

Different pre-treatments of chrome tanned leather waste and their use in the biogas production

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Abstract

Leather industry has undeniable economic and environmental importance converting by-products of the meat industry in value-added products. However, leather production generates huge amount of solid wastes. Usually, tanning process is done with chromium salts. Consequently a substantial part of the wastes are chromium tanned leather shavings (CTLW), which are mostly disposed of through landfill or incinerated. CTLW are collagen residues produced in tanneries which are very stable towards temperature and enzymatic degradation thanks to natural cross-links in the collagen structure and chemical cross-links between collagen fibers formed in the tanning step. As collagen is organic matter it can be considered for biogas production through anaerobic digestion but to ease enzymatic degradation and produce biogas a previous denaturation of the structure has to be carried out.

The goal of this study is to accelerate and improve biogas production when using CTLW. Autoclaving, extrusion, and hydrothermal treatment were performed as pre-treatments of the wastes. The pre-treated samples were analyzed regarding their degradation degree. Results showed that the pre-treatments accomplish to degrade the structure. Those that underwent autoclave treatment (120°C) show more than 90% enzymatic degradation after 192 minutes of pre-treatment. Results for the extruded samples vary with operation conditions, and it was possible to reach 35% of degradation

at 170 °C. The hydrothermally treated sample at 170 °C reached 90% of degradation. The untreated CTLW was only 6% degraded. During biogas production pre-treated samples were able to start production approximately five days before the untreated sample and presented higher biogas yield.

Keywords: Leather wastes, Biogas, Collagen

1. Introduction

1.1. Chromium tanned leather wastes and their disposal

In 2014, the manufacture of leather and related products in the European Union generated EUR 54 billion in turnover and employed 447.535 people (GROW 2016) highlighting the importance of the leather industry in this region. This industry also has an important environmental role, since its main raw material (hides) is a by-product of the meat industry.

Europe alone is responsible for the largest part of the global leather production, around 25%, generating about 170,000 ton of tanned leather wastes annually (Dahalayan et al. 2007). As the chromium-based tanning process is predominantly followed worldwide (Agrawal et al. 2006) most of these wastes will contain Cr³⁺ and need special handling. Currently, in most cases the chromium tanned leather wastes are disposed of through landfill or incineration processes, despite the ecological

consequences (Pati et al. 2014). In disposal sites the leaching of Cr³⁺ from wastes can pollute groundwater. The incineration at elevated pH (9-10), in the presence of an excess of oxygen, can lead to conversion of Cr³⁺ to Cr⁶⁺, which is a well known carcinogen (IULTCS 2008; Kolomaznik et al. 2008).

Increased environmental restrictions and escalating landfill costs have encouraged the leather industry to develop cleaner technology by minimizing wastes generated and maximizing those reused (Mu et al. 2003). Attempts have been made to replace the chromium in the tanning process but the obtained results cannot reach the quality of the chromium tanned leather. An option would be using vegetable agents in the tannery process, but those tanning agents cannot be considered more environmentally friendly than chrome tanning, due to the high waste water load and low treatability in conventional systems (IULTCS 2008). Therefore, the leather industry continues to face the handling and disposal problems of CTLW.

1.2. Alternative management of CTLW

Among the methods of reutilization of CTLW the biogas production through its anaerobic digestion stands out due to its ability to reduce the final amount of wastes and generate renewable energy simultaneously, low level of process complexity and low cost. Until present few studies about this subject have been published. They demonstrate that it is possible to produce biogas from CTLW but, due to very long times needed for the digestion, this method must be further developed to reach industrial feasibility.

The process is nothing more than anaerobic digestion of organic matter, a quite complex microbial process that takes place in the absence of oxygen with many types of strictly and facultative anaerobic bacteria (Murphy and Thamsiriroj 2013; Deublein and Steinhauser 2008). Biogas is the final product, which is a mixture of methane (55-70%) and carbon dioxide (30-45%) with traces of other gases (Deublein and Steinhauser, 2008). Mata-Alvarez et al. (2014) examined the papers about anaerobic digestion published between

2010 and 2013 and concluded that the most frequent main substrates studied are animal manures (54%), sewage sludge (22%) and the organic fraction of municipal solid waste (11%). At the same time, the most used co-substrates are industrial waste (41%), agricultural waste (23%) and municipal waste (20%).

As CTLW are considered complex wastes due their high chromium content, most of the biogas production papers analyzing the digestion of tannery wastes focus their efforts in the digestion of fleshings (Shanmugam and Horan 2009), sludge from the wastewater treatment (Kameswari et al. 2014a), wastewater (Banu and Kaliappan 2007), or the co-digestion of two of them (Zupancic and Jemec 2009; Thangamani et al. 2010 and 2015; Kameswari et al. 2011; 2012; 2014b and 2015; Ravindranath et al. 2015).

Tanned leather wastes are composed of organic matter, hence they can be used as raw material to produce biogas, even though leather itself is slowly biodegradable. The treatment to which hides undergo to produce leather with different chemicals (tanning process) makes them even more stable. This approach would become more feasible if a simple method to reverse the effects of tanning could be developed (Covington 2009).

More recently the investigation of CTLW's anaerobic digestion has started. Dhayalan et al. (2007) and Ferreira et al. (2010) studied the anaerobic digestion of CTLW. The former concluded that the degradation of this waste is possible using anaerobic sludge and it is better than vegetable tanned leather waste and the latter that the results are dependent on the anaerobic sludge concentration. Agustini et al. (2015) also studied the degradation of CTLW and detected 45% of methane in the produced biogas. In all cases, the experiments lasted one to four months, a time considered too long for industrial purposes.

Due to these difficulties there are currently no biogas plants in the industry using CTLW as main substrate. However, the tannery SÜDLEDER (Rehau, Germany) already has a biogas plant in operation using their own tanning wastes (hair, protein, fat, and waste water) to produce energy

(Schuberth-Roth 2013). This kind of initiative illustrates the interest of the industry in biogas production, nevertheless the use of a substrate as complex as CTLW needs to be further developed.

Chrome tanned leather is a collagen fibrous material. Hence to understand leather it is important to begin by understanding the structure of collagen, which is among the most common fibrous proteins and it is present in tendons, ligaments, bones, dentin, skin, arteries, cartilage, and in most of the extracellular matrix in general (Fratzl 2008).

1.3. Collagen structure

At present over 50 collagens and collagen-like proteins are known, type I collagen being the most common protein in mammals (Hulmes 2008). These molecules are assembled in different fibrous structures with quite different properties, such as elastic skin, soft cartilage, and stiff bone and tendon (Fratzl 2008). What all the collagen molecules have in common is that they are composed of three polypeptide chains forming a triple helix arrangement. Each of the chains contains one or more regions characterized by the repeating amino acid motif (Gly-X-Y), where X and Y can be any amino acid (Hulmes 2008).

Several collagen molecules are stabilized by the development of molecular cross-links between them forming the fibrils and, subsequently, different kinds of tissues (Wess 2008). The resulting high mechanical strength and resistance to heat and bacterial degradation of collagen fibers motivated their use in the leather industry. Despite the natural collagen features there is a need to further stabilize collagen fibers by chemical cross-linking increasing their mechanical strength, their denaturation temperature, and susceptibility to enzymatic degradation (Avery and Bailey 2008). This chemical cross-linking process applied to hides is known as the leather manufacturing process.

As mentioned above, collagen molecules are not susceptible to degradation by enzymes because of their stable structure, and the tanning process increases this stability. The anaerobic digestion is based on this kind of degradation, hence this characteristic would

preclude the digestion. To enable the process it is necessary to perform a prior degradation of the structure, which is normally accomplished increasing the temperature up to the denaturation temperature. Denaturation of collagen happens when this material is exposed to the denaturation temperature or higher. In this process the collagen structure collapses into gelatin chains (Avery and Bailey 2008). The random structure of gelatin loses the former high stability and can be easily degraded. However, CTLW has a denaturation temperature between 110 °C and 120 °C, which requires a denaturation process at these temperatures. After such treatment the chrome tanned collagen is as degradable as the raw collagen, and the denatured collagen behaves just like any other protein, but containing some inert Cr³⁺ (Covington 2009).

1.4. Objectives

The aim of this study is to accelerate and improve the biogas production process through anaerobic digestion of chromium tanned leather shavings (CTLW) enabling its application in the industry. For this purpose, CTLW underwent pre-treatment with different heating and mechanical technologies. The modifications caused in the collagen structure of this waste were evaluated with different methods, and some of the pre-treated samples were tested for biogas production.

2. Material and Methods

This study was developed in three different steps. At first, CTLW underwent pre-treatment to initiate material degradation. Thereafter, the pre-treated samples were assessed regarding their degree of degradation with different methods. Finally, the biogas building potential of some selected samples was investigated through biogas production trials in order to prove the feasibility of this method.

2.1. Material

Chromium tanned leather shavings (CTLW) samples from the shaving operation of the leather-making process were obtained from a local tannery and characterized regarding their volatile matter (DIN EN ISO 4684:2005

– Leather – Chemical tests – Determination of volatile matter), ashes (DIN EN ISO 4047:1998 Leather - Determination of sulphated total ash and sulphated water-insoluble ash), and chromic oxide content (DIN EN ISO 5398-1:2007 - Leather - Chemical determination of chromic oxide content). The results for the CTLW characterization are shown in Table 1.

Table 1: Leather shavings characterizations.

CTLW	
Volatile Matter (%)	20.9 ± 0.18
Ashes (%)*	11.0 ± 0.01
Chromium (%)*	4.4 ± 0.05

*Dry basis; mean ± standard deviation, n = 3

2.2. Pre-treatments

In order to denature the CTLW and favor the waste degradation and biogas production different heat and mechanical pre-treatment techniques were tested.

2.2.1. Autoclave

In order to reproduce the autoclaving conditions (high temperature and pressure) the trials were carried out using screw cap micro tubes tightly closed through O-ring sealing and a block heater (Stuart SBH130D) at 120 °C.

The CTLW were prior moistened with distilled water until saturation and left overnight at room temperature. This procedure is carried out in order to favor collagen denaturation, the main aim of this pre-treatment. All the samples were placed in the micro tubes, tightly closed, and subsequently placed in the block heater at 120 °C. The micro tubes were preheated for 3 minutes and 30 seconds, the estimated time necessary for the samples to reach the autoclaving temperature. Each sample was exposed to the autoclaving conditions for a predetermined time (3 to 384 minutes). Thereafter the samples were dried in a drying oven at 30 °C for one day.

2.2.2. Extrusion

Extrusion was performed with a co-rotating twin-screw-extruder Werner & Pfleiderer ZSK 25 at different temperatures (100 °C, 130 °C, 150 °C, and 170 °C) and humidity conditions (dry or wet) in a continuous

process. The wet CTLW were prior moistened with water, well homogenized and left overnight. The dry samples were handled without any humidification process, exactly as delivered from the tannery. This process starts by feeding CTLW from a hopper into the barrel of the extruder. Subsequently the material is gradually degraded by mechanical energy generated by turning screws and by heaters arranged along the barrel, taking approximately 3 minutes.

Samples originated from dry and wet CTLW differ in appearance. The extrusion of dry CTLW resulted in samples with granular appearance, on the other hand the wet CTLW gave rise to a powder sample.

2.2.3. Hydrothermal treatment

CTLW were subjected to hydrothermal treatment through a continuous autoclave system attached to a refiner (ANDRITZ) at different temperature and pressure conditions. The temperature was adjusted regarding the saturated steam relative pressure. However, due to technical reasons the temperature was not as exact as expected (140 °C, 150 °C, and 170 °C). The pre-treatment time was approximately 45 seconds.

2.3. Assessment of the pre-treated samples

The susceptibility to anaerobic degradation of the pre-treated samples and the leather shavings were evaluated with two methods. The enthalpy measured with the DSC (differential scanning calorimetry) method represents the enthalpy of the denaturation process. In other words, the necessary energy to break down the hydrogen bonds that stabilize the triple helix. The degradation by trypsin breaks down covalent bonds between carbon atoms, a process similar to the actual enzymatic digestion.

2.3.1. DSC

Thermal profiles of the pre-treated samples were taken from 0 to 130 °C using DSC (DSC 1 STAR[®] System Mettler Toledo) to assess thermal changes as a function of input temperature. pH was previously adjusted to 7 washing the samples with a KH₂PO₄/K₂HPO₄ buffer solution.

2.3.2. Degradation by trypsin

The denaturation degree of the pre-treated samples was measured with the aid of trypsin, an enzyme that acts to degrade protein. This enzyme test is based on the measurement of the degradation speed of heat treated leather. As the not denatured collagen is stable against enzyme degradation it is possible to determine the fraction of the samples which was denatured in the pre-treatment. The samples are placed in safe-lock microcentrifuge tubes with buffer solution and left overnight. Then the trypsin solution (1382 U/mL) was added at 37 °C (block heater Stuart SBH130D) during 5 hours. The degradation degree by trypsin at certain time (DD_t) is the portion of the sample that solubilizes in water after treatment with trypsin and it is represented by Equation 1:

$$DD_t = 100 - \left(\frac{w_f}{w_0}, 100 \right) \% \quad \text{Eq. (1)}$$

Where w_0 (mg) is the onset weight of the CTLW samples and w_f (mg) is the weight after the predefined treatment time, both weights were considered on a dry basis.

2.4. Biogas Production

Anaerobic digestion experiments were performed under mesophilic conditions (37 °C ± 2 °C) according to VDI 4630 (2006) in triplicate. The tests were conducted using 65 ml reactor flasks in two batches, with agitation (shaking water bath julabo SW-20C at 150 rpm) and without agitation (drying unit Fratelli Carlessi ARMADIO 5B). The gas production was monitored on a daily basis with a digital manometer (Leo 3 Keller). The mesophilic anaerobic inoculum was anaerobic sludge from the local sewage treatment plant. Biogas production is given in norm liters (273 K and 1013 hPa) per kg of organic dry matter ($I_N \cdot \text{kg}_{\text{ODM}}$).

At the end of the process the resulting biomass was analyzed regarding its pH, volatile matter (DIN EN ISO 4684:2005), ashes (DIN EN ISO 4047:1998), and chromic oxide content (DIN EN ISO 5398- 1:2007). The results were useful to develop the mass balance necessary to understand the ongoing processes in the biogas production and the actual final degradation of the substrates.

3. Results and Discussion

3.1. Assessment of the pre-treated samples

Based on analysis of DSC and degradation by trypsin results (Figure 1) it is possible to conclude that the pre-treatments accomplished to degrade the triple helical structure of the samples. In all cases the degradation by trypsin is more sensitive to evaluate the susceptibility of the pre-treated samples to enzymatic degradation than DSC. The good results presented by the pre-treated samples even with more than 4% chromium content indicate that chromium in this quantity is not toxic for trypsin, which implies that the waste will probably not be toxic for the enzymes in the anaerobic digestion.

The autoclaved samples (Figure 1.a) even with short pre-treatment times presented high degradation. After only three minutes of thermal pre-treatment the degradation of the wastes went from 6.7% to 25.8% and within only 24 minutes it was possible to have more than 50% of degradation reaching more than 90% after 192 minutes. After 192 minutes of heat treatment the degradation reaches a plateau and any longer autoclaving process would not be worthwhile.

Figure 1.b shows that with extrusion it is possible to increase the degradation degree by trypsin of the untreated sample from 6.7% up to 35.2% at the highest tested temperature. Results showed an increasing tendency of degradation with increasing extrusion temperature. The previously moistened extruded samples obtained slightly higher degradation levels. Nevertheless, it is still preferable to perform the process of humidification of the samples before the extrusion due to the ease of handling with granular samples instead of powder.

The hydrothermally treated samples showed a linear growth trend with the temperature. The sample pre-treated at 170 °C reached a degradation by trypsin of 90% (Figure 1.c). The samples also differed in appearance. The sample pre-treated at 170 °C, which reached the highest degradation degree, had its collagen structure affected by the high temperature turning completely into gelatin. Samples pre-treated at 150 °C and 140 °C are very similar, with a doughy appearance.

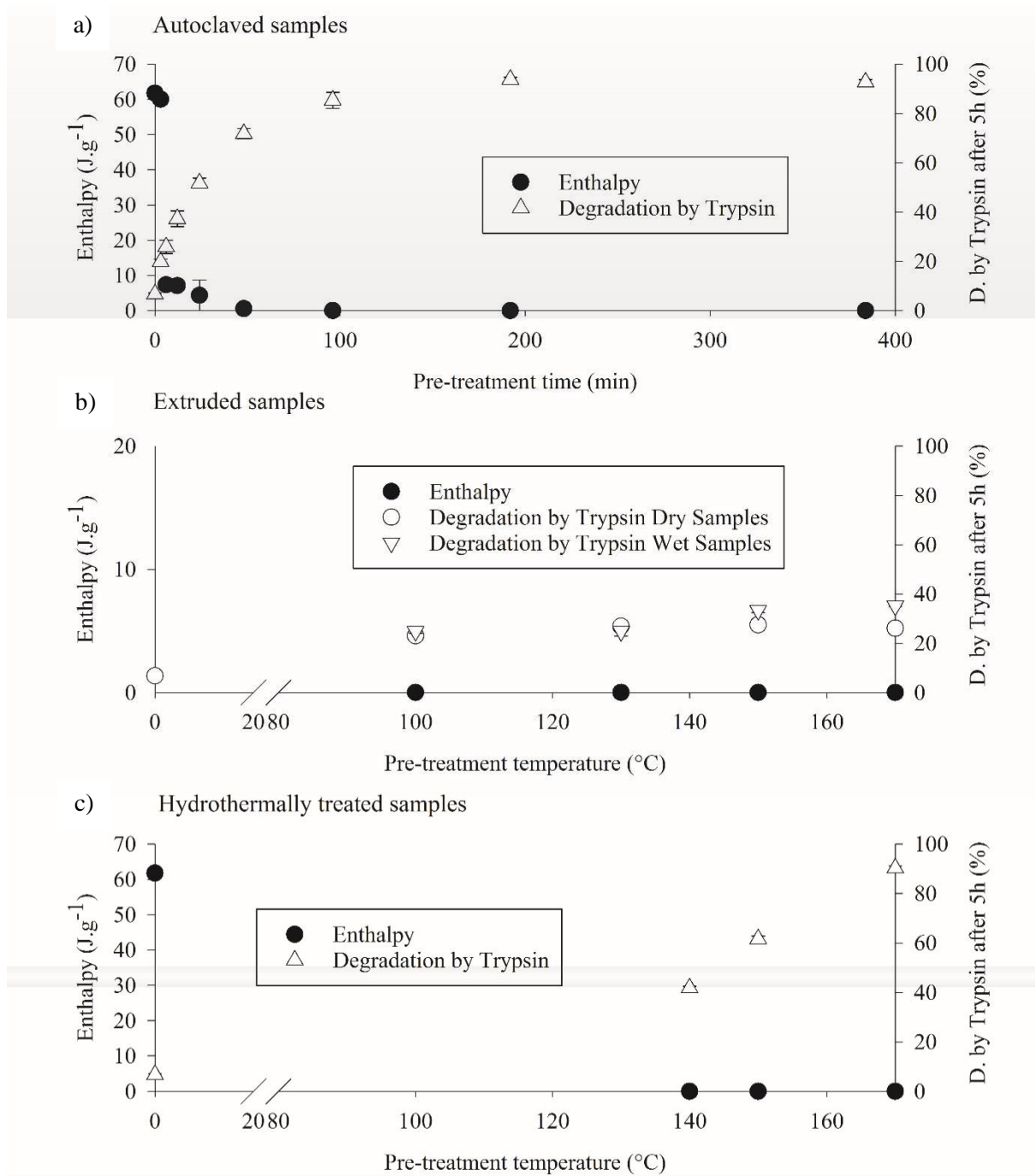


Figure 1: Enthalpy of the denaturation process and degradation degree by trypsin of CTLW and autoclaved samples as a function of the pre-treatment time (a), extruded samples (b), and hydrothermally treated samples as a function of the pre-treatment temperature (c).

3.2. Biogas Production

Two of the extruded samples and the untreated leather shavings were tested for biogas production. The sample extruded dry at 100 °C (E100D) and extruded wet at 170 °C (E170W) were selected as they represent the extremes of the extrusion treatment, being E100D the sample with the

lowest degree of treatment and E170W the highest degree of treatment. Results are represented in Figure 2.

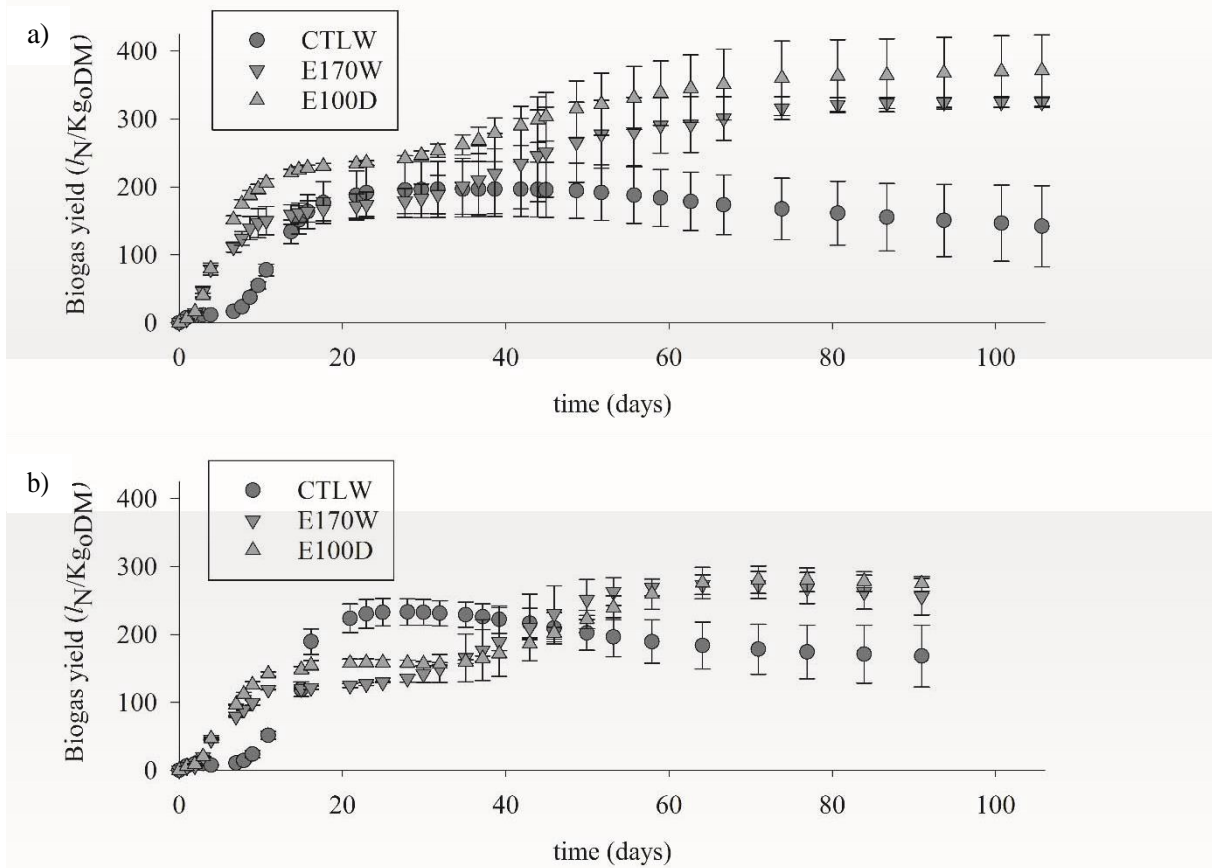


Figure 2. Cumulative biogas production for CTLW, E170W and E100D in agitated bioreactors (a) and in non-agitated bioreactors (b).

Comparing the untreated and the extruded samples for biogas production, the pre-treated samples were able to start production approximately five days before the untreated sample. Moreover after a lag- phase the extruded samples start to produce again, and diauxia (two phase decomposition) was observed, while the leather shavings remain stagnated. Diauxic growth is commonly seen in aerobic systems but not much information is available for anaerobic systems. Marin et al. (2010) reported diauxic growth curves for substrates containing protein and its occurrence was attributed to the presence of easily accessible biodegradable compounds that are digested first. The shape for the CTLW curve indicates a retarded degradation, what happens when the substrate degrades with difficulty (VDI 4630 2006).

In comparison with the untreated sample, the extruded samples presented higher final biogas yields in both cases indicating that the pre-treatment is able to ease the process. When comparing the extruded samples it is possible to see that they presented very similar results, which happened in the

agitated and non-agitated reactors, although E100D was less degraded by trypsin E170W. A reason can be, that this sample is a powder like material favoring the mass transfer inside the reactors and hence its contact with the inoculum and anaerobic bacteria.

A comparison of the results for both batches (with and without agitation) indicated that agitation favors the biogas production. The E170W sample had final biogas yields of 325.0 ± 7.6 and 273.4 ± 14.5 IN.kgoDM in the trials with and without agitation respectively. The E100D sample had final biogas yields of 371.2 ± 52.7 and 280.8 ± 20.1 IN.kgoD, an increase of more than 30% for the trials with agitation. For the untreated sample the final yield in both batches were very similar. Probably the agitation of the system facilitates the mass transfer in the bioreactors and favors the biogas production.

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Table 2: Biomass characterization after digestion and estimation of the final organic matter destruction.

Agitated bioreactors					
	pH	Volatile Matter (%)	Ashes (%)*	Chromium (%)*	Organic Matter Destruction (%)
Blank	8.07	97.9 ± 0.5	61.2 ± 0.2	0.9 ± 0.0	-
CTLW	8.50	94.7 ± 0.2	36.0 ± 0.1	2.2 ± 0.0	27.0 ± 0.4
E170W	8.56	96.2 ± 0.0	53.7 ± 0.1	3.9 ± 0.5	76.7 ± 1.4
E100D	8.57	95.7 ± 0.7	54.9 ± 0.6	2.2 ± 0.1	71.8 ± 0.4
Non-agitated bioreactors					
	pH	Volatile Matter (%)	Ashes (%)*	Chromium (%)*	Organic Matter Destruction (%)
Blank	8.05	97.8 ± 0.0	59.4 ± 0.6	0.6 ± 0.1	-
CTLW	8.58	95.1 ± 0.0	38.3 ± 0.2	2.1 ± 0.1	37.6 ± 2.4
E170W	8.65	96.4 ± 0.0	53.6 ± 0.1	3.1 ± 0.3	81.4 ± 0.5
E100D	8.66	96.5 ± 0.1	54.3 ± 0.1	2.1 ± 0.0	81.2 ± 0.1

*Dry basis; mean ± standard deviation, n = 3

The characterization of the final sludge enabled the estimation of the final organic matter destruction (Table 2). The extruded samples presented organic matter destruction between 70% and 82%, a very high destruction of the original substrate, while the untreated sample could only reach 27% to 38%. This indicates that the CTLW is a complex substrate and the pre-treatments are very important to assure the reduction of the final wastes.

4. Conclusion

Three different pre-treatments were carried out to ease the anaerobic digestion of chromium tanned leather shavings. The evaluation of the pre-treated samples showed that it is possible to increase the degradability of the wastes, reaching more than 90% of degradation by trypsin in the cases of the autoclaved and hydrothermally treated samples, and 35% for the extruded samples.

In the biogas production trials with extruded samples the pre-treatment decreased the onset time of biogas production of the leather shavings by 5 days. The extruded samples also presented higher biogas yields when compared to the untreated sample, reaching up to 370 $l_N.kgOD$ while the latter could only reach 233 $l_N.kgOD$. The agitated trials were

proven to have a better performance for the tested pre-treated samples, facilitating the mass transfer inside the reactors. The extrusion pre-treatment also increased the leather destruction while producing biogas. It was possible to destruct approximately 80% of the pre-treated samples.

Results up to now show that the pre-treatments can increase the efficiency of the biogas production out of chromium tanned leather shavings. The pre-treatments accelerate the process and improve the final yield apart from enhance the wastes destruction. All these improvements increase the suitability of this method for the industry.

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