ml of biogas/g of solid). Results are presented on Figure 1.

As can be seen in Figure 1, the largest volumes were generated in samples AP, AL and AE, (20.22 mL, 38.00 mL and 16.90 mL respectively), while for the other samples the volume was lower. There was a higher biogas generation in samples with lower chromium content, as the hide powder and sludge. It confirms the toxicity of this compound to the microorganisms responsible for anaerobic digestion.

The hide powder production process employs a minimum level of chromium for its chemical stabilization. This characteristic makes it chemically and biologically less stable when compared to chromium-tanned leather shavings. Therefore, hide powder is more susceptible to biodegradation.

This is evident in Figure 1, where it can be clearly noticed that the hide powder sample generated higher volumes of biogas when compared to the leather waste samples. The pretreatment conducted in the samples only broke the bonds between the tanning agent and the protein, but kept chromium in the solution.

Other authors compared biogas obtained from chromium-tanned leather shavings and hide powder. In all studies, hide powder samples generated higher volume of biogas. (Covington, Paul and Yagoub, 2003; Priebe 2014; Dhayalan et al., 2007).

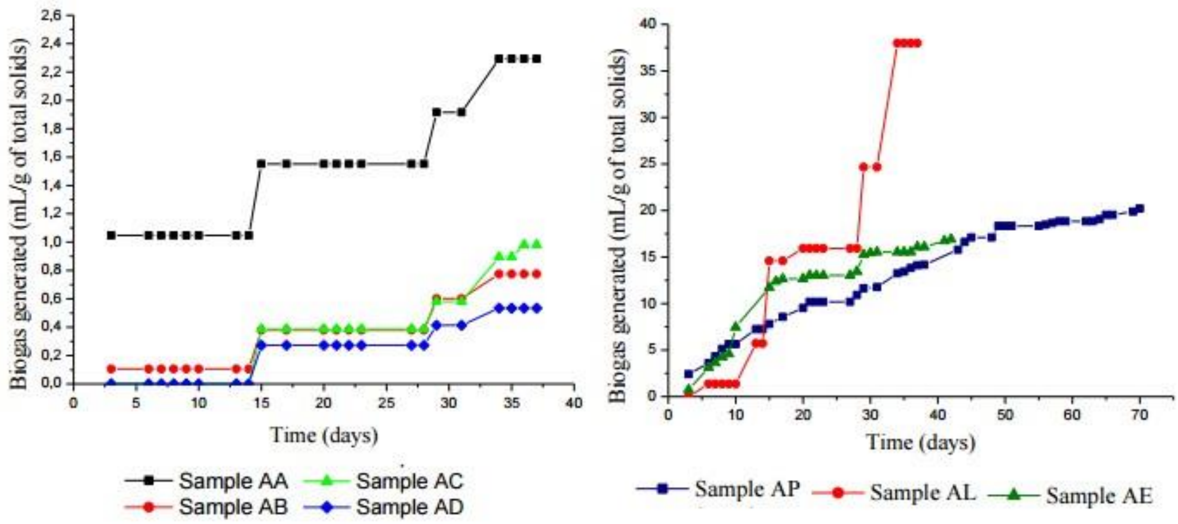
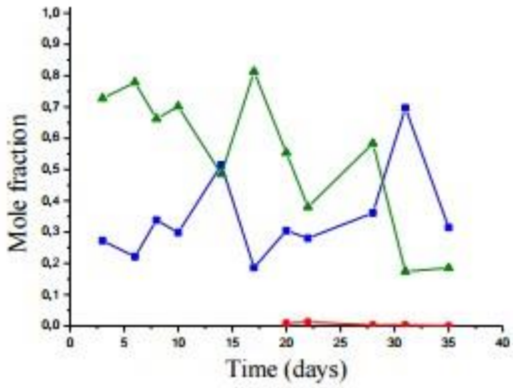


Figure 1 - Biogas volume

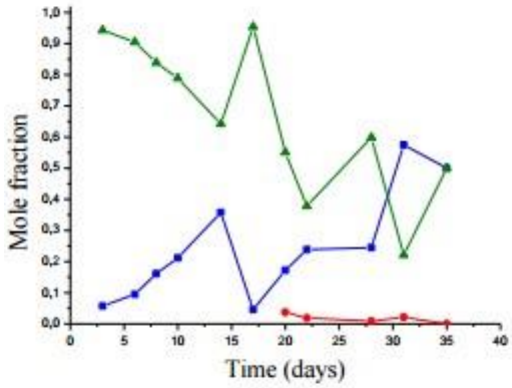
In samples where the chromium precipitation was carried out, the volume of biogas produced was higher when compared to the samples where there was chromium in higher concentration (without precipitation). Still, it was expected a higher biogas volume, similar to the volume produced from hide powder, which was not found.

This fact can be explained by the very high pH variations during chromium precipitation process, from pH 1 to 9. It may have led to protein denaturation or changes in the structure of other essential compounds for microorganisms. It can also be inferred that the pH variations can generate toxic compounds for the added microorganisms.

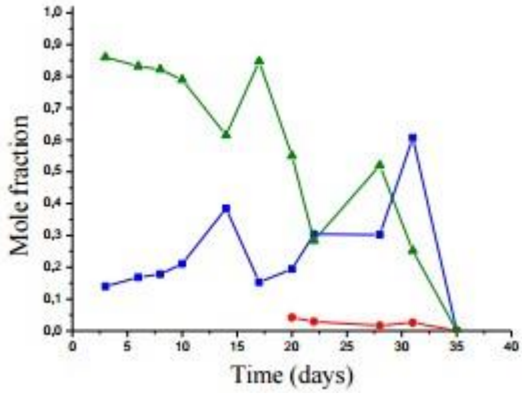
A) Mole fraction of the gas generated from the sample AA



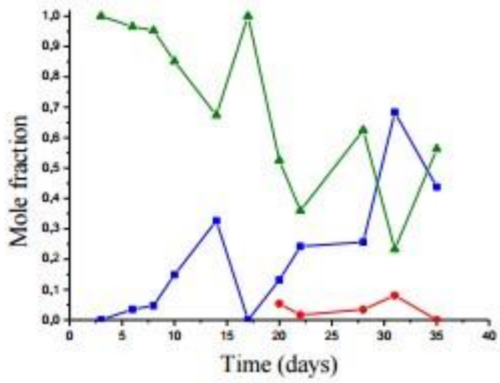
B) Mole fraction of the gas generated from the sample AB



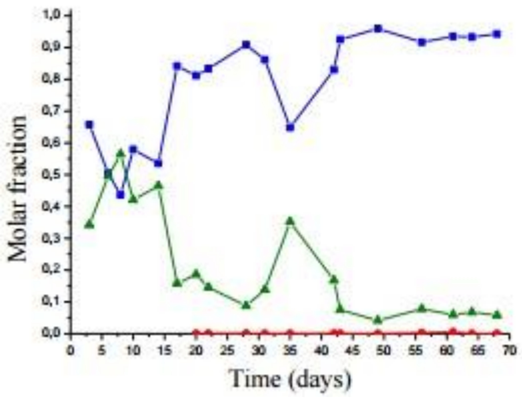
C) Mole fraction of the gas generated from the sample AC



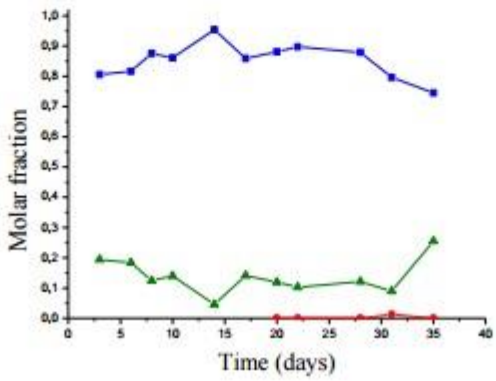
D) Mole fraction of the gas generated from the sample AD



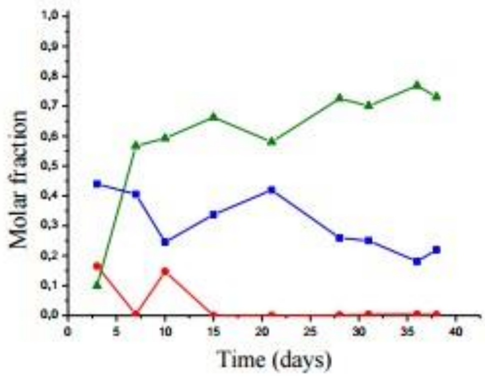
E) Mole fraction of the gas generated from the sample AP



F) Mole fraction of the gas generated from the sample AL



G) Mole fraction of the gas generated from the sample AE



Methane Hidrogen Carbon dioxide

Figure 2 - Mole fraction of gas generated in the different samples

The predominant compound in gas produced from chromium-tanned leather waste samples subjected to steam explosion was carbon dioxide. However, in all tests the concentration of methane reached values of about 50%. After the thirtieth day of tests, methane became the predominant molar fraction for some samples. This can be attributed to the added microorganisms, they may contribute to hydrolyzes and to enzymes production, which improve anaerobic digestion process.

The experiments conducted with hide powder and sludge from UCS' ETE showed high molar fraction of methane, thus presenting the mole fraction that best characterizes biogas, since it may contain up to 85% of methane. The leather wastes pretreated and subjected to chromium precipitation had greater volume of gas and methane fraction, up to 45%. In the sludge of UCS' ETE, methane fraction was 90%.

3 – Conclusion

Steam explosion as a pretreatment for the anaerobic digestion of chromium-tanned leather shavings proved to be a promising alternative for increased generation of biogas from these residues. The optimum condition of pretreatment, the one that generated the highest volume of biogas, is the temperature of 150°C and time of 20 min.

Hide powder samples generated higher gas volume, about 20.22 mL of biogas/g of total solids, when compared to samples of chromium-tanned leather shavings without precipitation. It happens due to the reduced chromium content present in this residue, showing the toxicity of this compound to microorganisms and how important it is to remove chromium before the anaerobic digestion process.Samples in which chromium was precipitated before the anaerobic degradation formed higher gas volumes, approximately 16.90 ml of biogas/g total solids, compared to samples where the chromium had not been precipitated, in which the volume of biogas varied from 0.53 to 2.29 ml of biogas/g of total solids. There was also an increase in the molar fraction of methane in the samples where chromium was not precipitated.

Carbon dioxide is the predominant mole fraction of the gases generated in the anaerobic digestion for both the samples that the chromium was precipitated and the samples that it remained in solution. The experiments with hide powder and sludge from UCS' ETE showed high molar fraction of methane, thus presenting the mole fraction that best characterizes biogas, since it may contain up to 85% of methane. Chromium-tanned leather shavings pretreated and subjected to chromium precipitation

generated greater volume of gas and methane fraction of up to 45%. In the gas produced from the sludge of UCS' ETE, methane fraction was 90%.

4 – Acknowledgements

The authors acknowledge the National Council for Scientific and Technological Development (CNPq), the Foundation for the Rio Grande do Sul State Research (FAPERGS) and the University of Caxias do Sul (UCS) for financially supporting this study.

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