2020 IULTCS Young Leather Scientist Grant

Identification: YLSG2020_applicantname

COMPLETE APPLICATION FORM (click application area)

☐ Basic Research ☐ Machinery/Equipment ⊗ Environmental/Sustainability

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By submitting this application, I commit to develop the project as outlined in the attached Research Project Plan and to complete a written report by February 28, 2021 with the following items:

1) Introduction
2) Materials and Methods
3) Results and Discussion
4) Conclusion
5) Suggestion for Future Work
6) References

2) Research Project Plan outline – Maximum 3 pages

Title: HYDROCARBONS RELEASE DURING THE BIODEGRADATION OF SOLID WASTE FROM TANNERIES FOR BIOGAS PRODUCTION

Introduction:

Anaerobic digestion (AD) of organic waste is a method of producing renewable energy, i.e. biogas, with simultaneous waste treatment. Despite the fact that biogas is widely used, in many countries in the southern hemisphere biogas is still not properly used and there is still a lack of scientific contributions and proper utilization, especially in the production of biogas from tanned waste from tanneries [1]. Biogas energy has the advantage of not having geographical limitations or requiring new technology for producing energy [2]. Biogas production is the first category of renewable energy where potential process innovations are sought and analyzed. Within this category a significant number of studies have been published over the last few years. Topics address various ways of enhancing, controlling and optimizing AD and improving biogas yield and/or biogas quality. Crucial points for improving the efficiency of biogas production that are frequently emphasized throughout the literature are associated with favoring access to cheap raw materials [3]. However, many biogas plants operate at sub-optimal loading rates to ensure a stable process at the expense of digester productivity [4]. There are issues during AD, such as process instability, long lag time, low biogas yield, and methane concentration. There are a number of factors that affect AD performance including environmental conditions (e.g., temperature, pH, carbon/nitrogen – C/N ratio), process by-products (e.g., volatile fatty acids and ammonia), and physical and chemical properties of the feedstock (e.g., VS (volatile solids), nutrient content, complex chemical structure) [5]. Biomass is a sustainable renewable energy source including a broad range of organic waste such as animal manure, forestry and agricultural residues, municipal and industrial solid waste [2]. Tannery wastes consist of wastewater, solid waste mainly shavings and sludge. The on-site anaerobic treatment of solid tannery waste to produce biogas has become an attractive option for the tannery industry, treating its waste avoiding its disposal in landfill and using it energetically, contributing to the prevention of global warming [6].

Research carried out on this issue has studied AD of tannery solid waste where thermophilic AD of fleshing, hide trimmings and wastewater sludge were investigated [6], with chromium, in 1,160 mL vessels; The specific methane production potential was estimated to be 0.617 m^3/kg of volatile suspended solids (VSS) for tannery waste sludge, 0.377 m^3/kg for tannery waste trimmings and 0.649 m^3/kg for tannery waste fleshing. Different proportions of waste fleshing and primary sludge were subjected to mesophilic AD in 100 mL bottles [7]; VS destruction between 41 and 52%, specific gas production between 0.419 and 0.635 L/g volatile solids feed and methane yield between 71 and 77% were achieved. In the AD of fleshing and mixtures of primary and secondary sludge in 650 mL bottles [8], biogas generated per gram of VS added was on average 410 mL/g. In mesophilic AD of substrates (soybean meal, hydrolyzed collagen, hide powder and wet-blue leather shavings) containing different concentrations of chromium in 300 mL bottles [9], the maximum rate of biogas production reached a yield of 162.2 mL/g of VSS and a methane fraction of 73.7%. These researches do not analyze in depth the initial and limiting stage of the process, the hydrolysis stage.

Some of our previous researches were focused on studying the feasibility of the AD of mixtures of shavings and sludge in co-digestion processes, addition of tannery wastewater for nutritional supplementation, assessment of a semi-pilot scale procedure, cost saving analysis, the influence of the presence of the tanning agent and high-throughput sequencing. Tannery waste with chromium presence proved to be significantly more suitable for AD than waste without chromium. Biogas yields between 21 and 30 mL/gVSS, maximum methane content of 59% v/v, and a total organic carbon (TOC) reduction between 68 and 76% were obtained. A linear consistency of methane production was found in the assessed scale-up and a two-fold biodegradation rate to a five-fold volume of treated waste. In the conditions studied in semi-pilot scale, a midsize tannery could reduce 6.8% of electric and 1.6% of thermal energy consumption besides the great cost savings of disposal of this waste. The highest amount of biomethane observed was related to the archaeal family *Methanosaetaceae* and bacterial order *Bacteroidales* [10,11,12].

Further studies focus on adding other residues for nutritional supplementation in addition to studies on the application of digestate as a fertilizer.

However, the quantities of biogas produced by tannery residues are still lower when compared to other more bioavailable residues, such as food residues [13], where the biogas production reaches up to 15 times greater. Once anaerobic digestion is fully established, as there is methane production, a gap remains in the initial stage of hydrolysis, where the organic load of the residues does not appear to be completely broken down into smaller hydrocarbons to be bioavailable for microorganisms.

Objectives:

The aim of this study is to evaluate the evolution of the hydrocarbon release, the energy efficiency and the efficiency of the treatment of the waste of the AD of the solid waste of tanneries. The originality of this study is gaining the innovation of how chemical, physical and environmental parameters work is an important step in improving the efficiency and process stability of anaerobic digesters to be able to adjust in which step of the batch process the continuous process must be designed and which pretreatments are most suitable to increase the carbon depletion of the waste.

Methods:

Batch digester and Periodic sampling: Chromium-tanned leather shavings and sludge with chromium salts will be incubated in 20 batch co-digestion assays. The ratio of the quantity of sludge/shavings of 25 mL/1 g in the assays is adapted to the proportional amount of waste produced in ensured favorable conditions. The bioreactors will be incubated at 35 °C in a microorganism culture oven. As the analyses are destructive and require a large volume of sample, every 10 days a duplicate of bioreactors will be opened for collection of the liquid and precipitate reaction medium, starting on day 0 and ending on day 100.

Biogas monitoring: Biogas volume will be measured every 2 days by water displacement with a device based on the Mariotte principle [10]. The proportion of biogas components will be accessed weekly through a gas chromatograph (GC-2014 Shimadzu, Japan) equipped with a ShinCarbon column (ST 100/120 2 m 1 mm ID 1/16" OD Silco) and TCD detector. Helium (White Martins 5.0, United Kingdon) will be used as the carrier gas at a flow rate of 10 mL/min. The injector and detector temperatures will be held at 200 and 250 °C, respectively. The oven program will be: 40 °C (3 min), ramp at 15 °C/min to 150 °C, and hold for 0.67 min.

Monitoring waste destruction: Total organic carbon (TOC), inorganic carbon (IC) and total nitrogen (TN) will be measured in a TOC analyzer (Shimadzu TOC-L, Japan) equipped with a TN measuring unit (Shimadzu TNM-L) and 8-port sampler (Shimadzu OCT-L). Biological oxygen demand (BOD5) will be manometrically measured with a VELP Scientifica BOD Sensor System 6 (VELP, Brazil). Solid contents (volatile suspended solids (VSS) and volatile dissolved solids (VDS)) will be determined with gravimetric method To determine the amount of hydrocarbons in tanned wastes, a FT-NIR Frontier spectrometer (Perkin Elmer), equipped with a quartz beamspliter, an air cooled NIR source and an InGaAs detector will be employed. Transmission absorbance spectra will be obtained in the wavenumber range from 14,000 to 3500 cm^{-1}, from sample in a 9.5 mm internal diameter glass cylindrical cell using a nominal resolution of 8 cm^{-1} and cumulating 32 scans per spectrum. A carbon-based mass balance will be conducted to calculate the percentage of carbon conversion throughout the experiment, taking into account the initial and final TC (converted to moles) and the carbon that left the system in the biogas (CH_4 and CO_2, in moles).

Hypothesis/Expected Results:

- Alternative for the use of the organic and nutritional load of solid tannery residues, instead of their disposal in landfills without any use, usual in Brazil;

- Energy use of solid tannery waste;

- Stages that the degradation process of tannery waste can be separated;

- Hydrocarbon release throughout the assays and relationship between hydrocarbon release and biogas production;

- Biogas cumulative production per gram of VSS added in the biodegradation tests of tannery waste;

- Mean biogas composition and daily production during the assays;

- Organic and inorganic load of the residues throughout the assays.

Research benefit for the local or global leather industry (one sentence only):

The main benefits for the Brazilian leather industry is the proposal of energetic using their waste in order to prevent them from being disposed of in landfills, the most common destination in the Country. In addition to all the contamination risks involved, disposal in landfills does not utilize of the organic and nutritional waste load. The main benefits for the global leather industry will be the description of the entire anaerobic biodegradation process of its residues, especially the initial limiting stage, which will make it possible to direct pre-treatments to the process that will make it economically viable and attractive.

Literature:

[1] C. Rieke, D. Stollenwerk, M. Dahmen, M. Pieper, Modeling and optimization of a biogas plant for a demand-driven energy supply, Energy. 145 (2018) 657–664. doi:10.1016/j.energy.2017.12.073.

[2] B. Ozer, Biogas energy opportunity of Ardahan city of Turkey, Energy. 139 (2017) 1144–1152. doi:10.1016/j.energy.2017.07.052.

[3] W.M. Budzianowski, A review of potential innovations for production , conditioning and utilization of biogas with multiple-criteria assessment, Renew. Sustain. Energy Rev. 54 (2016) 1148–1171. doi:10.1016/j.rser.2015.10.054.

[4] A.J. Ward, E. Bruni, M.K. Lykkegaard, A. Feilberg, A.P.S. Adamsen, A.P. Jensen, A.K. Poulsen, Real time monitoring of a biogas digester with gas chromatography, near-infrared spectroscopy, and membrane-inlet mass spectrometry, Bioresour. Technol. 102 (2011) 4098–4103. doi:10.1016/j.biortech.2010.12.052.

[5] C. Mao, X. Wang, J. Xi, Y. Feng, G. Ren, Linkage of kinetic parameters with process parameters and operational conditions during anaerobic digestion, Energy. 135 (2017) 352–360. doi:10.1016/j.energy.2017.06.050.

[6] G.D. Zupančič, A. Jemec, Anaerobic digestion of tannery waste: Semi-continuous and anaerobic sequencing batch reactor processes, Bioresour. Technol. 101 (2010) 26–33. doi:10.1016/j.biortech.2009.07.028.

[7] A. Thangamani, S. Rajakumar, R.A. Ramanujam, Anaerobic co-digestion of hazardous tannery solid waste and primary sludge: Biodegradation kinetics and metabolite analysis, Clean Technol. Environ. Policy. 12 (2010) 517–524. doi:10.1007/s10098-009-0256-x.

[8] S.B.K. Kanchinadham, C. Kalyanaraman, T. Kumarasamy, Optimization of organic load for co-digestion of tannery solid waste in semi-continuous mode of operation, Clean Technol. Environ. Policy. 17 (2015) 693–706. doi:10.1007/s10098-014-0826-4.

[9] G.P.S. Priebe, E. Kipper, A.L. Gusmão, N.R. Marcilio, M. Gutterres, Anaerobic digestion of chrome-tanned leather waste for biogas production, J. Clean. Prod. 129 (2016) 410–416. doi:10.1016/j.jclepro.2016.04.038.

[10] C. Agustini, M. da Costa, M. Gutterres, Biogas production from tannery solid wastes e Scale-up and cost saving analysis, J. Clean. Prod. 187 (2018) 158–164. doi:10.1016/j.jclepro.2018.03.185.

[11] C.B. Agustini, F. Spier, M. da Costa, M. Gutterres, Biogas production for anaerobic co-digestion of tannery solid wastes under presence and absence of the tanning agent, Resour. Conserv. Recycl. 130 (2018) 51–59. doi:10.1016/j.resconrec.2017.11.018.

[12] C.B. Agustini, M. da Costa, M. Gutterres, Biogas from Tannery Solid Waste Anaerobic Digestion Is Driven by the Association of the Bacterial Order *Bacteroidales* and Archaeal Family *Methanosaetaceae*, Appl. Biochem. Biotechnol. 192 (2020) 482-493. doi: 10.1007/s12010-020-03326-6.

[13] X. Fei et al., Enhancement effect of ionizing radiation pretreatment on biogas production from anaerobic fermentation of food waste, Radiat. Phys. Chem. 168 (2020) 108534. doi: 10.1016/j.radphyschem.2019.108534.