Co-digestion of tanning residues and sludge

Santino Di Berardino[1] and Alcino Martinho[2]

[1]Unidade de BIOENERGIA, LNEG, Est. do Paço do Lumiar, 1649-038 Lisboa, Portugal.
(e-mail: santino.diberardino@mail.ineti.pt)
[2] CTIC, Centro Tecnológico das Indústrias do couro. Apartado 158 – S. Pedro, 2384-909 Alcanena Portugal

Tanning Waste and Wastewater

- In the Alcanena Region: 100 tanning factories (about 75 % of national production).
- Large wastewater volume (70 000 m^3/day).
- Tanning processing huge waste producer. Only about 25-30 % by weight of primary matter is transformed into leather.
- The environmental degradation observed in the 70s decade has been attenuated.

Tanning Wastewater treatment Existing facilities

- Large collective wastewater treatment plant.
- Centralized chromium recovery unit.

Wastewater Treatment Plant (WWTP)

- Includes physicochemical separation and biological processes. Generates more solid wastes:
- Chemical sludge removed from precipitation
- Biologic sludge settled in the secondary settling tank.
- These wastes are today dewatered in a filter press (30 % T.S.) mixed with a lime based stabilizing agent and disposed in a controlled industrial landfill

General view of WWTP

Chrome recovery Plant

Tanning Waste treatment-facilities

- Industrial chrome containing and not biodegradable wastes are send in Industrial landfill.
- “Green” solid waste placed in soils
- WWTP Sludge is dewatered mixed with stabilizing chemical agent and sent in landfill

Sludge Dewatering and Stabilization

Old Sludge Pond

- Pond Coberture solved bad odours emissions

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Stabilized Sludge landfill

Landfill - not biodegradable SW

Existing Problems

- Controlled industrial landfilling is being restricted by recent environmental laws.
- The existing facilities are being filled and new uses or disposal solutions for the solid wastes and sludge had to be sought.
- No satisfactory solution for "green tanning Wastes"
- Cost of sludge stabilizing agent.

Aims of the project

- New uses or disposal solutions for the solid wastes and sludge had to be sought.
- Plan AD plant for sludge and tannery wastes to degrade OM, generate valuable biogas, alleviate environmental problem, giving time to set-up more sustainable treatment and disposal routes.
- Digested solid waste is biologically stabilized and can be reused in agriculture. Chrome free digested tannery sludge has a definite value as a fertilizer.
- AD can also incorporate any other domestic, industrial or agricultural wastes.

Objectives of the project

- Study of degradation of mixtures of "green" tannery solid wastes and sludge with the goals to:
- evaluate the degradation extent,
- define the acceptable organic load, and estimate the biogas yield,
- watch the occurrence of inhibition or operational problems and
- assess the technical feasibility of a full-scale facility. The studies were carried both at laboratory and pilot scale. In next stage, chrome containing SW addition.

Tanning “green” waste Valorisation

- Reuse of lime fleshing, rawhide and pelt trimmings in the production of animal glue or other valuable products, is frequently not feasible.

Pilot Plant Description

- The co-digestion pilot plant prepared to work in mesophilic and, also, in thermophilic temperature.
- Three storage 2 - 4m^3 volume polypropylene tanks equipped with hermetic covertures, mixer and recirculation, pH control and ventilation arrangement, to strip hydrogen sulphide.
- Maceration of chromium free tannery wastes required adjustment of the viscosity, with treated effluent and spent solution containing proteolytic enzymes. obtaining a proper pumpable mixture.

Pilot Plant Description

- Each substrate was joined in adequate proportion in the homogenization tank,
- Moderate hydrolysis and acidification of the feedstock spontaneously occurred.
- methanogenic reactor was upward spiral flow ensuring high solid retention time (SRT), good conditions for dissolution and efficient contact between food and organisms and no clogging.
- The heating system was constituted by a double pipe external exchanger

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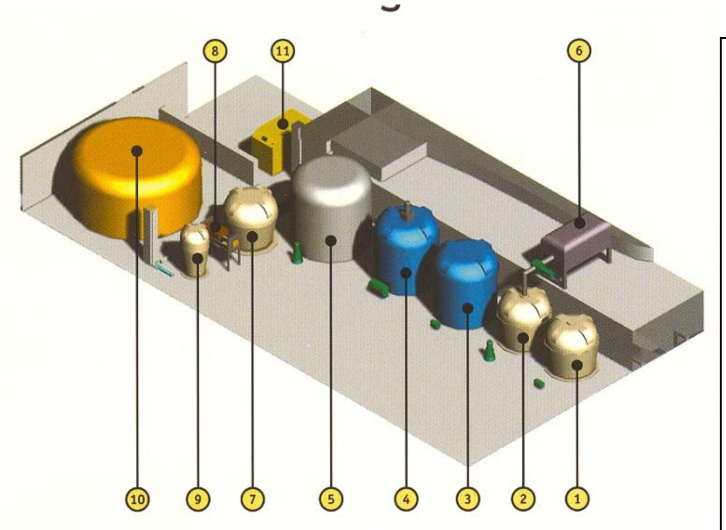
Pilot Plant



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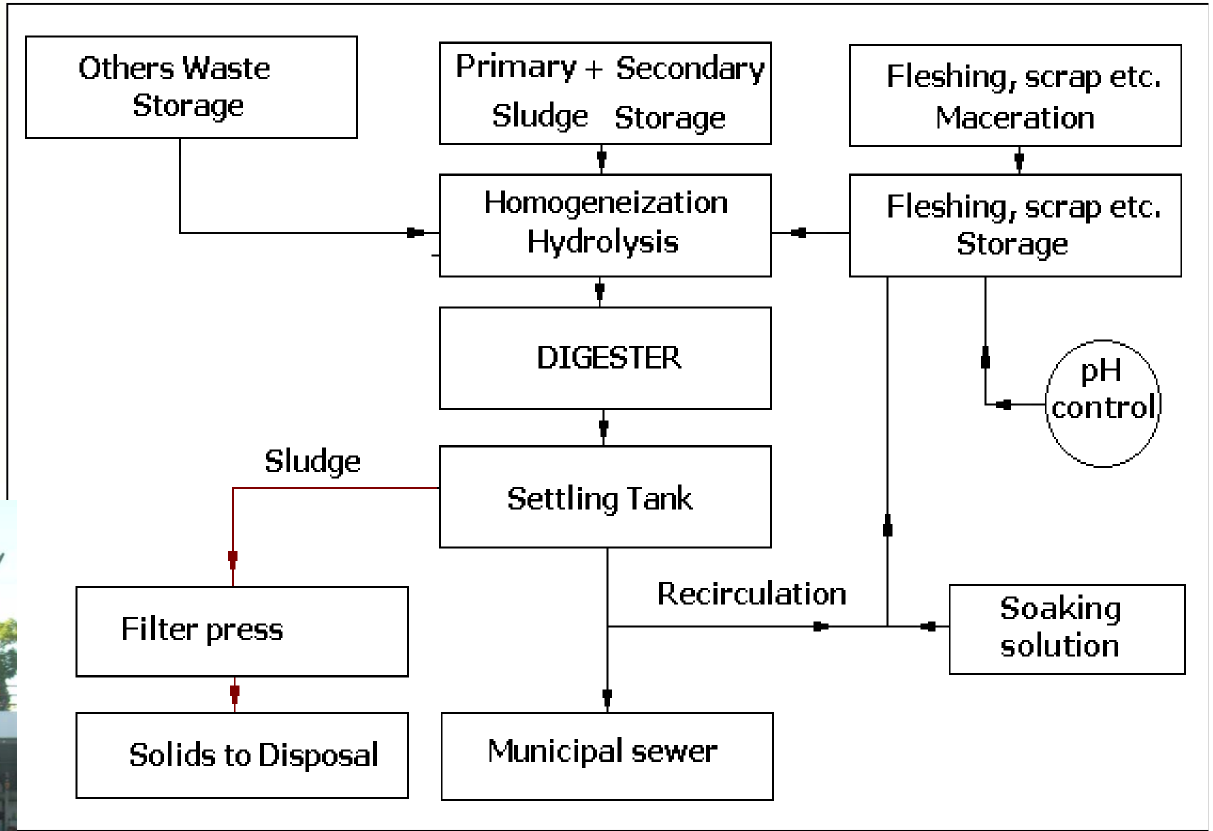
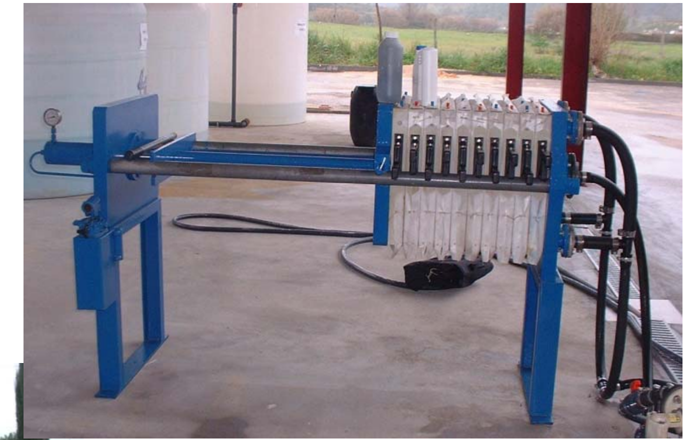


Others Waste Storage
Primary + Secondary Sludge Storage
Fleshing, scrap etc. Maceration
Homogeneization Hydrolysis
Fleshing, scrap etc. Storage
DIGESTER
pH control
Sludge
Settling Tank
Recirculation
Filter press
Soaking solution
Solids to Disposal
Municipal sewer

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Analytical and operational determinations

- The facility worked at HRT of 20 days and 35 ºC temperature.
- controlled parameters in the input and out-put line recorded daily: Mass flow, volumetric streams, biogas production, reactor and environmental temperatures, natural gas consumption and electricity consumption and production
- Liquid effluents were characterized in order to assess the efficiency of removal in terms of several parameters.

Analytical and operational determinations

- The digester stability was controlled by routine measurements of Volatile Fatty Acids (VFA), alkalinity, pH and REDOX potential.
- The biogas composition was controlled periodically by mean of gas chromatography.
- Analytical determinations were according to (APHA) standard methods.

Start-up procedure

- Hydrogen sulphide caused frequent inhibitions of the bacterial communities in the laboratorial reactor, making the digester incapable to run with efficiency and stability.
- Were carried-out preliminary activity tests, in order to find adequate available seeding sludge for the pilot plant facility. Its Methanogenic acetoclastic activity was: ACmax=0,105 gCQO-CH_4/gSSV.d.
- The methanogenic reactor was completely filled with this sludge, in order to accelerate the start-up and adaptation.

Sludge and Waste availability

Type of waste	Waste availability (ton/day)
Fleshing and trimming Splitting Shaving Unhairing and Liming	34 7,3 1,4 2,3
Total tanneries "green" waste (TW)	45
Primary sludge (PM)	320
Secondary sludge (SS)	60
Total Sludge (TS=PM+SS)	380
Swine manure (SM)	10
Total Waste	435

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Composition of feedstock

- The sludge collected after gravity thickening [3-6,1 % Total Solids (T.S.)].
- Some trivalent chromium is discharged in the sewer. This compound precipitates with the sludge in the chemical pre-treatment and is bio absorbed in the biologic sludge.
- Activated sludge is more efficient than chemical precipitation to remove chromium Cr^{+3}.

Fleshings Characteristics

- Fleshing with variable OM concentrations, due to water flushing (T.S.=36-120 g/l).
- About 65 % of the organic matter was as suspended solids. Hydrolysis plays important role.
- Fat content (8.4 g/kg) more than 35% of the TVS, promised high methane yield of the waste.
- pH average value 7.18, often very very high (>9), due to presence of lime-rich shavings, capable to create a scale problem in the anaerobic reactor.

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Nutrient and VFA

- Total organic (Kjeldahl) nitrogen (TKN) in relatively high quantities (2000 mg/l) but insufficient to establish ammonia inhibition.
- The Phosphorous content was low (70 mg $PO_4^{=}$/l), a situation of potential deficiency of this element.
- Intense acidification of the mixed feedstock occurred in the storage and in the homogenization tank, before the feeding (Redox potential -300 mV; AGV =1500-2000 mg/l), particularly in Summer time.

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Chromium in the Feedstock

- $Cr^{+3}$is much higher than value detected in the industrial wastewater but is lower than the limit for toxicity in anaerobic process (1500 mg/l).
- This compound reduces slightly the applicability of sludge in agriculture.
- Hexavalent chromium in the mixed sludge was lower than 0,6mg/l, the detection limit of method.
- pH value of this sludge (pH=7,9) and negative Redox (-0,172 mV), unfavorable to form Cr^{+6} compound in sludge, assumed as negligible.

Table 2: Chromium concentrations (mg/l) in the sludge

Substrate	Cr^{+3}
Biologic Sludge	303±193
Mixed Sludge	177±95
Sludge+Tanning Waste	120±117

Solid waste pre-treatment

- Fleshing and the other green tannery waste: a complex and hard substrate, offensive smell, repugnant look and high mechanical resistance.
- Maceration difficult, repeated operations. Frequent blockages required power increase.
- The macerated slurry (0.8 mm) looked like a viscous fluid. It was pumped by a volumetric progressive engine, which also displayed operational problems.
- This operation must be carefully evaluated at full scale plant.

Fleshings

Solid waste aeration

- The "green residue" was aerated, to avoid excess hydrogen sulphide concentration in the feed.
- The existing aeration facility reduced H_2S concentration from 22-77 mg/l range to 0-3 mg/l.

Performance of the system

- Addition of the “green” tannery wastes to sludge improved degradation, gas production, CH_4 content and efficiency.
- OL slightly increased outputs VS and COD
- The effluent still contained concentration of OM and SS (VS =8,5 g/l; COD 12 g/l; TSS=15,9 g/l; VSS=10,4g/l), but low solubles (TOCs=710 mg/l, CODs =1,8 g/l)), VFA (VFA=647 mg/l), and fats (Fats=1,6 g/l).
- Moderate decrease of TSS and VSS in the reactor effluent: low hydrolytic activity.

Performance of the system

- Fat degradation is apparently very efficient. low values in the effluent.
- "Green" tannery wastes considerably increased the alkalinity(16000 mg/l $CaCO_3$). possible calcium carbonate precipitation.
- Sulphate compounds ($SO_4^{=}$=300-1200 mg/l) stimulated SRB activity, decreasing the biogas quality.
- Hydrogen Sulphide concentrations (HS^{-}=0-57 mg/l), were always inside the limits of toxicity for AD (150 mg/l).

Efficiency of Removal

- Efficiency increased during the experimental period as a result of bacterial adaptation and improvement.
- In the last two month of operation, proteolytic enzyme containing solution, from washing tanning operations, in the feedstock, the efficiency of removal of SSV increased from 36,3 % to about 50,3 %.

Efficiency of removal (%) (Average)

Obtained average efficiency value of removal of several parameters, during the entire period.

Parameter	Removal Efficiency (%)
ST	47,5
SV	55,0
SST	36,1
SSV	36,3
COD	55,0
Fats	77,5
TOC	69,1
$SO4^{=}$	35,1

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Biogas production

- Biogas production was dependent from type of mixture and fleshing content in the feedstock.
- Addition of 30 % by weight of fleshing increased 4 times the biogas production (from 3.85 m^3/day to 14,62 m^3/day). 10 m3 more!.
- The maximum Biogas production rate was 28 liter/kg of feedstock.
- Fleshing biogas yield: 630 l/kg VS loaded, higher than the value of mixed sludge (280 l/kg VSloaded).
- Methane varied in the range 68 -77 % CH_4.
- Reactor biogas productivity: 1.49 l/l/day.

SW benefits and drawback

- Addition of fresh wastes (nutrients and positive additives), the sludge had undergone a better degradation.
- The “green” tanneries wastes provided increased the volume of biogas obtainable from the sludge.
- The maximum measured production was 19,6 m^3/day.
- H_2S concentration in biogas from SRB activity was, on average, 1829 ppm, considerably greater than the allowed limit for use in ICE (500 ppm). Its value varied between 831 e 3843 ppm.

Biogas production and organic load

Feedstock	Biogas Production (m^3/day)	Organic Load (Kg VS/day)
SM(40%)+TW(20%)+SS(40%)	6.24	**10.0**
SM(10%)+TW(25)+SS(65%)	7.12	**37.6**
25 % TW + 75 % SS	8.90	**28.0**
100 % TS	3.85	**8.0**
TW (30 %) + TS (70%)	**14.62**	31.4

Environmental and technical Benefits

- Biogas is a valuable renewable energy expected production: 11 500 m^3/day. electric production 20 000 kWh/day.
- Degradation of about 55% of the Volatile Solids (fleshing 70%, sludge 50%)
- Decrease of energy and chemical consumption for dewatering and transportation.
- Digester implementation will increase more than two times the foreseen useful life of industrial landfill.

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Environmental and technical Benefits

- Contribute to fulfillment of the European directive on organic matter landfilling (1999/31/EU)
- With a better control of the waste sources and chromium separation or changes in tanning technology, digestate can be adequate for agricultural purposes or to its incineration.
- The digestate is biologically stabilized and residue will be also safer, in pathogenic terms (providing hygienisation).

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Environ. and technical Benefits - Digestate

- It will release less unpleasant and dangerous odors, spread into the surrounding area and cause discomfort in the local population.
- The digestate contains chromium compounds that difficult agricultural reuse AD keeps chromium (Cr^{+3}) compounds in reductive conditions, reducing the possibility of oxidation to Cr^{+6}
- Can avoid any chemical conditioning of landfilled sludge to avoid chromium diffusion in the landfill.

Economic outcome

- The capital cost for the digestion facility includes the execution of the fleshing pretreatment tank, the digester, the gas recovery and treatment and the cogeneration units (2 x 500 kW motor generators).
- Construction works for infrastructure and equipment for dewatering of digested slurry were not included.
- Operational cost does not include waste collection, assumed to be already present, and chemical products for dewatering and conditioning, considered as equivalent to the actual consume

Cost and incomes evaluation

Cost	Value
Capital Cost	4.800.000 €
Energy +O & M costs	279.500 €/year
Electricity Sales	846.000 €/year
Reduction sludge disposal	98.500 €/year
Reduction fleshing disposal	345.000 €/year
Net annual income	1.010.000 €/year

Balance

- The economic balance revealed the anaerobic digestion plant refundable within 5 years
- Recent incentives on electric energy sale from renewables (0.116 €/kWh), improved revenue,
- The saved landfill disposal costs were evaluated about 30 €/ton.

Conclusions-1

- Codigestion of “green” tannery wastes with sludge and others residues revealed technically feasible and a low cost solution.
- The sludge contains some compounds moderately inhibitory, requiring bacterial adaptation and appropriate mixtures of substrate during the start-up period.
- The experiment demonstrated good compatibility between the waste and sludge. “Green” tannery wastes exerted a favorable effect on biodegradation and gas production, after overcoming any inhibition phenomena.

Conclusions-2

- Sulphide rich “green” T. W. must be pretreated in order to avoid smell, corrosion and inhibition.
- Calcium hydroxide must be watched, in order to prevent calcium carbonate precipitation.
- The equipment for maceration and transfer of solid wastes must be carefully selected.
- Degradation of suspended organic solids is moderate. Addition of proteolytic enzyme containing tanning wastewater can improve degradation and gas production.

Conclusions-3

- The insertion of a hydrolisation-acidification step or the thermophilic anaerobic digestion process can be recommendable.
- Protein and fat degradation proceeded better than suspended solids.
- AD premised favorable incomes by electric energy sell.

Conclusions-4

- Codigestion achieved also substantial reduction in bio solids volume, pathogens, and odor. An important evolution on current solution in terms of transport and increase of landfill useful life.
- This alleviates the current situation and gives some time to plan and implement new sustainable projects, recovery of valuable compounds contained in the waste and fertilizer capacity of degraded biomass.

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