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Anaerobic Digestion of High-Nitrogen Tannery By-products in a Multiphase Process for Biogas Production

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Industrial by-products and wastes can be very challenging substrates for anaerobic digestion, since their composition in terms of nutrient content can be strongly unbalanced. Tannery by-products, for instance, are biomasses of animal origin with high nitrogen content since their composition is dominated by proteins, peptides and amino acids. The use of this biomass as main substrate to feed anaerobic digestion is limited because of the high concentrations of ammonia formed during fermentation. Ammonia is originated from the biological degradation of proteinaceous materials in anaerobic environment. Free ammonia permeation into bacterial cells can cause intracellular pH change, inhibition of specific enzymatic activities and increased energy requirement for cell maintenance. Therefore, high ammonia amount cause severe inhibition or failures of anaerobic digestion, with important consequences for both process stability and productivity.
The aim of this study was the development of a multiphase anaerobic digestion process for tannery by-products, characterized by a C/N ratio below 5, in order to convert them into biogas. The process needed an acclimation phase of anaerobic microorganisms due to high concentrations of ammonia (NH_4^+/NH_3), above 9,000 mg/L, and the low C/N ratio. Implication for process stability, microbial activity and for the achievement of the target performances are discussed.

1. Introduction

Tannery is often considered one of the most polluting industry since the production process generates huge quantities of liquid and solid effluents, together with frequent smell problems. Environmental policy regarding Italian leather districts has enforced many controls and defined several strict rules in order to mitigate the impact of leather manufacturing on soil and rivers, leading to a “zero impact” approach. While liquid effluents are often treated in dedicated wastewater treatment plants, solid residues are usually converted in useful by-products like fertilizers. Nevertheless, energy recovery from leather by-products and wastes can represent a bonus for the energy balance of many production sites, avoiding significant fossil fuel inputs. Thus, renewable energy production can be a very positive option for the enhancement of leather industry environmental balance.
As in many other conditions where high-moisture wastes and by-products are available, anaerobic digestion for biogas production is a first-choice solution for energy recovery. Anaerobic digestion (AD) is a convenient way to manage biogas production from organic waste, leading to almost complete methane and CO_2 recovery from the process, virtually without losses to the atmosphere (Lyberatos and Skiadas, 1999). AD can be described as a sequence of metabolic steps involving several microbial populations, to form a complex metabolic interaction network, resulting in the conversion of organic matter into methane, carbon dioxide and other compounds. The improvement of the established green technologies to attain lower costs and better environmental performances may pass through the adoption of two-phase anaerobic digestion (TPAD) processes (Salomoni et al., 2011a), since acidogenic and methanogenic microorganisms exhibit different growth rates and pH optima (in the range 4.0-6.0 and 6.5-8.0, respectively) (Ghosh et al., 1987). Two-phase systems for the anaerobic degradation of organic matter

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have shown several advantages over conventional single-stage processes, the main being increased stability of the overall process (Ghosh et al., 1987). Separation of phases allows optimization of the hydraulic retention time and organic loading rate, according to the requirements of the different microbial populations of each phase (Koutrouli et al., 2009). It is then possible to keep shorter retention times in hydrolytic–acidogenic reactor, while keeping longer retention time in methanogenic reactors (with no risk of washing out for the slow-growing methanogenic microorganisms). TPAD can handle high-solid containing waste as liquefaction occurs along with acidification, widening application of anaerobic digestion to municipal solid wastes (Vieitéz et al., 2000). Moreover, TPAD is more flexible and robust toward toxicity and inhibition phenomena, a very positive feature when the substrates are industrial by-products. A wide variety of inhibitory compounds can be present in industrial by-products, and many others can originate during anaerobic digestion in specific conditions (Chen et al., 2008). These compounds can be the cause of process upset or failure, or simply represent a limiting factor for performance enhancement.

Fleshing and other organic solid residues from leather industry can be treated to separate a valuable fatty component, awkward for AD treatment (Lauwers et al., 2012) but often suitable for rendering. The aqueous fraction is a high-strength, nitrogen rich liquid, mainly composed of semi-hydrolysed proteinaceous material. High concentrations of salts are also present due to the use of lime and other chemicals in the production process. The use of this tannery by-product as main substrate to feed anaerobic digestion is limited because of the high concentrations of ammonia formed during fermentation, in a way similar to other animal-derived by-products like slaughterhouse waste (Palatsi et al. 2011). Ammonia inhibition can be extremely detrimental when combined to other negative factors like inhibition by Long Chain Fatty Acids (LCFA), leading eventually to process impairment and failure.(Cuetos et al., 2008). Ammonia is originated from the biological degradation of proteinaceous materials in anaerobic environment. Free ammonia permeation into bacterial cells can cause intracellular pH change, inhibition of specific enzymatic activities and increased energy requirement for cell maintenance (Chen et al., 2008). Therefore, high ammonia amount cause severe inhibition or failures of anaerobic digestion, with important consequences for both process stability and productivity. Nevertheless, process conditions have a strong influence on ammonia inhibition effect as demonstrated by the very different "inhibiting concentrations" that can be found in literature, ranging from less than 2 to 14 g/L of total ammonia nitrogen. Temperature (Angelidaki and Ahring, 1994), pH, inoculum origin and acclimation (Van Velsen, 1979) are the main factors, among many others.

In previous works we described successful energetic conversion processes for several industrial and municipal by-products like cheese whey, alcoholic wastewaters (Salomoni et al., 2011b) crude glycerol (Salomoni et al, 2012) and sewage sludge (Salomoni et al., 2011a). In this work we show the set-up of a multiphase anaerobic digestion process at pilot scale for the conversion of tannery nitrogen-rich by-products into biogas for renewable energy production.

2. Set-up and start-up of pilot plant

2.1 Pilot plant structure

The project involved the use of a pilot plant (Figure 1) within the Bologna municipal WWTP, in which determination of operational parameters and performance was realized during demonstration activity. The pilot plant is composed of two main anaerobic reactors, named DIG1 and DIG2, equipped with monitoring and operating industry-derived instruments. DIG1 and DIG2 are quite similar in structure and equipment. They are cylindrical, cone-bottomed, jacketed stainless steel reactors. Internal volumes are 850 L.

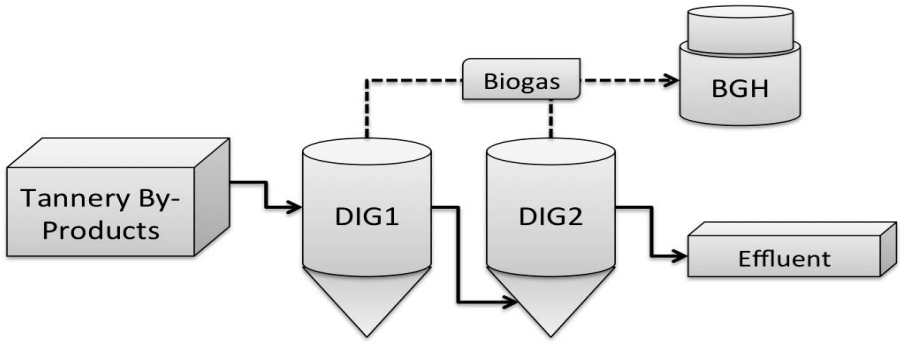

Figure 1: Outline of the configuration of the pilot plant

Table 1: Analytical data about the tannery by-products (TBP) batches used in the work

	u.m.	TBP batch 1	TBP batch 2	Mean value
Dry matter	% w/w	11.3	11.4	11.3
Nitrogen	% w/w	1.4	1.3	1.3
Organic carbon	% w/w	5.1	5.1	5.1
C/N ratio		3.6	3.9	3.8
pH		6.7	6.7	6.7
sCOD	gO_2/L	109	115	112
Cl^-	g/L	13	13	13
Na^+	g/L	12	13	12.5
Ca^{++}	g/L	4.4	4.2	4.3
SO_4^{2-}	g/L	10	14	12

Temperature, pH, pressure and hydraulic level probes allowed online monitoring of essential parameters. Internal mixing, when required, can be accomplished by means of both an axial-flow impeller and a recirculation pump. Biogas exhausts from DIG1 and DIG2 are collected through water traps to the Bio-Gas Holder (BGH). Sampling points for gas and liquid phases are available. Liquid transfers between reactors are performed by progressing cavity pumps. The Biogas holder (BGH) is a floating-head polypropylene pressostatic vessel, filled with acidic saline solution (NaCl 1.7% w/w, pH set to 2.0-3.0 with HCl) to limit CO_2 dissolving. The gasholder can accommodate 900 L gas storage. All fill and draw operations are managed by a PC control unit equipped with LabVIEW X.1 plant managing software.
At the beginning of the demonstration setup, the reactors were inoculated with active biomass obtained from the existing full-scale anaerobic digestion plant, operated at 35-37°C in single-stage configuration. pH of the inoculum was close to neutrality (7.2) and total solid content around 3 % (w/w). After inoculum transfer, residual oxygen was removed from both reactors and temperature was set to 40 °C. Hydrochloric acid was added in DIG1 to shift to acidic pH. Hydraulic Retention Time (HRT) was gradually decreased as the main parameters stabilized. After an adaptation period (35 days) no pH correction was needed anymore in DIG1, being the culture conditions quite stable. Biogas production in DIG2 increased, as well as the methane fraction therein. As a result of microbial adaptation and selection, a steady-state operating condition was achieved.

2.2 Substrates

The first demonstration run was carried out with tannery by-products (TBP), without any additional integration. TBP is a liquid solution that is obtained by the combination of at least two different industrial streams, both originating from a major tannery by-product treating plant. Consequently, its main features can vary as the combination varies. The combination used for this work is described in Table 1, where different values for different batches are reported. The most striking feature is the extremely low C/N ratio that is far outside the optimal range for anaerobic digestion (20-30). As mentioned before, nitrogen rich substrates can lead to ammonia toxicity. pH is close to neutrality and concentrations of salts are quite high, especially Cl^-, Na^+ and SO_4^{2-}.

2.3 Analytical methods

Sampling of TBP as well as DIG1 and DIG2 cultures were regularly carried out. Samples were refrigerated at +4 °C until analysis. Volatile Fatty Acids (VFA) and soluble ions concentrations in TBP (Na^+, Ca^{++}, Cl^- and SO_4^{2-}) were determined by external labs with various methods. The determination of dry matter and pH were carried out according to APHA, AWWA, EF ,1995. Soluble Chemical Oxygen Demand (sCOD) and ammonium concentrations were measured by specific wastewater analysis kits (HACH-LANGE, Germany). The biogas produced by each digester was measured by Elster diaphragm gas flow meters (Essen, Germany). Raw data were corrected for actual pressure and temperature to conform to normal conditions (100 kPa, 0 °C).
Biogas composition (CH_4, CO_2, O_2, CO, H_2S) was regularly analysed by means of GA2000 hybrid IR/electrochemical portable gas analyzer (Geotechnical Instruments, Warwickshire, UK).

2.4 Description of process parameters

The analytical values determined in each digester show a sharp separation of anaerobic digestion phases (Table 2). In the first digester, the pH is stably below 5.0 while in second the pH is in the range 7.5-8.0. This difference is caused by intense acidogenic and acetogenic activity in DIG1 that leads to accumulation of VFA. In DIG2, on the other hand, VFA are almost completely converted into biogas and pH rises. Ammonia release by the conversion process is also a main driver of pH increase in methanogenesis.

Table 2: Analytical description of digester microbial cultures of DIG1 and DIG2

	unit	DIG1	DIG2
Dry matter	% w/w	10.2	5.8
pH		4.0-4.5	7.6-8.0
sCOD	gO_2/L	106	13.5
VFA (as acetic acid)	g/L	28.1	4.0
NH_4^+	g/L	3.32	8.94

VFA production in DIG1 is extremely important for stability and efficiency of the entire process. First, organic matter is converted into a relatively homogeneous, easily degradable mix of low molecular weight compounds. This conversion step act as a shield for methanogenic microbes against loading shocks, sudden variations of input composition and inhibitors. The result is an easier and safer management of inputs to the anaerobic digestion process. Second, the hydrolytic activity in the first phase can convert recalcitrant substances present in industrial by-products into more degradable intermediates, improving the overall conversion efficiency.

Ammonium concentrations are 3.32 and 8.94 g/L, respectively, in DIG1 and DIG2. Nitrogen metabolism during biogas production leads to a very critical ammonium level, considered by some author as completely unsuitable for anaerobic digestion (Chen et al., 2008). Nevertheless, the multiphase process described here could handle these high ammonium concentration with limited inhibitory effects, due to flexibility and effective acclimation of the microbial population.

The main operative parameters at steady-state are shown in Table 3. The organic loading rate (as COD) was kept between 2 and 2.5 $kg/m^3 \bullet d$ to avoid overload, but higher levels are likely to be reached after accurate process optimization. Specific methane production expressed on input sCOD was 0.312 Nm^3/kg_{input}, while overall conversion of sCOD was 88 %.

More than 95 % of biogas production occurred, as expected, in the methanogenic phase, while a minor gas stream (mainly CO_2) was produced in the acidogenic/acetogenic phase (Table 4). CH_4 concentration in the mixed gas was 64 %, while H_2S concentration exceeded 2,000 ppm. Desulphurization of biogas is then required before energetic use, and can be achieved by several means: the first step should be biological desulphurization, capable of a reduction of sulphide down to less than 400 ppm; final treatment can be accomplished by chemical and/or absorption methods, according to the specific condition of each application.

2.5 Residual biogas production

To asses the presence of any residual methane potential production that could be recovered from the effluent with further digestion, samples from the DIG2 digester were taken and incubated in lab batch digesters for extra time (up to 25 days additional HRT) in identical conditions. The results in terms of metabolites concentration and methane residual production are shown in Table 5. A slight increase in ammonium concentration and pH is reported, in parallel with minimal reduction of dry matter and sCOD.

Table 3: Main operative parameters of pilot plant at steady state

	Unit	
Organic loading rate as sCOD	$kg/m^3 \bullet d$	2.0-2.5
Specific methane production (versus input sCOD)	Nm^3/kg_{input}	0.312
Overall conversion of sCOD	%	88

Table 4: Biogas production in DIG1 and DIG2

	unit	DIG1	DIG2	Overall
Share of biogas production	%	3 %	97 %	100 %
Methane conc.	% v/v	11 %	66 %	64 %
Carbon dioxide conc.	% v/v	88 %	34 %	36 %
Oxygen conc.	% v/v	0.1 %	0.0 %	0.0 %
Hydrogen sulphide conc.	ppm	n.d.	2,040	2,020
Carbon monoxide conc.	ppm	425	211	216
Others (comprising H_2, N_2)	% v/v	0.9 %	< 0.5 %	< 0.5 %

Table 5: Residual biogas production in extended digestion experiment

	unit	Pilot plant	Extended digestion	Overall
Share of biogas production	%	93 %	7 %	100 %
Share of Methane production	%	91 %	8.6 %	100 %
Methane conc. in biogas	% v/v	64 %	77 %	65 %
Carbon dioxide conc. in biogas	% v/v	36 %	23 %	35 %
Dry matter	% w/w	5.8	5.5	-
pH		7.6-8.0	7.9-8.1	-
sCOD	gO_2/L	13.5	10.1	-
VFA (as acetic acid)	g/L	4.0	2.1	-
NH_4^+	g/L	8.94	9.08	-

The biogas residual production represents less than 10 % of total production in the pilot plant. Careful consideration of this residual biogas production must be taken in a full-scale plant design in order to verify if the realization of an additional methanogenic stage is economically convenient.

After the additional digestion step, that extends digestion time up to 65 days, a residual sCOD concentration is still present (Table 5), indicating that a fraction of the input TBP is highly recalcitrant to biological conversion. Since TBP has undergone harsh chemical treatments before use in anaerobic digestion, it is likely that a fraction of organic matter has been converted into xenobiotic compounds that don't fit easily into the main metabolic pathways.

2.6 Process design

The operational data obtained during the pilot scale demonstration can be the base of a full-scale process design in order to present the capability of multiphase anaerobic digestion for tannery industry. In Figure 2 is shown a possible process design for renewable electric energy production from TBP. TBP are collected from tannery waste and by-products treatment facilities. As verified by long-term analysis, storage of TBP is possible under suitable conditions (not shown). The multiphase anaerobic digestion process is composed of at least two digesters, in series, with pumps and piping to perform liquid transfer and recirculation if needed. Extra methanogenesis modules (EM) can be added to optimize organic matter conversion if convenient. One or more digesters are covered by double-membrane domes where biogas is stored before utilization. Within the dome(s), biological desulphurization of biogas is accomplished by controlled air injection, allowing sulphide conversion into elementary sulphur by resident sulphide-oxidising bacteria. Effluent from the anaerobic digestion can be treated in several ways, allowing separation of valuable compounds (e.g. ammonia, carbonate) and/or production of nitrogen-rich fertilizers.

The biogas stream, after final moisture and contaminant removal in a dedicated skid, is then delivered to the cogeneration facility. Electric energy is then dispatched to the grid to benefit of renewable energy feed-in tariff. A fraction of thermal energy is used for digester heating, while excess thermal energy can be used in any adjacent facility. Alternatively, if thermal energy is the main requirements, biogas can be used as fuel, alone or mixed with natural gas.

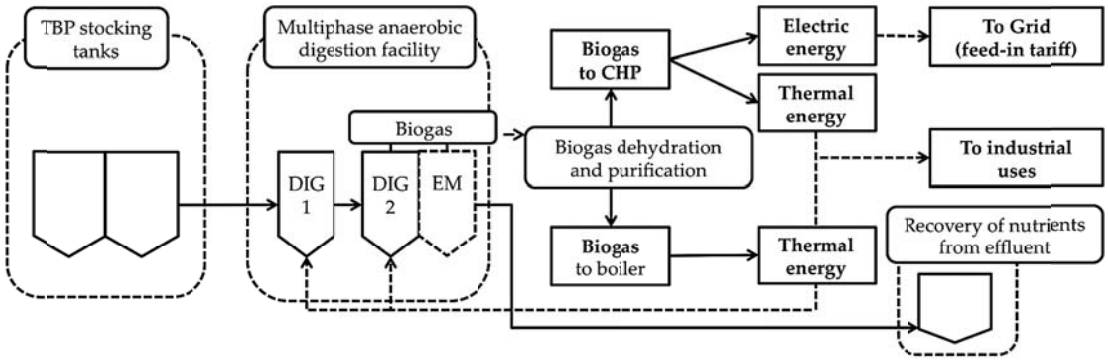

Figure 2: Concept design of a full-scale facility for renewable energy production from TBP

3. Conclusions

The work described in this paper shows that tannery by-products can be successfully converted into biogas for renewable energy production. High nitrogen and salts represent a serious challenge for anaerobic digestion, since they can trigger important inhibitory phenomena. Moreover, C/N ratio is significantly unbalanced with respect to standard conditions for anaerobic digestion. Multiphase anaerobic digestion was able to overcome these issues, limiting inhibitory effect of ammonia by efficient microbial acclimation and by effective process control. Concentrations of ammonium up to 9 g/L could be tolerated with minimal inhibitory effects. Nevertheless, process conditions that reduce ammonium concentration under 7.5 are now under investigation to improve performance. From a yield-oriented standpoint, the results from the pilot plants are excellent since 88 % of input sCOD is converted into biogas; further enhancement on this aspect is possible (over 90 % conversion) adding an extra methanogenesis module. Residual sCOD could not be converted even with longer digestion times because it is probably due to the presence of xenobiotic compounds. The concept design presented here shows how a renewable energy facility can be designed to provide electric and/or thermal energy for industrial use or for sale.

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