Leather industry waste material energetic valorisation by anaerobic digestion thanks to a Multi-Phase Process

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Abstract. Consumption enhancement brings forth large amounts of waste materials, which are now considered to be reusable or can be used as resources. By natural biodegradation, the organic waste materials release greenhouse gases, especially methane (a gas whose greenhouse effect is more than 20 times greater as compared to the carbon dioxide). For the tanning industry, embracing environmentally friendly technologies of recycling waste materials as an energetic resource has become an attractive option. This paper here aimed at obtaining biogas by the anaerobic fermentation of the waste materials from the leather industry. The technology put in place is a multi-phase process of anaerobic digestion, characterized by a C/N ratio lower than 5. The process sets out a phase of incubation and conditioning anaerobic microorganisms, because of the high concentrations of ammonia (NH_4^+/ NH_3) – more than 9,000 mg L^{-1} – and of a low C/N ratio. We used two phases of anaerobic digestion, because the acidogenic and methanogenic microorganisms have got different rates of growth and an optimal pH: 4.0-6.0 and 6.5-8.0, respectively. Phase separation enables us to optimize the hydraulic retention time and the organic loading rate. The initial substances are incessantly decomposed into substances with smaller molecules, each stage involving specific groups of microorganisms. To this end, we have made an experimental plant, composed of 3 digesters, which carry out hydrolysis, acidogenesis and methane genesis processes. In terms of yield, the outcomes of the experimental plant are very good, 88% of the amount of COD being turned into biogas.
Key Words: anaerobic digestion, biogas, acidogenic and methanogenic microorganisms, C/N ratio.

Introduction. One of the most important environment problems of today is the fact that the quantity of organic waste grows constantly. In many countries the sustainable management of waste as well as the prevention to pile up waste and to reduce its quantity became priorities of major politics and represents an important contribution to the commonly made effort to reduce pollution, emission of greenhouse gases and the diminishing of climate changes on world level (National waste management strategy-2013).

The tanning industry produces huge quantities of organic waste such as meat remains, cuttings, and stripes or parts of raw skin as well as sludge as a result of the treatment of waste water. The waste from raw skin can be changed into useful products. The sludge of waste water proves much more problematic. The conventional manipulation of sludge means that you have to store the waste. By biodegrading, the organic waste emits hothouse gas, especially methane (a gas with a hothouse effect 20 times higher than carbon dioxide) and smaller quantities of nitrous oxide (300 times more than hothouse effect). We have to add the smell and the problem of soil contamination (http://www.unido.org/fileadmin/import/userfiles/timminsk/leatherpanel14ctcwastes.pdf).

For the tanning industry it is a necessity to adopt a new ecological recycling technology of this waste and in the same time, by using such technology, the waste resulted can be used for creating new energetic resources. Thus they are going to adopt a cleaning technology based on anaerobic digestion of the waste in watery environment for getting biogas (Seadi et al 2008).

The anaerobic digestion of biodegradable waste for tanning workshops. The biogas that is obtained in the anaerobic digestion process is cheap and is a source for regenerating energy as this procedure produces combustion neutral CO_2 and offers the opportunity to treat and to recycle a large variety of waste, of various bio-waste, of organic waste waters coming from industry and sludge in a sustainable and „environment friendly" way. In the same time biogas brings about a great many benefits for the social and economic branches as well as at the level of the whole society (Mocanu et al 2016).

Conditioning of the raw matter. Before the raw material is introduced into the installation it is chopped and water is added in order to homogenize and fluidize it and afterwards it is pumped into the installation. The digestion process goes faster when particles are smaller. Nevertheless the dimensions of particles influence the digestion time but it does not determine necessarily a higher quantity of methane (Seadi et al 2008).

The anaerobic digestion is a biochemical process during which the complex organic matter is decomposed in various types of microorganisms without the help of oxygen. By performing these processes under control, the organic matter is stabilized as fermented sludge and so they get biogas that is a mix of methane (50-65%), water steam (5%), hydrogen sulphide (up to 1%) and carbon dioxide (Seadi et al 2008).

The efficiency of the anaerobic digestion depends on a few critical parameters. It is therefore important to ensure development conditions for anaerobic microorganisms. The functioning of the process depends thus on the existence of an optimum medium for the development of methanogen microorganisms. This means a neutral pH, a constant temperature, total lack of oxygen (methanogenic bacteria are strictly anaerobic), a certain number of nutrients and the homogenization of the content of the fume hood. The process is also influenced by the existence and the quantity of inhibitors (Seadi et al 2008).

There are two possible temperature regimes in which the anaerobic digestion can be carried out: mesophilic, about 37°C and thermophile, about 55°C. Although the efficiency of the degrading of the substrates is the same with both temperatures, the thermophile way has the advantage of a higher degradation speed of the organic matter and needs a retention period of about 15 days, a half it needs for a mesophilic functioning, that means that the volume of the fume hood needed is two times smaller resulting in lower investment costs. The thermophile conditions also ensure the cleanness of the waste. On the other hand, the thermophile ways of functioning is less robust and more sensitive towards the variation of operating conditions. Temperature variations and the growth of ammonium chloride concentrations have a negative effect on the production rate of methane. A high temperature needs extra consumption of energy (Zupancic & Jemec 2010).

The multiphase anaerobic fume hood. Out of practical reasons we introduced the reactors into a thermostatic bath of de 1.2m x 0.5m (Figure 1). The internal environment is kept at a pH of 4.0-5.0 in the acidogenic reactor and 7.0-8.0 the methanogen reactors by dosing hydrogen chloride and solution of caustic soda depending on the pH sensors, if necessary (Mocanu et al 2016).

The biogas installation (multiphase anaerobic fume hood) is made of a stainless steel vat with heating insulation where the reactors are introduced (the acidogenic reactor and methanogen reactors 1 and 2) made of stainless steel, the lids are bell-shaped to gather the biogas (Figure 2).

The temperature is given and maintained by warm water that is produced in a boiler and recirculated by means of a pump. The reactors are endowed with a vertical mixing system and pH and temperature sensors.

In order to simplify the installation, the reactors are identical but as the hydrolyze speed is twice compared to the methanogenic digestion two methanogenic reactors with one acidogenic reactor were introduced. The mix introduced in the first reactor determines the cascade evacuation of the reaction compounds after the methanogenic reactor 2 and then we get the final deposit (Mocanu et al 2016). The circulation takes place in the final tank (R3F) at the entrance in the reactor 1.

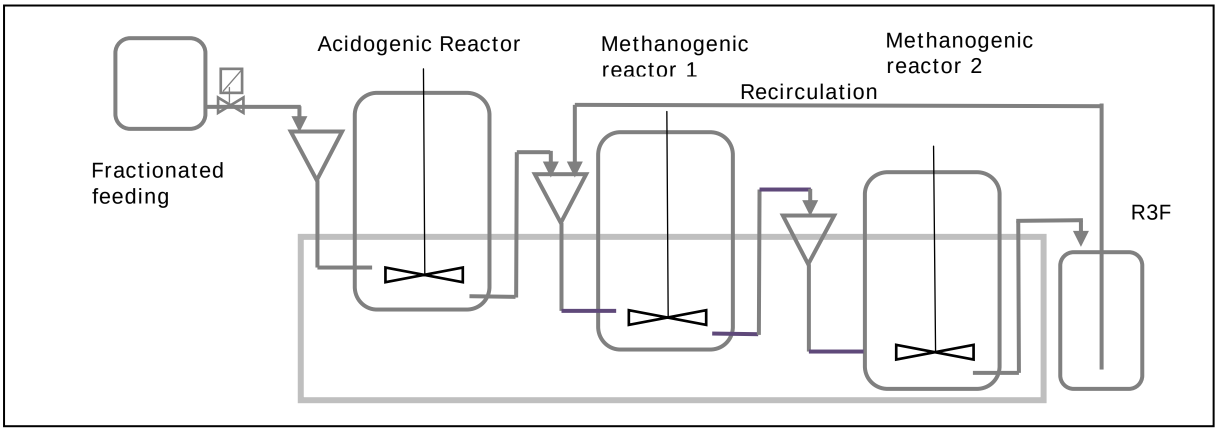

Figure 1. Biogas installation (multiphase anaerobic fume hood) scheme (Mocanu et al 2016).

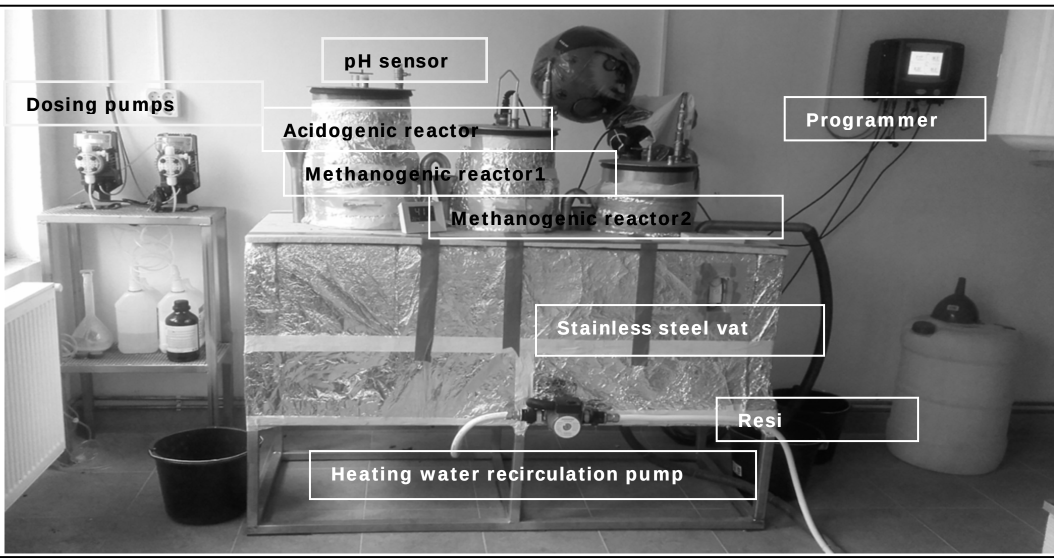

Figure 2. Biogas installation (multiphase anaerobic fume hood).

Description of the process. There is a discontinuous anaerobic digestion process that is an alternative to the conventional system where the fume hood can be fed directly with waste and thus eliminating the necessity of a buffer tank. This process increases the global methane output.

The designed installation is based on a technology with an anaerobic digestion multiphase process, with discontinuing feeding and circulation. We adopted this solution in order to separate the acidogenic phases from the methanogenic ones and to have control pH and temperature more efficiently. For the methanogenic phase we designed two digesters in order to regulate the methanogenic digestion time compared to the acidogenic one and to raise the output of biogas transformation.

The waste from tanning used in the anaerobic installation has a C/N ratio under 5, thus the process needs an adaptation phase of the anaerobic microorganisms because of the high concentration of ammonium chloride (NH_4^+/NH_3) of more than 1,100 mg L^{-1}. In the process by digestion of the organic matter into methane gas, carbon dioxide and ammonium products, the organic carbon (CBO_5) is reduced and the concentration due to ammonium products is increased in the mix in the reactor, thus the C/N ratio becomes even smaller.

The ammonium results from the biological degradation of protein matter in an anaerobic environment. The ammonium that was absorbed in bacterium cells may alter the intracellular pH, it may inhibit the activity of enzymes and increase the need of energy to entertain the cell (Chen et al 2008). A large quantity of ammonium causes a severe inhibition or the failure of anaerobic digestion, having important consequences both for the stability of the process and for its productivity. The fact that the volume of the methanogenic reactor was allocated into 2 smaller reactors causes that the load of ammonium products gets smaller in the first methanogenic reactor and prolongs the optimum time of biogas production. Nevertheless, the process conditions are of great importance on the inhibition effect of the ammonium as we can clearly see in the "inhibiting concentrations" that are quoted in the specialty literature varying from less than 2 g L^{-1} to 14 g L^{-1} total nitrogen from ammoniac (Banoli et al 2014). The temperature (Angelidaki & Ahring 1994), pH, the inoculum and the adaption (Van Velsen 1979) are the main factors that are taken into account for a correct working of the anaerobic digestion. In this work we are going to describe a multiphase anaerobic digestion on experiment scale to convert into biogas products from the secondary tanning industry into nitrogen and biogas used to produce energy from reusable sources.

Material and Method. Waste was collected from a leather processing factory in Bucharest. The waste was characterized by analyses, with standard methods, the substrates were gathered and chilled at -4^{o}C prior to the analysis and other tests. The material chosen to serve as substrate to produce biogas were solid waste of leather that was cleaned from fat and traces of hair.

Preparation of the samples. In order to carry out the hydrolysis, the waste is cut into 2-5 mm pieces (in order to make the matter more digestible) in an electric chopping device, then it was mixed with water at a ratio of 1 to 10 and then introduced into a reactor of acidogenic digestion in order to accelerate decomposition (Craciun et al 2016).

The pre-digestion material was developed in the hydrolysis reactor and acidogenic digestion by introducing the basic and acid substrate in order to stabilize the pH at a value of ≤4.5. Acetic acid and industrial ethylic alcohol were used in various ratios as substrate in order to maintain the C/N and pH ratio (Mocanu et al 2016).

In order to start the process in the methanogenic reactors we introduced active household sludge that was thickened to 4-6%. This sludge contains the whole range of anaerobic microorganisms, including methanogenic bacteria.

On the samples taken from the reactors 1 and 2 we carried out the following analyses s: CCO-Cr (SR ISO 6060-1996), total nitrogen (STAS 7312-83), ammonium nitrogen (SR ISO 7150/1-01) and total phosphorus (SR EN ISO 6878).

We determined the quality of biogas by means of a portable analyzer (Biogaz 5000).

Results and Discussion. The tests were carried out for 10 weeks, between 9 March 2016 and 16 May 2016; this period of time includes the first and the second part of the experiment with the support of an anaerobic multiphase fume hood. In order to feed the fume hood, we used 0.15 kg substrate day^{-1} at a volume of 1.5 L water.

The experiments were carried out in the mesophilic interval for temperatures of 36-38°C, an interval where the pH was maintained in the optimum functioning zone of 7.5-8 and did not need to be corrected from the outside, save the acidogenic reactor, where once a week (average) we had to reduce the pH from 5 to 4 with phosphoric acid, acetic acid or chlorohydrin acid. We also added carbon by means of technic ethylic alcohol in the first methanogenic reactor.

We daily registered the data concerning pH, the temperature in thermostatic areas, the temperature and concentration of de CO_2 in the environment as well as the electric energy needed to maintain the temperature constant.

The fact that the efficiency to produce biogas diminished was mainly due to the piling up of the ammonium products that slowly decreased the C/N ratio from 5 to 2 or lower as this process was spoiled at this level, mainly in methanogen reactor 2. By regulating the process in a way that should keep the ratio constant or even to increase it (by eliminating the nitrogen ammonium) it would be possible to get a constant functioning of the fume hood.

We took samples every week at the exit of the reactors and calculated the concentrations of CCO-Cr, total nitrogen, ammonium nitrogen and total phosphor (the first part of experiment - working period: 09.03.2016-13.04.2016).

From the biogas produced we made determinations to measure the CH_4, CO_2 and O_2 concentration in order to determine the quality and the efficiency of the anaerobic digestion process. To this end we used a portable analyzer (Biogaz 5000).

We could show the variations of concentration of dissolved organic matter that was chemically oxidable (CCO-Cr) at the crossover from reactor 1 to reactor 2 and at the evacuation depending on the time. We could state that the organic carbon, that was dissolved in reactor 1 by the hydrolysis of the introduced raw material, increased in time, it partially decreased in reactor 2 and then at the exit by building biogas (Figure 3, left).

Figure 3 (right) shows the variation of total nitrogen concentration (Nt) at the passage from the reactor 1, from reactor 2 and its evacuation depending on time. The value of total nitrogen increased in time by accumulation.

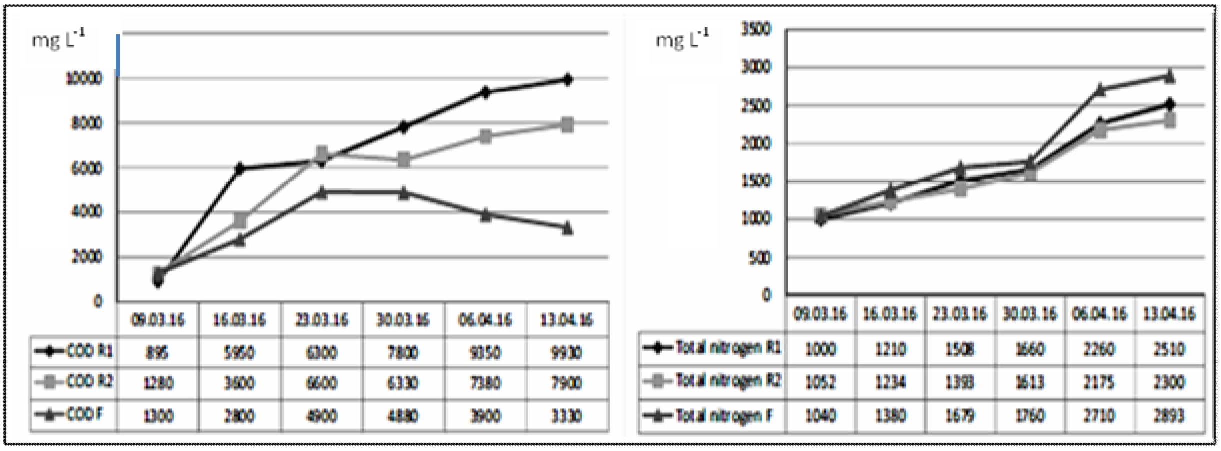

Figure 3. CCO-Cr concentration variation (left) and total nitrogen (right) in reactors 1 and 2.

Figure 4 (left) shows the variation of concentration of ammonium nitrogen (NH^{4+}) from the reactor 1, from reactor 2 and its evacuation depending on time. We could find that ammonium nitrogen came out by anaerobic alteration of total organic having a relatively constant concentration in reactor 1, and then an accumulation occurs in reactors 2 and tank 3 F (R3F).

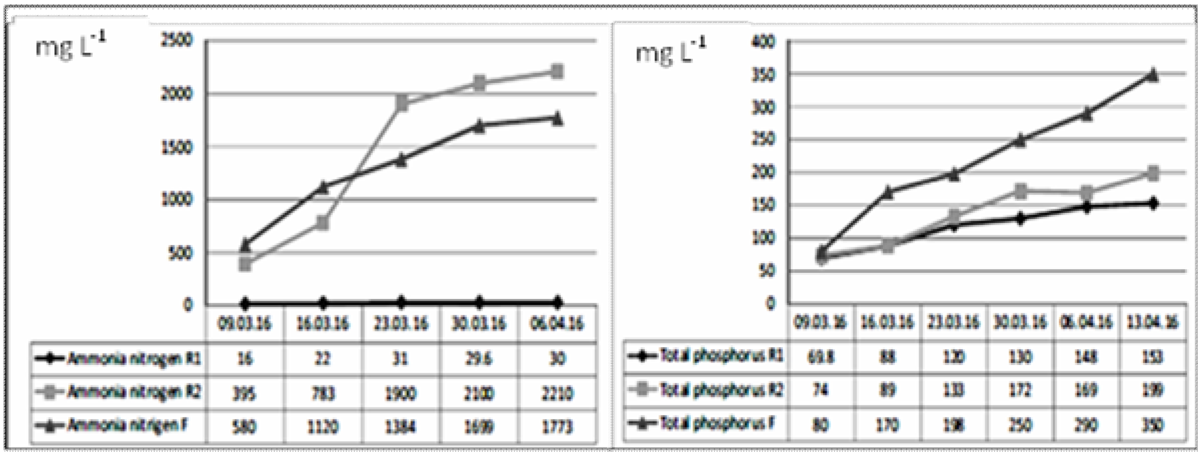

Figure 4. Variation of the concentration of ammonium nitrogen (left) and total phosphor (right) in the reactors 1 and 2.

The variation of total phosphorus concentration (Pt) at the passage from reactor 1, from reactor 2 and its evacuation depending on time is shown in Figure 4 (right). We found that it grows in time by accumulation.

By means of hydrolysis the raw material decomposes, the organic carbon, proteins and phosphorus enter in their dissolved form into CCO-Cr, total nitrogen and phosphorus. Later they are transformed partially into biogas mainly with a content of methane CH_4 and carbon dioxide CO_2.

The waste that remains contains the other compounds: ammonium nitrogen and phosphor that were not assimilated in the digestion process and organic carbon that did not become methane gas.

After the first week of functioning the pH the reactor 1 and 2 stabilizes at a slightly basic value between 7 and 8; a chemical regulation is not necessary. The temperature in the first methanogen reactor was at average at 36°C compared to 38°C in the second methanogen reactor. Although the temperature is lower in the first methanogen reactor, the quantity of biogas was higher than in the second methanogen reactor. Practically 70% of the quantity was obtained from the first reactor. Figure 5 shows the quantity of biogas obtained under these conditions and the volume of CH_4 achieved.

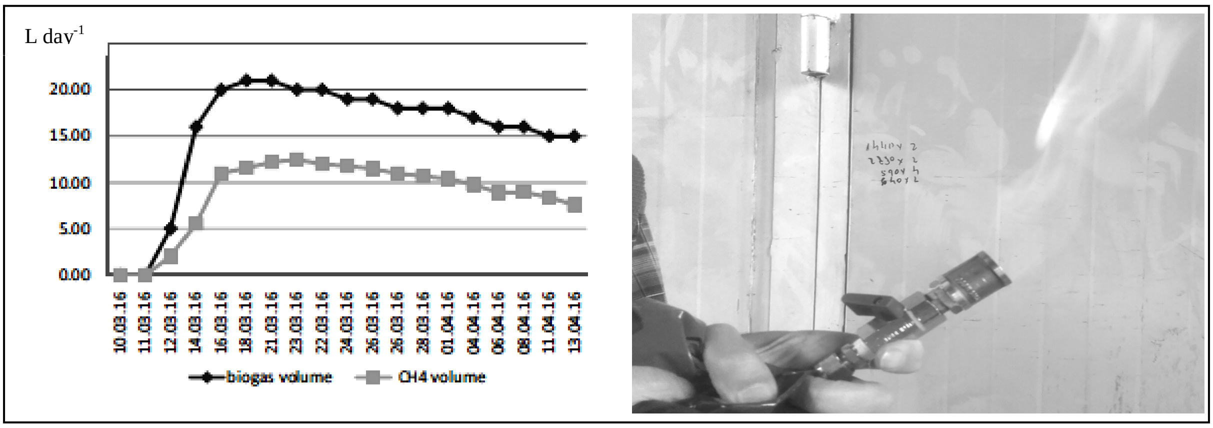

Figure 5. Volume of biogas and ammonium obtained.

Efficiency achieved. In the second part of the experiment (working period: 15.04.2016-16.05 2016) we did not make a recirculation (working period: 15.04.2016-30.04 2016) of the biological matter from the F (R3F) tank in reactor 1, the volumes of biogas obtained was at a maximum 14 L day^{-1} (Figure 6 left). In the case shown in Figure 6 (right) we recirculated the matter in the final tank (R3F) in reactor 1 between 25.04.2016-16.05 2016 when we got a growth of the biogas volume compared to the previous situation up to a maximum of 23 L day^{-1}.

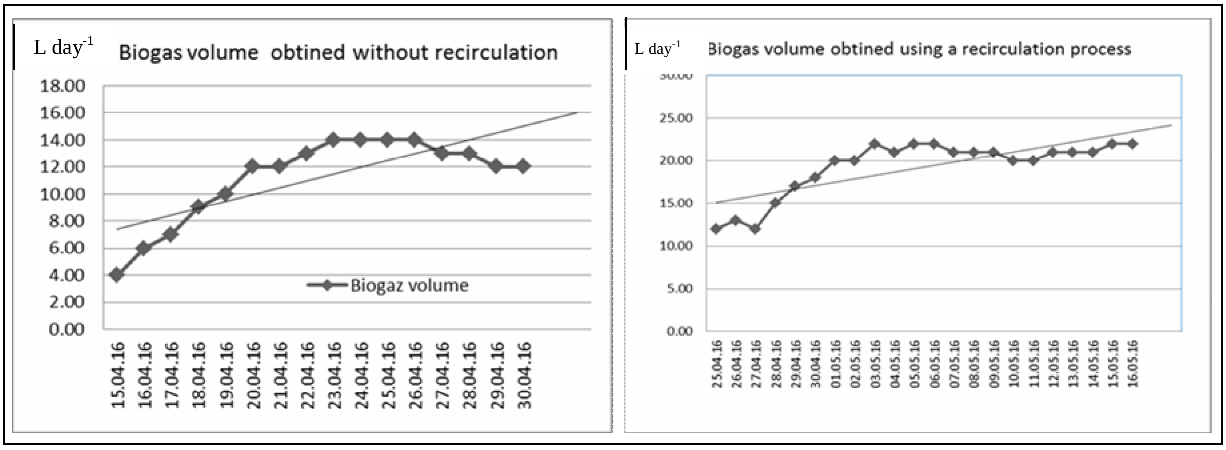

Figure 6. The volume of biogas obtained the process without recirculation (left) and with recirculation (right).

The enhancement of the amount of biogas by liquid biomass recirculation is achieved thanks to the improvement of the environmental conditions for the micro-organisms recirculated from the final reactor, where the carbon-nitrogen ratio has dropped to the limit of the metabolic inhibition, to the primary reactor, where the C/N ratio is higher. The micro-organisms from the final reactor are activated and start competing with the micro-organisms that get developed in the first methanogenic reactor. As a result, biogas increase and the adaptation of the methanogenic micro-organisms to the enhanced ammonia nitrogen conditions.

Conclusions. The tests carried out in the installation to produce biogas (anaerobic installation with multiphase digestion) proved that the waste from the tanning industry can successfully turned into biogas to produce energy from renewable sources. The digestion of the waste from the tanning industry in the installation of biogas production (anaerobic installation with multiphase digestion) proved feasible when the starting conditions are supported by active household sludge.

The high concentration of nitrogen and of salts is a serious challenge for anaerobic digestion as this digestion may generate important inhibitory phenomena. And what is more, the C/N ratio is seriously out of balance what standard conditions concern. The anaerobic installation with multiphase digestion was capable to overcome these problems by limiting the effect of the nitrogen inhibitor for the development of an efficient microbial flora by acclimatization and real control of the process.

For a proper running of the installation we made from time to time a correction of the pH at the beginning and then every time it was necessary during the acidogenic phase; the methanogenic phase did not need any pH correction as its value was neutral or slightly basic, that means the reactions were at their best.

The installation functioned properly even if the C/N ratio stayed at values twice as high. When the values of the ammonium products increased significantly we found the inhibition process. In this case we needed some support from external carbon.

From the data of the experiment we can conclude that the anaerobic digestion process with the outcome of biogas using tanning waste is feasible; it is practically possible to get biogas in a high concentration out of methane gas.

Acknowledgements. This work was supported by a grant of the Romanian National Authority for Scientific Research CNCS – UEFISCDI, project ID PN-II-PT-PCCA-2013-4-1017, “Green Tannery – Methods for energetic recovery of biodegradable wastes”.

References

Angelidaki I., Ahring B. K., 1994 Anaerobic thermophilic digestion of manure at different ammonia loads: effect of temperature. Water Research 28(3):727-731.

Bonoli M., Salomoni C., Caputo A., Francioso O., Palenzona D., 2014 Anaerobic digestion of high-nitrogen tannery by-products in a multiphase process for biogas production. Chemical Engineering Transactions 37:271-276.

Chen Y., Cheng J. J., Creamer K. S., 2008 Inhibition of anaerobic digestion process: a review. Bioresource Technology 99:4044-4064.

Craciun M., Mocanu R., Lăzăroiu G., Mavrodin M. E., Ignat D., Somesan M., Ciuban V., 2016 Anaerobic digestion of tanneries wastes. 5th International Conference on Thermal Equipment, Renewable Energy and Rural Development, TE-RE-RD 2016, Golden Sands Bulgaria, 2-4 June 2016, ISSN: 2457-3302, ISSN: L 2457-3302, pp. 459-464.

Mocanu R., Lăzăroiu G., Mavrodin M. E., Craciun M., Ignat D., Somesan M., Ciuban V., 2016 Biogas modern technology by using biodegradable waste from tanneries. 5th International Conference on Thermal Equipment, Renewable Energy and Rural Development, TE-RE-RD 2016, Golden Sands Bulgaria, 2-4 June 2016, ISSN: 2457-3302, ISSN: L 2457-3302, pp. 479-482.

Seadi T. A., Rutz D., Prassl H., Köttner M., Finsterwalder T., Volk S., Janssen T., Ofiţeru A., Adamescu M., Bodescu F., Ionescu D., 2008 [Biogas - practice guide]. Big-East: biogas for Eastern Europe, 152 pp. [in Romanian]

Van Velsen A. F. M., 1979 Adaptation of methanogenic sludge to high ammonia nitrogen concentrations. Water Research 13(10):995-999.

Zupancic G. D., Jemec A., 2010 Anaerobic digestion of tannery waste: semi-continuous and anaerobic sequencing batch reactor processes. Bioresource Technology 101(1):26-33.

*** SR ISO 6060-1996 [Determination of Chemical Oxygen Demand]. [in Romanian]

*** STAS 7312-83 [Determination of total nitrogen]. [in Romanian]

*** SR EN ISO 6878 [Determination of total phosphorus. Ammonium molybdate spectrometric method]. [in Romanian]

*** SR ISO 7150/1-01 [Determination of ammonia nitrogen. Spectrophotometric method]. [in Romanian]

***http://www.unido.org/fileadmin/import/userfiles/timminsk/leatherpanel14ctcwastes.pdf.

*** National Waste Management Strategy, 2013 Ministry of Environment and Climate Change.

Received: 17 January 2017. Accepted: 10 March 2017. Published online: 15 March 2017.

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How to cite this article:
Crăciun I. M., Vlad G., Ignat D., Mocanu R., Berkesy C. M., Someşan M., 2017 Leather industry waste material energetic valorisation by anaerobic digestion thanks to a Multi-Phase Process. AES Bioflux 9(1):37-44.