Special Review: Anaerobic Digestion of Leather Industry Wastes – An Alternate Source of Energy

by

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Abstract

Advances in environmental protection legislation, along with the awareness of societies, leads industrialists, environmentalists and scientists, to search for production methods or industrial processes with lower environmental impacts. Within this philosophy, the maximum utilization of raw materials, wastes and by-products should be considered as a target for the leather industry. The anaerobic digestion of solid leather wastes may represent a possibility for energy recovery through biogas production. This gaseous fuel (biogas) is considered a renewable and carbon-free since the basic raw material is classified as biomass. This paper presents the potential for energy recovery through anaerobic digestion of different tannery wastes, tanned and untanned, based on the potential for biogas generation available in scientific literature using recent publications. The results show that collagenous materials can be efficiently degraded biologically to obtain a gas with high calorific value in sufficient quantities to supplement the energy demand of tanneries as a complementary source. The average heating values (Higher Heating Value, HHV) of biogas obtained under controlled conditions was found to be between 13.1 and 29.4 $MJ.Nm^{-3}$ allowing an estimated energy potential of around 123 to 485 kWh per metric ton of rawhide processed. Considering the tannery energy consumption, the biogas may represent from 0.9 to 15% of the total energy demand or from 6 to 31% of the electrical demand. This initiative aims to increase the energy efficiency and improve the environmental quality of the tanning industry.

Introduction

The tanning industry is recognized as a sustainable solution provider through commodity production using meat industry by-products as raw material.[1] This industrial activity requires large amounts of resources generating substantial quantities of solid wastes, liquid effluents and air emissions.[2] The solid wastes generated in the leather transformation process from rawhides and during the manufacturing of leather goods (leather production chain) are well known and studied. For several decades, the improvements in waste processing technologies have been focused on the utilization of these materials.[3,4,5,6] These technologies are based on the recovery of its constituents to obtain new materials or products for direct application in the leather chain, or other applications (protein and metals) by destroying the leather structures for further processing.[7,8,9] Such processes have elevated costs and require the creation of a consumer chain which hampers its implementation. Other forms of waste processing have been proposed, based on energy recovery processes through combustion, pyrolysis and gasification. However, difficulties associated with the ash disposal due to the presence of chromium metal are reported.[10-1]

Another approach to this problem, recognizing the need for replacement of the energy model based on the use of fossil fuels, is for a model that employs renewable energy sources (from biomass). Biogas can be produced from almost all types of biological materials including the primary sector (agriculture) and various organic wastes. The most abundant resource is animal excrements. Waste and sludge resulting from cattle and pig production units as well as poultry and fish. If managed properly these wastes can provide a considerable resource for renewable energy (biogas and biodiesel) and as a source of nutrients for agriculture.[14,15]

Anaerobic degradation/digestion processes have been one of the most widely employed technologies in chemical and biological stabilization of wastewaters and bio-solids since the early 20th century and are continuously being developed and expanded. Several research groups worldwide have studied the biological degradation of solid wastes from the leather industry aimed at biogas production; however, implementation of these technologies on industrial scale appears to still be underutilized, despite its proven applicability.[16,17]

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This paper aims to assess the different possibilities for biogas production through anaerobic degradation of various leather wastes focused on energy recovery. The compilation of data published in journals and scientific literature related to anaerobic biological degradation of different leather wastes, exploring its potential for biogas and energy production reveals it to be a valuable tool to increase tannery energy efficiency. The average calorific values and degradation potential (in terms of composition and generation rates of biogas) allows evaluation for possible application as thermal energy source or in power generation systems.

Critical Parameters for Biogas Production

Despite the many benefits of anaerobic digestion (AD), the process is burdened by complexity, poor practical and operational stability, high sensitivity to changes in environmental conditions and toxic substances, long retention and start-up times, and undesired sludge dewaterability. Many researchers have investigated various methods to eliminate the above-mentioned problems.[18]

The AD process includes four distinct chronological steps: hydrolysis, acidogenesis, acetogenesis and methanogenesis. These steps can occur sequentially, after the process starts, and simultaneously in continuous processes. The hydrolysis step can control the whole process due to its relationship with substrate solubilization.[19] When the substrate is leather fiber, the hydrolysis step is crucial and the methanogenesis step is the most sensitive or unstable. In terms of microorganism interaction, syntrophy is a fundamental concept of this complex process.[20]

Substrate Characteristics

The potential for biogas production and its composition are both dependent on the characteristics of the substrate used and the specific features of microbiological processes.[21] The biogas production depends on the waste/substrate composition - its chemical composition and heterogeneity - and some specific physicochemical conditions that the substrate brings to the reaction medium.[16] These aspects are deeply associated with the final energy content of produced biogas.

The solid wastes generated in leather production in tanneries are characterized by high protein content (collagen) and water (free and water of hydration). Protein levels vary by type of waste and the production method employed, ranging between 23 and 44% by mass, and between 10 and 87% in humidity.[22,23] The phosphorus and potassium concentrations are negligible, which leads to the necessity of complementary additions of these chemicals when this substrate is submitted to anaerobic digestion. Other essential trace elements such as Ni, Co, Mo and Se may also be required.[24]

Chrome tanned leather is highly stable and its use as a substrate is particularly difficult. The formation of coordinated cross-links between the collagen matrix (side-chain carboxyl groups of aspartic and glutamic acids) and chromium results in a very stable complex, conferring it hydrothermal and enzymatic stability.[25,26] The bacterial, or more specifically the bacterial enzyme degradation of these complexes is hindered by the tannage, making it difficult to hydrolyze these chemical structures. The effectiveness of leather AD is directly affected by dispersion in water, water solubility, and degree of chrome-tanning. The adoption of previous processes to destabilize the chrome-collagen complexes and/or mixture with readily degradable materials can significantly improve the biogas production by anaerobic digestion.[19]

Another characteristic to be considered when leather wastes are used for biogas production is the C:N ratio. C:N ratios are considered adequate in a range between 16:1 and 25:1. Due to low production of biomass in anaerobic processes, an acceptable and sufficient ratio for C:N:P:S nutrients is approximately 500-1000:15-20:5:3. Leather fleshing's present a C:N ratio of near to 3.5:1, a very low value, but this represents a good example of the C:N ratio of proteinaceous materials.[27]

Inhibitory Substances

Inhibitory conditions/processes are dependent on the inhibiting substance concentration in the substrate and in solution and the capacity of the biota to adapt to a specific inhibitor. The effect on the anaerobic process is complicated for certain reasons, such as: 1) Microorganisms are adaptable to the environment; 2) Inhibitors have different effects depending on the form of exposure; 3) Effect of interactions or crossover effects (inhibitors are affected by several factors, including inhibition by other bacterial species). Usually anaerobic processes can develop some resistance and frequently adapt to certain inhibitory agents.

Ammonium

Nitrogen containing substrates submitted to AD processes tend to increase the ammonia and ammonium concentration causing inhibition of the methane production by raising the pH value. The equilibrium between ammonia and ammonium ions is dependent on the concentration of hydrogen ion (H^+). Both present inhibiting effects to the biota at higher concentrations. Ammonium presents an inhibiting effect at concentrations above 1,500 $mg.L^{-1}$ and its effect occurs predominantly on the availability of species whose concentration depends on the pH value. This negative effect increases at high pH values. The ratio ammonium to ammonia is 99:1 at pH 7 and 70:30 at pH 9.[28,29]

High concentrations of nitrogen and chromium are present in leather substrate. The inhibition of methanogenesis due to the simultaneous presence of trivalent chromium ($Cr^{(III)}$) and ammonium is demonstrated for concentrations higher than 12 $mg.L^{-1}$ of total Cr and 4,000 $mg.L^{-1}$ of NH_4^+, which causes a 50% reduction in bacterial activity.[30]

Sulfur Content

The minimum influence on biogas production with increase in sulfide concentrations is a process delay and manifests itself mainly with methanogenesis. In a continuous reactor, concentrations of 100 mg.L^{-1} of hydrogen sulfide can inhibit and reduce efficiency by at least 15%.[31] The toxicity of sulfides is strongly dependent on the pH since only the un-ionized forms of hydrogen sulfide (H_2S) can pass through the cell membrane (closely dependent on the pH). The inhibition limits over methanogenic processes are low, near 200 mg.L^{-1} when biomass is acclimatized and 50–100 mg.L^{-1} in shock load conditions.[32] Sulfite is another inhibitory compound that can inhibit the biological process if it is present in concentrations higher than 132 mg.L^{-1}.[33]

Oxidized forms of sulfur exhibit some inhibition characteristics on methane formation. Sulfate reducing microorganisms are dominant over methanogenic ones. Sulfate degradation (reduction) is energetically favored when compared to methane formation. Therefore, sulfate-reducing microorganisms can utilize acetate more efficiently than methanogens at low acetate concentrations, resulting in a predominance of these microorganisms under acetate limited conditions. Methanogens exhibit higher maximum growth at higher acetate concentrations.[34] These behaviors explain the high concentrations of hydrogen sulfide in biogas when sulfur rich substrates are used and the negative effect over methane production when the sulfate concentration in the substrate is increased.[35]

Metals

Heavy metals at low concentrations give a stimulating effect for some anaerobic processes. Toxic or inhibitory effects are observed at higher concentrations. Particularly, lead, cadmium, copper, zinc, nickel, and chromium can promote disturbances in biogas production plants. In the presence of sulfides at 1 - 2 mg.L^{-1} some metal species are bound or precipitated. In other cases, the metals can be made inert by using complexing agents such as polyphosphates or EDTA.[29]

The presence of high chromium concentration in leather substrate must be taken into consideration. The $Cr^{(VI)}$ species represents significant toxicity compared to $Cr^{(III)}$ due to its higher mobility. $Cr^{(VI)}$ can cross cellular membranes and influence intracellular biochemical processes. Some biological processes are stimulated at concentrations up to 15 mg $Cr^{(III)}$.L^{-1} with lethal doses above 160 mg.L^{-1}. $Cr^{(VI)}$ is reported as toxic at concentrations above 5 mg.L^{-1} with the lethal dose identified as near 80 mg.L^{-1}.[30,36] Generally, microorganisms present a tolerance to Cr species in the range of 0 - 100 mg.L^{-1}, however, some types of *Bacillus* spp. can tolerate around 500 – 5,000 mg.L^{-1}of $Cr^{(VI)}$.[37] In the absence of ammonium, chromium does not show toxicity until concentrations of 140 mg.L^{-1} are reached.[30]

Other Organic Compounds

The presence of certain cations in sufficient concentrations is toxic to the anaerobic process. There are a large number of these substances, too numerous to list. However, high concentrations of halogenated organics can be harmful.[38]

Another type of organic material that influences biological process are the vegetable tannins. Vegetable extracts are widely used as tanning agent in chrome free leathers.[39] The performance of the anaerobic bioreactor can be hindered by the presence of vegetable tannins in concentrations above 915 mg.L^{-1}.[33]

Operational Conditions

The operational control of anaerobic reactors or digesters should take into consideration the average temperature of the bioreactor, the nutrient and micronutrient concentrations necessary for the growth of microorganisms, the pH in order to ensure favorable conditions for microbial growth, and the presence of inhibitors such as sulfur and nitrogen compounds, and metals in their reduced forms. A moisture content of 40% or higher based on the wet weight of the waste input promotes maximum biogas production.[20]

The temperature inside the digester has a major effect on the biogas production process. Anaerobic processes can be carried out at three different temperature ranges, psychrophilic (< 20°C), mesophilic (20 - 45°C) and thermophilic (> 45°C). However, anaerobes are most active in the mesophilic and thermophilic temperature range.[40] Mesophilic microorganisms show a quick reduction of 50% in biogas yield when the temperature is reduced from 35°C to 25°C.[30]

Another crucial parameter that needs attention - since a slight change may result in reduction of biogas production - is pH. The formation of volatile fatty acids beyond a particular range hinders methane production.[40] Volatile Fatty Acids (VFA) are produced during acidogenesis and their concentration depends on the characteristics of the substrate and on the equilibrium between acidogenic and methanogenic bacteria. The stability parameter may be expressed and assessed by variations in acetate concentration. Its rapid increase indicates an evolution to the acidogenic phase with an increase in the organic matter to be treated.[41] In these cases, the pH can be used as a control parameter for the biological growth phases inside the reactor/digester. Volatile fatty acids inhibit the growth of methanogens if their concentration rises above a certain level. Additionally, different volatile fatty acids show different behaviors when inhibiting methanogens.[18]

The optimum pH for the methanogens is in the range of 6.5 - 7.5. Metabolism is considerably suppressed at pH < 6 and pH > 8.3. If the pH value is below 6.5, the production of organic acids causes an increase of hydrolytic bacterial metabolism and the anaerobic digestion processes may cease. Normally, the pH value must be held within the neutral range.[16]

Anaerobic Digestion Residues (Digestate)

Anaerobic digestion of wastes focused on biogas production allows the recovery of a fraction of the energy contained in the wastes and a post-digestion sludge with high fertilizing value. The digested substrate contains undegraded organic waste, microorganism cells and structures formed during digestion, as well as some inorganic matter and a high content of water. Studies have shown that composts are valuable fertilizers having a much higher content of N, P, Ca, Zn and Cu compared to farmyard manure.[42] The digested slurry or sludge contains 2-12% of solids; wet waste from solid-state digestion contains 20-25% solids. This is potentially an alternative source of humic material, nutrients and minerals for agricultural soil.[24]

A solid-liquid separation is performed to obtain aqueous and semi-solid fractions. The semi-solid fraction may be used for fertilizing purposes. The final aqueous solution is considered as wastewater. Sludges from tannery waste anaerobic digestion may contain as much as 10 times more phosphorus and nitrogen than any average manure.[43]

Biogas Utilization

Biogas characteristics, such as storage simplicity and low costs for transportation, permit a wide range of applications. As examples, it can be used as a fuel for direct combustion in boilers and steam generating systems or for power generation in internal combustion engines (ICEs), in microturbines, in some specific fuel cells, for hot gas generators like sludge dryers, or for chemical synthesis of other fuels like hydrogen by steam reformer process. Therefore, knowledge about its specific properties is useful for optimizing biogas utilization.[44-46]

Utilization Forms

The most common way for biogas to be used as an energy source is its direct use as a gas of medium calorific value for power generation (electricity) or distribution through gas grids. The chemical energy can be converted to heat and/or mechanical energy in a controlled combustion system. The mechanical energy activates an electric generator producing electrical power.

The power generation can be achieved using classic Rankine Cycles (RC) through biogas combustion to produce high-pressure steam in boilers. However, gas turbines (or microturbines) and internal combustion engines (ICE) are the most common technologies for power generation using biogas. In general, engines are more efficient than turbines and even more efficient when operating in cogeneration cycles, producing electricity and heat.[42] ICEs can work with biogas, natural gas, mixtures of both fuels, and in a combination of these gaseous fuels with diesel fuel.[47] For microturbine applications, the biogas has to present a heating value (HV) above 200 Btu.ft^{-3} (7,456 kJ.Nm^{-3}). Gaseous fuels with Lower Heating Value (LHV), near these values have greatly restricted flammability limits when compared to methane.[48]

For thermal generation only, the gas calorific value, purity, and its adaptation to the available firing system are considered. The efficiencies associated with these processes are varied. Typically, such processes present high levels of energy conversion to steam, of the order of 75% or more. When the electric power generation using steam turbines coupled to electrical generators is considered, the overall efficiency is reduced to between 20 and 31%.[49] Alternately, power generation can be achieved by the use of internal combustion (ICE, Otto cycle) or rotating (gas turbine, Brayton cycle) engines. These configurations operate at 30 to 40% of conversion efficiency, the remaining power is lost internally (cooling and friction) or rejected through the gas exhaustion system.[50]

Other available technologies are combined heat and power systems (CHP), in which a piston engine or a turbine drives an electrical generator. The biogas can be converted in typical CHP systems to electricity (35% efficiency) and heat (50% efficiency) with 15% of energy loss.[20] The most efficient engines, hybrid diesel and hybrid hydrogen fuel cell, achieve nearly 50% efficiency. Further, emissions for hybrid hydrogen fuel cell are substantially less than diesel and gasoline engines.[51] Figure 1 presents an overview of the diverse forms of biogas utilization as an energy source, with necessary adaptations.[52]

Another clean and efficient technology is the high temperature fuel cell. Specifically, this type of fuel cell is a molten carbonate fuel cell (MCFC) working at 600°C with an electrical efficiency of 47%. The biogas is internally reformed into hydrogen and carbon monoxide, which is consumed at the anode as a fuel. In addition, the MCFC consumes carbon dioxide at the cathode side. The heat recovered can be used to produce steam for power generation in a typical RC.[53]

An efficient way of integrating the biogas into the energy sector is the upgrading of biogas to natural gas quality (biomethane) and injecting it into the existing natural gas grid. As biogas cannot always be used nearby the production facilities (such as farming areas) injecting upgraded biogas such as biomethane into natural gas grids widens up the opportunities for transport and utilization of biogas in larger energy consumption areas – e.g. areas where population concentration is higher.[15] A technology that is undergoing current research and development is the production of methanol from biogas.[54]

Cleanup Requirements

Biogas cleanup requirements for use in diverse ways vary by the aim and type of energy utilization. The cleanup requirements for each case vary as function of the equipment construction materials, storage conditions, and/or process conditions. Initially the biogas has to be cooled, drained and dried immediately after production. Another essential operation is the lowering of the hydrogen sulfide (H_2S) content. Table I presents a summary of the main contaminants of biogas and purity requirements (limit concentration) for some typical applications.

Ammonia

The concentration of ammonia in biogas is usually lower than 0.1 mg.m^{-3}. The maximum concentrations observed are between 1 and 1.5 mg.m^{-3} when nitrogen rich substrates are degraded (typically protein-based substrates such as leather or poultry excrements). Its presence can raise the NOx emissions of direct burners, damage fuel cells, and increase the anti-knock properties of engines.[55]

Hydrogen Sulfide

For energy conversion purposes, the H_2S content needs to have concentrations lower than 500 ppm to avoid damaging equipment.[15] Similarly for other contaminants the content of H_2S in biogas depends on the process conditions and the type of substrate. In its raw state, the biogas may have H_2S concentrations exceeding 1,500 ppm by volume.[51]

For biogas application, it is essential that H_2S content be maintained at the lowest level possible to prevent damage to plant components downstream. To reduce the H_2S formation inside the bioreactor, the substrate can be manipulated in terms of sulfur concentration and process conditions. With effective control, the content can be maintained below 70 mg.m^{-3}.[56,57]

The H_2S has to be removed in order to avoid corrosion in compressors, gas storage tanks and engines. In addition, it can contaminate the equipment used in upgrading processes - it is poisonous to catalysts. The most widespread processes for H_2S removal are adsorption using iron oxide and liquid phase oxidation processes (physical or chemical absorption using alkalis or iron salts).[58] Another cleanup system consists of a biological plant with aerobic bacteria capable of converting the H_2S into sulfur and sulfuric acid. The reduction of the H_2S concentration can be very high (up to 95%) and the low operation and maintenance cost balances the high investment cost.[53]

Siloxanes

The siloxanes represent a group of biogas contaminants formed from silicon. Siloxanes are found in water in its soluble form, inside the digester these materials are carried over by the biogas. In leather wastes, the silicon oxide (SiO_2) represents near 20%wt of total ashes.[13] Concentrations of the order of 18 mg.m^{-3} of methylcyclosiloxane have been measured. In biogas combustion processes, at high temperatures, siloxanes and its oxidized form (SiO_2) may deposit or remain on hot surfaces of the equipment. It results in friction, flow reduction and can cause abrasion of ICE pistons. The recommended limit value of polysiloxane in biogas, for heating and power plants, is near 0.2 mg.m^{-3}.[29] Siloxanes can cause fatal degradation of fuel cells if not removed.[59]

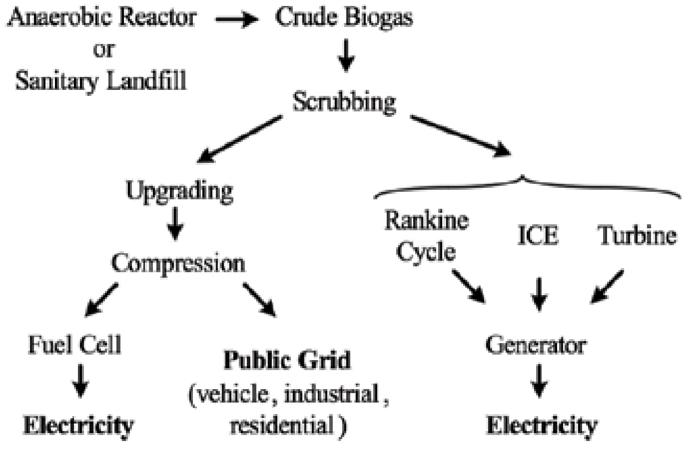

Figure 1. Overview of biogas utilization.

Methodology

The main objective was the calculation of the biogas potential of different wastes from leather manufacturing. A search was conducted of works by renowned authors and research groups (recent literature) to find experimental results of AD that contain sufficient reliable information. Information was selected and evaluated to represent the state-of-the-art for research in this area.

Works performed since the 1980's were investigated, in which the solid wastes from rawhide up to wetblue leather was assessed. Data about waste generation and anaerobic degradation potential (biogas production) in different process stages were computed and energy potential was calculated. The generated data uses the waste generation amounts, the potential for biogas generation by each type/class of waste, and the biogas characteristics (methane concentration) for each type/class employing standard methods.

Solid Waste Generation

Considering the whole leather production process, the following wastes representing the larger amounts generated can be highlighted: rawhide trimmings, limed trimmings, limed fleshings, wetblue shavings, wetblue trimmings and sludge from wastewater treatment plants. The amounts of waste generated in

Table I
Biogas cleanup requirements.

Contaminant	Boiler Burners	Internal Combustion Engines	Turbines	Fuel Cells
H_2S (ppm)	< 1,000[3]	< 200 [1]	700[4]	< 10 [1]
NH_3 (ppm)	-	150 [2]	-	< 1,000 [1]
Siloxanes (mg/m^3)	-	< 15 [1]	-	0 [1]

Source: [1]Castell et al., 2009[53]; [2]Deublein and Steinhauser, 2008[29]; [3]Drapcho et al., 2008[51]; [4]Boyce, 2006[48].

leather processing and its volatile solids fractions (VS) were investigated and expressed considering one metric ton of rawhide processed. Waste materials were categorized according to the steps mentioned, rating them into: (1) rawhide wastes, (2) limed hide wastes, (3) chrome tanned leather wastes and (4) leather wastes subjected to pre-treatments prior to use as a substrate for biogas production. From these data were calculated the VS mass of each material (approached by its organic matter) per ton of rawhide processed, for each category.

The inventory data related to the quantities of waste produced per ton of rawhide processed, as well as their characterization allows quantification of the VS fractions of wastes, as shown in equations (1) and (2).

$$m_{VSW} = m_W \times X_{VSW} \tag{1}$$

$$X_{VSW} = 1 - X_{Ashes} \tag{2}$$

where: m_{VSW}: is the waste VS mass per ton of rawhide processed, on dry basis ($kg_{VS}.ton^{-1}$); m_W: is the waste amount (mass) on dry basis (kg); X_{VSW}: is the VS fraction of the waste on dry mass basis; X_{Ashes}: is the ash fraction of the waste on dry basis.

The values for the VS mass produced per ton of rawhide allow the calculation of the biogas potential by each waste category.

Biogas Production

Several works have described the potential for anaerobic degradation of different wastes generated by the leather industry. However, the potential for biogas production has been secondary information, not the focus. Thus, obtaining sufficient and reliable data is difficult.

As the results for biogas production potential are expressed as volume of biogas per mass of volatile solids (VS) ($m^3.kgVS^{-1}$), the potential biogas per ton of feedstock processed can be obtained by multiplying the potential for biogas production by the VS mass fraction of each waste per ton of rawhide processed.

Biogas Heating Value

To determine the Higher and Lower Heating Values (HHV and LHV) of the biogas, from the mole fractions of its components, a methodology based on a standard test method from American Society for Testing and Materials was employed (ASTM D 3588-98 – Standard Practice for Calculating Heat Value, Compressibility Factor and Relative Density of Gaseous Fuels). The results were expressed on dry weight basis and used to calculate the energy potential of biogas from each substrate.

Considering the average quantities of biogas production ($mL.gVS^{-1}$) and the average concentrations of methane in the generated gas (% molar) it is possible to obtain the heating values (HV) of the biogas produced, expressed as $MJ.Nm^{-3}$ and $MJ.kg^{-1}$, based on the HV's of the pure substances. The higher and lower heating values of methane (HHV of 55.54 $MJ.kg^{-1}$ and LHV of 50.05 $MJ.kg^{-1}$) and its fractions in the biogas were considered to obtain the heating values of the produced gases employing different wastes as substrate. For calculation purposes, the biogas was considered as a mixture of methane (CH_4) and carbon dioxide (CO_2) without considerable loss in terms of reliability. The higher heating values of biogas (HHV_{Biogas}) were calculated by using equation (3), and considering the mole fraction of its components.

$$HHV_{Biogas} = \frac{\sum_{j=1}^{n} x_j.M_j.HV_j}{\sum_{j=1}^{n} x_j.M_j} \tag{3}$$

where: HHV_{Biogas} is the biogas higher heating value per unit mass ($MJ.kg^{-1}$); *xj* is the mole fraction of Component *j*; *Mj* is the molar mass of Component *j* of the gaseous mixture; *n* is the total number of components (gases); HV_j is the higher heating value per unit mass of pure Component *j* ($MJ.kg^{-1}$).

The HHV_{Biogas} per unit volume is calculated multiplying the higher heating value per unit of mass by its density ($kg.m^{-3}$). The equation (3) can be used to calculate the LHV_{Biogas}, substituting the HV_j by the LV_j - lower heating value per unit mass of pure Component *j* ($MJ.kg^{-1}$).

Energy Potential

The potential values for overall energy production by the different wastes was obtained from the multiplication of the HV's of the biogas by its yield and VS mass of each waste per ton of rawhide processed. The equation (4) shows the method used to obtain these values. Thus, when the biogas production potential from different materials is considered, it is possible to delimit a range, expressing the conditions of maximum and minimum potential for biogas and energy production. These tabulated results allow an estimate of the potential for each waste class and its full potential for energy recovery (sum of contributions from each class). It is worth mentioning that the energy losses associated both with the operation/maintenance and biogas cleaning and compression processes were not estimated.

$$E_{Potential} = Q_{Biogas} \times HV_{Biogas} \times x_{VSW} \times 277.7 \times 10^{-3} \tag{4}$$

where: $E_{Potential}$: is the energy potential of biogas per ton of rawhide processed ($kWh.ton^{-1}$); Q_{Biogas}: biogas produced per mass of substrate ($L.kg_{VS}^{-1}$); HV_{Biogas}: is the biogas heating value per unit mass ($MJ.kg^{-1}$); x_{VSW}: VS fraction of the considered waste.

The potential for electric power generation through internal combustion engines, gas turbines and steam cycles, were assumed using conversion efficiencies (η) of 33% for internal combustion engines,[60] 27% for simple combustion turbine,[45] 32% for combined cycle combustion turbine and 25.5% for steam RC.[61]

Results and Discussion

This section presents the quantification of wastes generated at the various stages of leather making, the potential for biogas production using these wastes as substrate and the potential for biogas utilization as an energy source. This information includes values on the potential for energy recovery considering different ways of conversion and power generation and compares these with the energy demand of the leather industry.

Solid Wastes Inventory

Table II presents the data reported by different authors relative to solid waste generation at different stages of leather processing in tanneries. These data refer to industrial processes that use chromium salts as tanning agent, a characteristic representing the vast majority of tanning establishments worldwide.

It is possible to observe that the values presented vary considerably when different types of wastes from distinct process steps/groups are compared. The variability is large but the average values are closer when considering the same process step. Some of the variation can be attributed to the technologies used in processing the raw material or diverse characteristics associated with the feedstock (calf hides, adult hides, and hides from different species).

Table II

Waste generated per metric ton of rawhide.

Process/Step	**Mass of waste per ton of rawhide / Volatile Solids fraction (kg.ton^{-1}, wet basis) / (%VS)**			
	Author			
	Buljan *et al.* **(2000)**[63]	**Stoop (2003)**[64]	**Sundar** *et al.* **(2011)**[7]	**Thangamani and Parthiban (2011)**[65]
Rawhide				
Raw Trimmings	-	120/29.2	120/-	80 – 100/30.0
Raw Fleshings	-	-	70 – 230/-	
Limed Hide				
Fleshings	155/16.5	75/32.7	-	90/13.9
Trimmings			-	20/13.9
Tanned Leather				
Splits	107/45.5	115/40.9	115/-	110/29.6
Trimmings and Shavings	119/45.4	102/40.2	100/-	30/29.6

The waste mass produced by the processing of one metric ton of rawhides is high, and adding other losses during the industrial process confirms the estimate that only 20 - 25% of the total feedstock is effectively transformed into the final leather.[12] Chrome free residues represent 75 - 80% of the entire quantity of solid wastes as fleshings, trimmings, unused splits, and hair residues.[62] In beamhouse operations, the average values are 115 kg.ton^{-1} of rawhide waste (trimmings + fleshings), 113.3 kg.ton^{-1} of limed waste (fleshings + trimmings) and 199.5 kg.ton^{-1} of chrome tanned leather waste (wetblue waste). The maximum values according to the Table II are 420, 155 and 226 kg.ton^{-1} respectively.

The average values of waste generation and its VS fractions can be used to estimate the total volatile solids produced during beamhouse operations. The VS average values are 29.6% for rawhide wastes, 21.1% for limed wastes and 38.5% for wetblue wastes. These results enable an estimate of the quantities of wastes available for use as substrates to AD aimed at biogas production.

Biogas Generation

The results obtained by various authors related to the potential for biogas generation using leather industry wastes are presented in Table III. The potential yields are expressed as the volume of biogas produced per mass of VS added (mL$_{Biogas}$.g$_{VS}^{-1}$) and the heating values calculated using equation (3), according to the categories. Together with the biogas potential, the main process parameters, controlled and/or monitored, during experiment execution are exhibited. This information allows comparison of the operational conditions and similarities between different types of waste.

A review of Table III information indicates that the higher heating values of biogas range between 13.12 and 29.42 MJ.Nm^{-3} (8.45 and 28.28 MJ.kg^{-1}). The biogas generated from these wastes has comparable heating values to combustibles such as ethanol, wood and forestry waste, as shown in Table IV. Furthermore, when the biogas heating values are compared to the raw solid wastes on dry basis (limed hide, chrome leather trimming and shavings) the same magnitude range can be observed, *i.e.* 17.6 and 24.9 MJ.kg^{-1} (Table IV).

The potential for biogas production presented by the authors varies from 2.4 and 910 mL.g$_{VS}^{-1}$, with an average value of 361.5 mL.g$_{VS}^{-1}$. Comparing these values to the theoretical maximum methane yield from carbohydrate, protein and lipid, that is 1.37, 1.0 and 0.58 m^3.CH$_4$.kg^{-1} of organic dry matter respectively, the observed results are promising.[51] Considering the average potential for biogas methane production by leather wastes (361.5 mL.g$_{VS}^{-1}$, with 61.2% of methane fraction) compared to the average yield from protein based substrates, it represents nearly 22% of the maximum yield. As leather waste substrates contain several characteristics capable of destabilizing the biological process, these results are positive.

When the biogas yield is compared to results obtained for the complete anaerobic biodegradation of municipal solid wastes (MSW), the conclusion is encouraging.

Table III

Biogas Production according to various authors.

Author	Substrate	Source	*Inoculum*	C:N Ratio	Temperature (°C)	Biogas (mL/g VS)	Methane Fraction (mol %)	Average Methane Fraction (mol %)	Time (days)	HHV (LHV)	of Biogas
										(MJ. Nm^{-3})	(MJ. kg^{-1})
Rawhide											
Lalitha *et al.* (1994)[67]	Rawhide	Bovine/ Calf	Effluent anaerobic sludge	-	30	648.2	62.7 - 71.8	70.0	80	27.83 (25.08)	25.86 (23.01)
Pulavendran *et al.* (2004)[68]	Rawhide	-	Effluent anaerobic sludge	6	28	308.0	60 - 65	62.5	40	24.85 (22.39)	20.99 (18.92)
Zupancic and Jemec (2010)[2]	Rawhide	Bovine	Sewage anaerobic sludge	-	55	617.0	55 – 70	62.5	30	24.85 (22.39)	20.99 (18.92)
Limed Hide											
Cenni *et al.* (1982)[69]	Limed trimmings	Bovine/ Calf	Swine manure	-	35	825.0	74	74.0	134	29.42 (26.51)	28.28 (25.49)
Urbaniak (2006)[43]	Limed trimmings	Bovine	Sewage anaerobic sludge	12	35	690.0	70 - 71	70.5	25	28.03 (25.26)	25.86 (23.30)
Zupancic and Jemec (2010)[2]	Limed fleshings and trimmings	Bovine	Sewage anaerobic sludge	-	55	377.0	56 – 70	62.5	31	24.85 (22.39)	20.99 (18.92)
Shanmugam and Horan (2009)[70]	Limed trimmings	Bovine	-	3.2		242.6	33	33.0	30	13.12 (11.82)	8.45 (7.619)
Basak *et al.* (2014)[23]	Limed trimmings and sewage anaerobic sludge	Bovine	Swine manure	17	30	476.0	-	-	60	-	-
Chrome Tanned Leather											
Dhayalan *et al.* (2007)[71]	Chrome tanned leather	Bovine	Tannery UASB sludge	1.57	-	3.2	-	-	30	-	-
Priebe *et al.* (2016)[19]	Chrome tanned leather	Bovine	Slaughter-house anaerobic sludge	2.7	35	162.2	53.8 – 73.7	63.8	62	25.36 (22.86)	21.72 (19.59)
			Aerobic activated sludge			162.2	21 – 61.1	42.0	60	16.70 (15.05)	11.60 (10.45)

Table III continued on next page.

Table III continued.

Pretreated Leather											
Urbaniak (2006)[43]	Limed trimmings (thermal hydrolysis at 100°C)	Bovine	Sewage anaerobic sludge	12	35	910	70 - 72	71	25	28.22 (25.44)	26.19 (23.60)
Dhayalan *et al.* (2007)[71]	Detanned chrome tanned leather	Bovine	Tannery UASB sludge	1.52	-	6.6	-	-	30	-	-

Table IV

Lower and higher heating values of various fuels.

Fuel/Substance	**LHV (MJ/kg)**	**HHV (MJ/kg)**	**Specific Mass (kg/Nm^3)**
Methane[1]	50.04	55.83	0.716
Hydrogen[1]	120.01	141.85	0.089
Limed hide (dry)[2]	24.91	-	-
Chrome leather trimmings (dry)[2]	17.58	-	-
Chrome leather fleshings (dry)[2]	22.73	-	-
Natural gas (NG)[3]	47.14	52.23	0.78
Conventional gasoline[3]	43.45	46.54	744.70
U.S. conventional diesel[3]	42.79	45.77	836.64
Ethanol[3]	26.95	29.85	789.35
Liquefied petroleum gas (LPG)[3]	46.61	50.15	508.00
Wood (dry basis)[3]	19.55	20.59	-
Forest residues (dry basis)[3]	17.21	18.12	-

Sources: [1]Perry's Chemical Engineering Handbook - 5th Edition (1980)[72]; [2]Biomass Energy Data Book - 4th Edition (2011)[73]; [3]Tomaselli and Mora (1992)[22].

The MSW generates approximately 122 Nm^3 of $CH_4.ton^{-1}$ of dry biomass when completely degraded,[66] an increment of near 80%.

For each group of residues, the average biogas production was 520, 533.6, 108.5 and 349.9 $mL.g_{VS}^{-1}$ for rawhide wastes, limed wastes, chrome tanned wastes and pre-treated wastes respectively. The assessment of these data reveals that the rawhide wastes are more suitable to biological degradation compared to other raw wastes. As the leather processing steps advance, the wastes generated become less degradable, resulting in inferior values of final biogas production. The adoption of processes for leather destabilization before it is used as substrate (considering limed and wetblue leather wastes) may be an alternative to improve the substrate in terms of bioavailability.

Among the values presented, attention is drawn to the fact that only one study employs thermophilic microorganisms (T > 45°C) and all the others performed their experiments in mesophilic temperature range (20 - 45°C) with no significant differences in terms of total biogas yield or methane concentration.

In general, the reported values for the C:N ratio shown in Table III are lower than those cited as optimal conditions. The experiments performed with higher C:N ratios showed better potential for biogas production, as expected. The reported pH ranges are set in a narrow range between 7 and 7.9, suggesting little influence in terms of production of ammonia.

According to the data presented in Table IV, a process focused on leather biogas cleanup and upgrading permits this fuel to achieve heating characteristics near to natural gas or liquefied petroleum gas. In these cases, it can be used directly in boiler burners for steam production.

Energy Potential

The potential for biogas use as an energy source depends on the biogas calorific value and available technologies for energy conversion. Table V shows the gross energy potential (thermal) calculated by comparing data from the AD of wastes from processing one metric ton of rawhides and the potential for biogas production using these wastes. The values represent the application of equation (4) for each biogas yield and HV presented in Table III, using the average values for waste generation and VS fractions presented in Table II (according to the waste groups).

The variation ranges were presented as average values and interval limits (min and max values) due to the limited number of authors and the variance of the available data. In terms of gross energy potential (thermal), the sum of the relevant waste groups show that on average 279.12 kWh.ton^{-1} can be produced by degrading solid wastes generated from processing one ton of rawhides. An asymmetrical dispersion is observed presenting max and min values of 123.1 and 484.95 kWh.ton^{-1} respectively.

The observed variability, in terms of minimum and maximum potential, must be associated with the natural variations when using different *inocula* and process conditions adopted in the work cited in Table III. In case of AD of industrial leather wastes, little variations in the tannery process along with different raw substrate characteristics can greatly influence the final biogas yields. This variability results mainly from the wide ranges presented in Tables II on waste generation. For all intents, the lower limits are more reliable than the higher ones. The higher limits are estimated but are considered good approximations.

The assessment of the data presented in Table V allows the observation that the highest energy potential is associated with the rawhide waste, followed by limed waste. These substrates are less stable chemically and biologically, being more susceptible to hydrolysis of the collagen chains.[19] The chrome tanned waste presents the lowest potential for biogas production, this is related to the stabilization of the material using chromium salts.

The power consumption (electrical and thermal fractions combined) of a typical leather finishing tannery reveals an energy demand of 0.21 - 0.37 kW.m^{-2}.day^{-1} (18.1 – 32 MJ.m^{-2}). Of these, the electrical fraction is shown to be 33.5%, suggesting the adoption of cogeneration systems.[50] Considering all process steps and utilities involved in leather tanning, the average energy consumption required is in the order of 80 MJ.m^{-2} of finished leather or 10 GJ.ton^{-1} of rawhide.[64] Values of 33 and 52 MJ.m^{-2}, respectively, have been reported for Asian and European energy consumption in tanneries.[74]

The annual Brazilian leather production, according to data from the year 2015 was 44.5 million hides.[75] Assuming average values of 25 kg.rawhide^{-1} and 4 m^2.rawhide^{-1}, the mass of rawhides processed per year approaches 1.113×10^6 kg or 1.780×10^8 m^2.[63] Considering an average value of 5.6 GJ.ton^{-1} for rawhides processed as the tannery energy consumption (1,555.6 kWh.ton^{-1}),[50] it can be inferred that the Brazilian leather industry uses 1.72 TWh (1,721 MWh.year^{-1}) annually.

Table VI shows the potential net electricity through biogas conversion using different conversion technologies from thermal to electric energy. The biogas yield employed in the calculation is the result of the sum of the three groups of wastes. Furthermore, the percentage values result from the comparison between the energy consumption of Brazilian leather industry and the potential production using the biogas as energy source (energy recovery).

The systems considered for energy conversion were Internal Combustion Engines (ICE), Combustion Turbines (CT), Combined Cycle Combustion Turbines (CCCT) and Steam Rankine Cycles (SRC). Considering the closeness of efficiency values for thermal to electric conversion, the variations observed in generation potential are directly dependent on the potential raw energy (Table V). It is worth mentioning that losses related to the biogas production process, such as cleaning and conditioning, were not considered (process losses and operating costs). A complete and definitive assessment would require a detailed analysis considering plant maintenance and operating costs as well as the investment return rate.

Table V
Biogas raw energy potential from tannery wastes per metric ton of rawhide.

Substrate	**Raw Energy Potential (kWh.ton^{-1})**		
	Min.	Average	Max.
Rawhide	64.77	116.32	153.81
Limed pelts	14.13	89.78	226.75
Tanned Leather	44.20	73.02	104.39

Table VI
Biogas net electric power potential from tannery wastes per metric ton of rawhide.

	Net Electric Power (kWh.ton^{-1}) / (% of electric input)			
	ICE (η = 0.33)	**CT (η = 0.27)**	**CCCT (η = 0.32)**	**SRC (η = 0.255)**
Max.	160.0/30.9	130.9/25.3	155.2/29.9	123.7/23,9
Mid.	92.1/17.8	75.4/14.5	89.3/17.2	71.2/13.7
Min.	40.6/7.8	33.2/6.4	39.4/7.6	31.4/6.1

The results presented in Table V allow a maximum estimate of raw energy potential of 14.7% (min 0.9%) of total energy consumption of the leather production. Taking into account that 33.5% is the electricity fraction of the total energy consumption of a tannery, the conclusion that all biogas produced could be used in electrical generation is well founded. This statement makes sense as the vast majority of companies use biomass (wood) as fuel for steam production. The conversion of biogas into electricity would result in minimal process changes, but with considerable gains in terms of input saving and would make the adoption of these practices easier. On the other hand, the adoption of biogas production processes and its conversion into electricity can represent a reduction of between 6.1 and 30.9% of the total electricity consumed. This, depending on the scale factor, could represent significant economic values.

Conclusions

The assessment of different possibilities for biogas production through anaerobic digestion of various leather wastes focused on energy recovery reveals the potential for use of this fuel as an energy source for tanneries.

In terms of average calorific values and degradation potential (composition and generation rates of biogas) a positive statement is concluded, especially the application as thermal energy source or in power generation systems. The waste inventory shows that 115 kg of rawhide waste (trimmings + fleshings), 113.3 kg of limed waste (fleshings + trimmings) and 199.5 kg of chrome-tanned leather waste (wet-blue waste) are produced per ton of rawhide processed. A methane rich biogas can be obtained representing high heating values that range between 13.12 and 29.42 $MJ.Nm^{-3}$ (8.45 and 28.28 $MJ.kg^{-1}$).

The potential for biogas production vary from 2.4 and 910 $mL.g_{VS}^{-1}$, with an average value of 362 $mL.g_{VS}^{-1}$, representing for each beamhouse group of wastes an average biogas yield of 520, 534, 109 and 350 $mL.g_{VS}^{-1}$ for rawhide wastes, limed wastes, chrome tanned wastes and pre-treated wastes respectively.

Considering the total energy consumption of leather processes, it is estimated that the maximum energy provided using biogas can reach 10.3% (min 2.0%) of the total energy demand. When considering the electrical fraction of the total tannery demand for energy, the adoption of biogas production processes and its conversion into electricity can represent from 6.0 to 30.7% of the electricity consumption. This may represent significant economic values with reduction of other inputs and promote best industrial practice in tanneries.

It is concluded that the implementation of anaerobic processes for biogas production using tannery wastes presents a powerful tool for future technological developments in energy recovery and implementation of sustainable tannery practices.

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References

1. Pati, A., Chaudhary, R.; A review on management of chrome-tanned leather shavings: a holistic paradigm to combat the environmental issues. *Environmental Science and Pollution Research* **21**, 11266-11282, 2014.
2. Zupancic, G.D., Jemec, A.; Anaerobic Digestion of Tannery Waste: Semi-continuous and Anaerobic Sequencing Batch Reactor Processes. *Bioresource Tec*hnology **101**(1), 26-33, 2010.
3. Gomes, C.S., Piccin, J.S., Gutterres, M.; Optimizing adsorption parameters in tannery-dye-containing effluent treatment with leather shaving waste. *Process Safety and Environmental Protection* **99**, 98-106, 2016.
4. Piccin, J.S., Gomes, C.S., Mella, B., Gutterres, M.; Color removal from real leather dyeing effluent us*ing tannery waste as an adsorbent. Journal of Environmental Chemical Engineering* **4**, 1061–1067, 2016.
5. Priebe, G.P.S., Gutterres, M.; Olein production from pre-fleshing residues of hides in tanneries. *Latin American Applied Research* **42**, 71-76, 2012.
6. Tahiri, S., La Guardia, M.; Treatment and valorization of leather industry solid wastes: A review. *JALCA* **104**, 52-67, 2009.
7. Sundar, V.J., Gnanamani, A., Muralidharan, C., Chandrababu, N.K., Mandal, A.B.; Recovery and utilization of proteinous wastes of leathermaking: a review. *Rev. Environ. Sci. Biotechnol* **10**, 151-163, 2011.
8. Ferreira, M.J., Almeida, M.F., Pinho, S.C., Santos, I.C.; Finished Leather Waste Chromium Acid Extraction and Anaerobic Biodegradation of the Products. *Waste Management* **30**(6), 1091-1100, 2010.
9. Galarza, B.C., Cavello, I., Greco, C.A., Hours, R., Schuldt, M.M., Cantera, C.S.; Alternative Technologies for Adding Value to Bovine Hair Waste. *Journal of the Society of Leather Technologists and Chemists* **94**, 26-32, 2009;
10. Dettmer, A., Nunes, K.G.P., Gutterres, M., Marcílio, N.R.; Obtaining sodium chromate from ash produced by thermal treatment of leather wastes. *Chemical Engineering Journal* **160**, 8-12, 2010.
11. Kolomaznik, K., Adamek, M., Andel, I., Uhlirova, M.; Leather waste - Potential threat to human health and a new technology of its treatment. *Journal of Hazardous Materials* **160**, 514-520, 2008.

12. Yilmaz, O., Kantarli, I.C., Yuksel, M., Saglam, M., Yanik, J.; Conversion of leather wastes to useful products. *Resources, Conservation and Recycling* **49**, 436-448, 2007.
13. Godinho, M., Marcilio, N.R., Vilela, A.C.F., Masotti, L., Martins, C.B.; Gasification and combustion of the footwear leather wastes. *JALCA* **102**, 182-190, 2007.
14. Kolomaznik, K., Pecha, J., Barinova, M., Sanek, L.; Economic Aspects of Biodiesel Production from Tannery Waste Fats. *JALCA* **105**, 327-333. 2010.
15. Holm-Nielsen. J.B., Al Seadi. T., Oleskowicz-Popiel, P.; The future of anaerobic digestion and biogas utilization. *Bioresource Technology* **100**, 5478-5484, 2009
16. Fonseca, J.A., Teixeira, M.M.; Biological Reactors: Fundamentals and Applications. Lidel – Technical editions, Lisbon, Portugal, 483 p., 2007.
17. Vasudevan, N., Ravindran, A. D.; Biotechnological Process for the Treatment of Fleshing from Tannery Industries for Methane Generation. *Current Science* **93**(11), 192-194, 2007.
18. Amani, T., Nosrati. M., Sreekrishnan, T.R.; Anaerobic digestion from the viewpoint of microbiological, chemical and operational aspects — A review. *Environmental Reviews* **18**, 255-278, 2010.
19. Priebe, G.P.S., Kipper, E., Gusmão, A.L., Marcilio, N.R., Gutterres, M.; Anaerobic digestion of chrome-tanned leather waste for biogas production. *Journal of Cleaner Production* **129**, 410-416, 2016.
20. Speight, J.G. Synthetic fuels handbook: properties, process and performance 1st Ed., McGraw-Hill Companies Inc., Arima, Trinidad and Tobago, 2008.
21. Agustini, C.B., Lourenço Neto, W., Priebe, G.P.S., Costa, M., Gutterres, M.; Leather solid waste biodegradation and manipulation of methanogens chromium resistant microorganisms. *JALCA* **112**(1), 2017.
22. Tomaselli, M., Mora, R.; Heating power of hides and tannery residues. *Cuoio, Pelli, Materie Concianti* **68** (1), 73-78, 1992.
23. Basak, S.R., Rouf, M.A., Hossain, M.D., Islam, M.S., Rabeya, T.; Anaerobic digestion of tannery solid waste by mixing with different substrates. *Bangladesh Journal of Scientific and Industrial Research* **49**(2), 119-124, 2014.
24. Zupancic, G.D., Grilc, V.; Anaerobic Treatment and Biogas Production from Organic Waste, Management of Organic Waste. Dr. Sunil Kumar (Ed.), InTech Europe, Slavka Krautzeka 83/A, 51000 Rijeka, Croatia, 2012.
25. Gutterres, M., Mella, B.; Chromium in tannery wastewater. In: Sharma, S.K. (Ed.), Heavy Metals in Water: Presence, Removal and Safety. The Royal Society of Chemistry, v.1, pp. 315-344, 2014.
26. Gayatri, R., Sharma, A.K., Rajaram, R., Ramasami, T.; Chromium(III)-Induced Structural Changes and Self-Assembly of Collagen. *Biochemical and Biophysical Research Communications* **283**(1), 229-235, 2001.
27. Kameswari, K.S.B., Kalyanaraman, C., Porselvam, S., Thanasekaran, K.; Optimization of Inoculum to Substrate Ratio for Bioenergy Generation in Co-digestion of Tannery Solid Wastes. *Clean Technologies and Environmental Policy* **14**, 241-250, 2012.
28. Westerholm, M., Levén, L., Schnürer, A.; Bioaugmentation of syntrophic acetate-oxidizing culture in biogas reactors exposed to increasing levels of ammonia. *Applied and Environmental Microbiology* **78** (21), 7619-7625, 2012.
29. Deublein. D., Steinhauser, A.; Biogas from waste and renewable resources 2nd Ed., Verlag GmbH & Co. KGaA, Weinheim, Germany, 2008.
30. Mannucci, A., Munz, G., Mori, G., Lubello, C.; Anaerobic treatment of vegetable tannery wastewaters: A review. *Desalination* **264**, 1-8, 2010.
31. Wiemann, M., Schenk, H., Hegemann, W.; Anaerobic Treatment of Tannery Wastewater With Simultaneous Sulphide Elimination. *Water Research* **32**(3), 774-780, 1998.
32. Chou, H., Huang, J., Chen, W., Ohara, R.; Competitive reaction kinetics of sulfate-reducing bacteria and methanogenic bacteria in anaerobic filters. *Bioresource Technology* **99**, 8061-8067, 2008.
33. Banu, J.R., Kaliappan, S.; Treatment of tannery wastewater using hybrid upflow anaerobic sludge blanket reactor. Journal of Environmental Engineering Science **6**, 415-421, 2007.
34. Yoda, M., Kitagawa, M., Miyaji, Y.; Long term competition between sulfate-reducing bacteria and methane producing bacteria in anaerobic biofilm. *Water Research* **21**, 1547-1556, 1987.
35. Harada, H., Uemura, S., Momonoi, K.; Interaction between sulfate- reducing bacteria and methane-producing bacteria in UASB reactors fed with low strength wastes containing different levels of sulfate, *Water Resource* **28**(2), 355-367, 1994.
36. Vaiopoulou, E., Gikas, P.; Effects of Chromium on Activated Sludge and on the Performance of Wastewater Treatment Plants: A Review. *Water Research* **46**, 549-570, 2012.
37. Pillai, P., Archana, G;. A novel process for biodegradation and effective utilization of chrome Shavings, a solid waste generated in tanneries, using chromium resistant Bacillus subtilis P13. *Process Biochemistry* **47**, 2116-2122, 2012.
38. GTRI, Georgia Tech Research Institute. Biogas Utilization Handbook. Atlanta, Georgia 30332, 133 p., 1988.
39. Gutterres, M.; Analysis of vegetable tannin absorption during the tannage of hide/hide powder. *JALCA* **102**(7), 216-221, 2007.
40. Yadvika, S., Sreekrishnan, T.R., Kohli, S., Rana, V.; Enhancement of Biogas Production from Solid Substrates Using Different Techniques - A Review. *Bioresource Tec*hnology **95**, 1–10, 2004.
41. Fantozzi, F., Buratti, C.; Anaerobic digestion of mechanically treated OFMSW: Experimental data on biogas/methane production and residues characterization. *Bioresource Technology* **102**, 8885-8892, 2011.
42. Ahmad J., Ansari, T.A.; Biogas from Slaughterhouse Waste: Towards an Energy Self-Sufficient Industry with Economical Analysis in India. *Journal of Microbial and Biochemical Technology* **12** (1), 2012.
43. Urbaniak, M.; Gaseous Efficiency Of Methane Fermentation Of Chromium-Free Tannery Wastes. *Journal of the Society of Leather Technologists and Chemists* **91**, 5-62, 2006.
44. Klass, D.L.; Biomass for Renewable Energy, Fuels, and Chemicals 1st Ed., Academic Press, San Diego, California, USA, p.445 – 491, 1998.

45. Salomon, K.R., Lora, E.E.S.; Estimate of the electric energy generating potential for different sources of biogas in Brazil. *Biomass and Bioenergy* **33**, 1101-1107, 2009.
46. Rao, P.V., Baral, S.S., Dey, R., Mutnuri, S.; Biogas generation potential by anaerobic digestion for sustainable energy development in India. *Renewable and Sustainable Energy Reviews* **14**, 2086-2094, 2010.
47. Pulkrabek, W.W.; Engineering Fundamentals of the Internal Combustion Engines. University of Winsconsin, Prentice Hall, Upper Saddle River, New Jersey 07458.
48. Boyce, M.P.; Gas turbine engineering handbook 3rd Ed. Elsevier, 30 Corporate Drive, suite 400, Burlington, MA01803, USA, 2006.
49. Environmental Protection Agency – USEPA. Turning a liability to an asset: A landfill gas-to-energy project development handbook, Landfill Methane Outreach Program. EPA 430-8-96-0004, Energy Efficiency and Renewable Energy Section, 401 M Street, SW, Washington DC 20460, USA, 1996.
50. Gutterres, M., Schneider, P.S., Vielmo, H., Marcílio, N. R., Danieli, R., Conceição, S. T.; Using natural gas to supply energy using co-generation. *Leather International* **206**(4742), 25-30, 2004.
51. Drapcho, C.M., Nhuan, N.P., Walker, T.H.; Biofuels engineering process technology 1st Ed., McGraw-Hill Companies Inc., 2008.
52. Al Seadi, T.; Biogas Handbook. University of Southern Denmark Esbjerg, Niels Bohrs Vej 9-10, DK-6700 Esbjerg, Denmark, 2008.
53. Castell, A., Medrano, M., Cabeza, L.F., Morera, J.M., Bartolí. E.; Economic Viability of Using Biogas from Tannery Wastes in Molten Carbonate Fuel Cells. *Journal of the Society of Leather Technologists and Chemists* **94**, 93-97, 2009.
54. Roe, Stephen M., Joel Reisman, Randy Strait, Michiel Doorn, E. H. Pechan, Rancho Cordova, Work Assignment No, and Susan A. Thorneloe.; Emerging Technologies for the Management and Utilization of Landfill Gas. Citeseer, 1998.
55. Kohl, A.L., Nielsen, R.; Gas Purification, 5th Ed., Gulf Publishing Co., Houston, Texas, pp. 279-326, 1997.
56. Aguilar-Virgen, Q., Taboada-González, P., Ojeda-Benítez, S., Cruz-Sotelo, S.; Power generation with biogas from municipal solid waste: Prediction of gas generation with in situ parameters. *Renewable and Sustainable Energy Reviews* **30**, 412–419, 2014.
57. Environmental Protection Agency – USEPA. A manual for developing biogas systems at commercial farms in the United States. 2nd Ed., EPA-430-B-97-015, AgSTAR Program - Managing Manure with Biogas Recovery Systems, Washington DC 20460, USA, 2004.
58. Kapdi, S.S., Vijay, V.K., Rajesh, S.K., Prasad, R.; Biogas scrubbing, compression and storage: perspective and prospectus in Indian context. *Renewable Energy* **30**, 1195-1202, 2005.
59. Bocci, E., Di Carlo, A., McPhail, S.J., Gallucci, K., Foscolo, P.U., Moneti, M., Villarini, M., Carlini, M.; Biomass to fuel cells state of the art: A review of the most innovative technology solutions. *International Journal of Hydrogen Energy* **39**, 21876-21895, 2014.
60. Barros, R.M., Filho, G.L.T., Silva, T.R.; The electric energy potential of landfill biogas in Brazil. *Energy Policy* **65**, 150-164, 2014.
61. Environmental Sanitation Technology Company - CETESB. Biogas: projects and research in Brazil. State Environmental Department, 184p., São Paulo, Brazil, 2006.
62. Bezama, A., Szarka, N., Navia, R., Konrad, O., Lorber, K.E.; Lessons learned for a more efficient knowledge and technology transfer to South American countries in the fields of solid waste and contaminated sites management. *Waste Management and Res*earch **25**, 148-161, 2007.
63. Buljan. J., Ludvik. J., Reich. G.; Mass Balance in Leather Processing. United Nations Industrial Development Organization - UNIDO, Regional Programme for Pollution Control in the Tanning Industryin South-East Asia, US/RAS/92/120, 2000.
64. Stoop, M.L.M.; Water management of production systems optimised by environmentally oriented integral chain management: case study of leather manufacturing in developing countries. *Technovation* **23**, 265–278, 2003.
65. Thangamani, A., Parthiban, R.; Management if industrial tannery solid waste for biogas production. Lambert Academic Publishing GmbH & CO, Saarbrücken, Germany, 2011.
66. Themelis, N.J., Ulloa, P.A.; Methane generation in landfills. *Renewable Energy* **32**, 1243-1257, 2007.
67. Lalitha, K., Swaminathan, K.R., Padma Bai, R.; Kinetics of Biomethanation of Solid Tannery Waste and the Concept of Interactive Metabolic control. *Applied Biochemistry and Biotechnology* **47**, 73-87, 1994.
68. Pulavendran, S., Ganesh, R., Thangamani, A., Thirumaran, K., Ramanujam, R.A.; Anaerobic Digestion of Animal Glue Industry Solid Wastes. *Journal of the Society of Leather Technologists and Chemists* **89**, 67-70, 2004.
69. Cenni. F.; Dondo. G.; Tombetti. F.; Anaerobic Digestion of Tannery Wastes. *Agricultural Wastes* **4**, 241-243, 1982.
70. Shanmugam, P., Horan, N.J.; Optimising the Biogas Production from Leather Fleshing Waste by Co-digestion with MSW. *Bioresource Technology* **100**, 4117-4120, 2009.
71. Dhayalan, K., Fathima, N.N., Gnanamani, A., Rao, J.R., Nair, B.U., Ramasami, T.; Biodegradability of Leathers through Anaerobic Pathway. *Waste Management* **27**, 760-767, 2007.
72. Perry, R.H., Green, D.W.; Perry's Chemical Engineering Handbook 5th Ed., McGraw Hill, New York, 1980.
73. Boundy, B., Diegel, S.W., Wright, L., Davis, S.C.; Biomass Energy Data Book 4th Ed., U.S. Department of Energy, Oak Ridge, Tennessee, USA, 2011.
74. Redwood, M.; Corporate social responsibility and the carbon footprint of leather. *Journal of the Society of Leather Technologists and Chemists* **97**, 47 - 55, 2013.
75. Brazilian Leather Book, Center of Tannery Industries of Brazil, Available at: http://brazilianleather.com.br/wp-content/uploads/2014/04/bl-book-mobile-port.pdf, accessed on June 27, 2016.