Valorisation of the organic content of tannery sludges to produce energy vectors

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Introduction

The Italian leather industry counts about 1.200 companies. In 2020, the production of finished leathers amounted to 97 million square meters, for a total value of 3.5 billion euros, of which ov 70% generated by exports. The tannery district is nowadays using advanced treatment plants, that are reaching high level of specialization for tannery discharges. The huge volume of sludg generated with solid wastes, poses economic and environmental issues associated with their landfilling.

In the circular economy perspective, the valorization of the organic content of tannery sludge to produce energy vectors is a promising strategy Sludge-to-Energy StE.

The growing interest in renewable energies due to climate change concerns have led research towards liquid fuels production from renewable energy resources. The conversion of tannery sludg into syngas via gasification in Fluidised Bed reactor can simultaneously provide a replacement to non-renewable crude-oil while dealing with waste disposal issues. Gasification is a StE process carrie out under partially oxidising conditions and allow to produce syngas together with the reduction of the amount of sludge to be landfilled, and the potential to reuse ashes in the constructio materials industry.

Aim of the work

In this work various tannery sludges from wastewater treatment plant, has been characterised by several techniques to preliminary assess the sludge composition and properties prior to its energet valorisation by gasification. A lab-scale plant consisting in fluidized bed reactors is used as gasifiers; gasification was carried out under two different operating conditions to the most performin sludge choice. Syngas, tar, bottom and fly ash streams were analysed, and their characteristic critically discussed with relation to the parent sludge properties and the gasification conditions.

Characterisation of a tannery sludge

Proximate/ultimate analysis and higher heating value of various italian WWTP

	Sludge n.1	Sludge n.2	Sludge n.3	Sludge n.4	Sludge n.5
Carbon	37,0%	38,6%	29,4%	23,5%	33,8%
Hydrogen	4,9%	5,7%	4,0%	4,5%	4,2%
Nitrogen	2,3%	5,0%	4,6%	3,1%	3,5%
Sulfur	3,4%	1,6%	3,2%	n.d.	n.d.
HHV (KJ/kg)	16,3	17,1	12,0	9,1	13,7

Proximate/ultimate analysis and higher heating value of tested sludge

	Test 1	Test 2	Test 3	Mean value
Moisture	18.51%	18.12%	18.74%	18.46%
Volatile	50.13%	50.07%	50.19%	50.13%
Fixed C	n.d.	n.d.	n.d.	n.d.
Ash	31.36%	31.81%	31.07%	31.41%
C (d.b.)	33.52%	33.53%	33.78%	33.61%
H (d.b.)	5.33%	4.99%	4.97%	5.10%
N (d.b.)	2.49%	2.38%	2.45%	2.44%
S (d.b.)	4.10%	4.05%	4.06%	4.07%
HHV [MJ/kg]	15.26	14.66	14.79	14.90

ICP-MS analysis on wet and dry tanning sludge

Metal	C [mg/kg] w.b.	C [mg/kg] d.b.
Mg	826.45	1013.55
Al	3886.60	4766.60
Ca	40479.02	49643.15
Ti	587.98	721.10
Cr	18366.18	22524.13
Fe	20202.41	24776.07
Si	7128.83	8742.74
K	377.21	462.61
Na	3523.96	4321.76
Zn	945.4	1160.09
Co	5.48	7.17
Ni	10.18	12.48
Cu	56.43	69.21
As	1.85	2.27
Zr	253.86	311.33
Cd	n.d.	n.d.
Sb	0.60	0.74
Ba	31.40	38.51
Hg	0.0026	0.0032
Pb	16.32	20.01

Cr, the main tanning agent in the leather production process, is the most abundant metal after Ca and Fe.

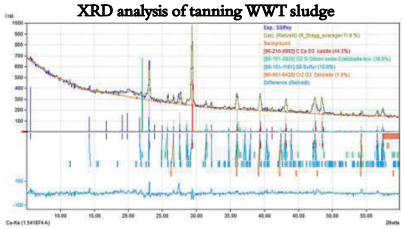
The UV-vis spectrophotometric technique did not detect the presence of the highly harmful Cr(VI) in the solution containing the sludge.

Detection limit by this technique:

Cr(VI)= 0.05 mg/L

Equivalent to a Cr(VI) content in the starting sludge ≤ 2 mg/kg, if present.

XRD analysis of tanning WWT sludge

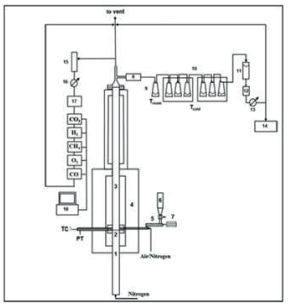


The XRD spectrum highlights four main crystalline species:

- Calcite, $CaCO_3$;
- Cristobalite, SiO_2;
- Sulphur;
- Eskolaite, Cr_2O_3.

Degree of crystallinity (DOC): 7.90%

Design of a lab-scale Fluidized Bed reactor



Layout of the lab-scale fluidised bed gasifier

1. Preheater
2. Distribution plate
3. Reactor
4. Electrical furnace
5. Feeding screw
6. Hopper
7. Variable speed engine
8. Steel net filter
9. T_{room} condenser
10. Refrigerated condensers
11. Walter filter
12. Cotton filter
13. Pump
14. Micro GC
15. Filter
16. Pump
17. Fridge
18. Data acquisition system

Role of operating parameters on the performances of gasification

NETL-DOE, Department of energy USA, reports LHV values in the range 8.3–13.0 MJ/Nm³ for syn-gas as energy vector.

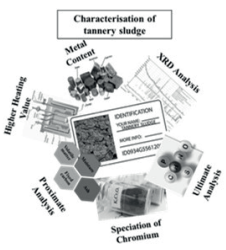
Dry and N_2 free basis	Test 1 (*ER*=0.15)	Test 2 (*ER*=0.24)
CO	35.49%vol. ↑	27.05%vol.
H_2	41.58%vol. ↑	32.69%vol.
CH_4	3.67%vol.	5.15%vol.
C_2H_4	2.89%vol.	4.66%vol.
C_2H_6	0.09%vol.	0.09%vol.
CO_2	16.16%vol. ↓	30.10%vol.
Total	99.88%vol.	99.74%vol.
SO_2	193 ppm	137 ppm
H_2/CO (vol/vol)	1.17	1.21
CH_4/H_2 (vol/vol)	0.09	0.16
Higher Heating Value (HHV)	13.1 MJ/Nm³ ↑	12.6 MJ/Nm³
Lower Heating Value (LHV)	12.0 MJ/Nm³ ↑	11.6 MJ/Nm³
Tar concentration in syn-gas [g/Nm³]	26.4 g/Nm³	22.3 g/Nm³
Elutriated stream flow rate (fly ash) [g/h]	7.57 g/h	4.24 g/h

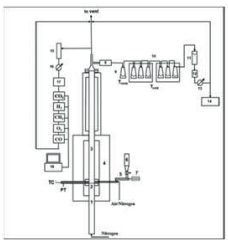
Tar was produced in limited quantity
(ENEA reports values of 200 g/Nm³ for gasification of coal, biomass and sludge).

The more reducing conditions (ER=0.15) resulted in a syn-gas with higher LHV and lower concentrations of unwanted species (e.g. CO_2).

Conclusions

The gasification technique applied to a tannery sludge is a promising conversion route to obtain a syngas.
The process successfully allows to limit undesired oxidation of chromium.
The evaluation of the energetic yield of the process, along with the investigation of possible recycle routes for gasification ash (e.g. as adsorbent material, or in the materials construction industry), will help to increase the circularity of the proposed process.





Characterisation of fly ash

	Test 1 (*ER*= 0,15)	Test 2 (*ER*= 0,24)
Cr_{tot} [mg/kg]	53.300	56.400
Cr(VI) [mg/kg]	4,1	7,1

Characterisation of bottom ash

	Test 1 (*ER*= 0,15)	Test 2 (*ER*= 0,24)
Cr_{tot} [mg/kg]	11.800	8.000
Cr(VI) [mg/kg]	8,2	9,6

