Valorisation of metal contaminated biomass by hydrothermal liquefaction: The case study of tannery sludge

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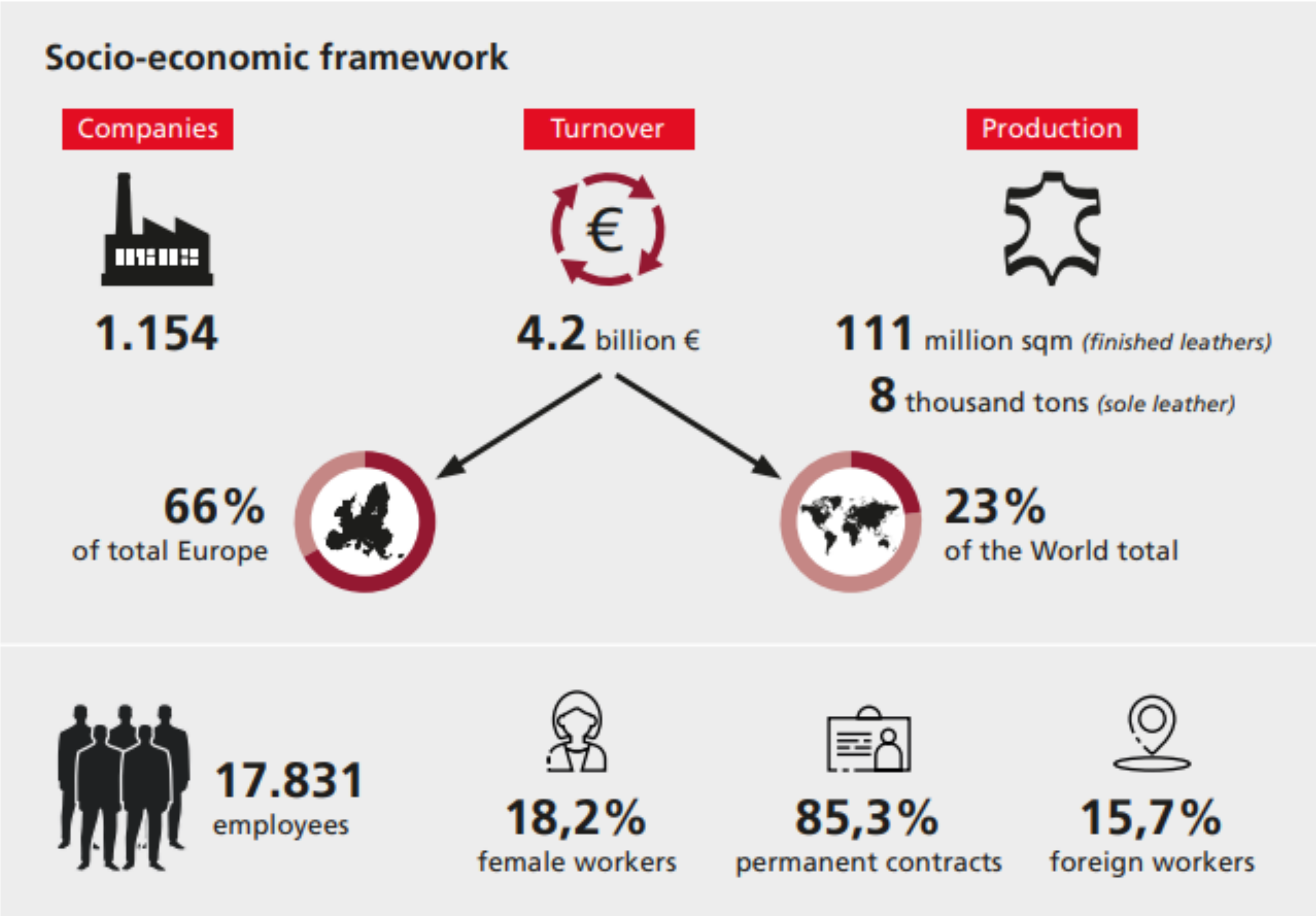
The Italian tanning industry

Italy is an important supplier of leather with a 66 and 23% share of the European and world production



[1] UNIC Sustainability Report 2022

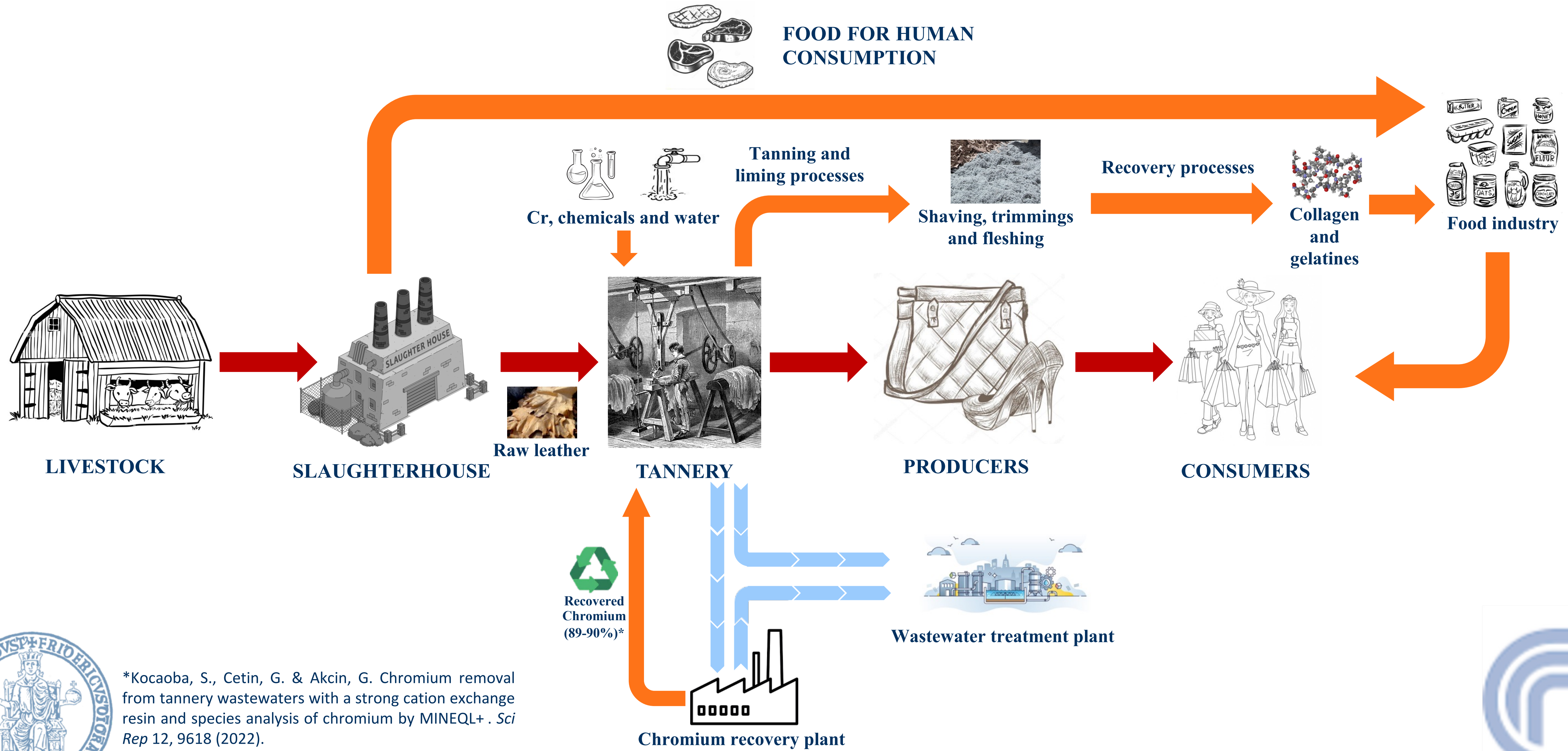
Italian tannery companies statements about leather sustainability:

1) The material is a waste by-product of the food industry (defined as ABP Animal by-products by EU Reg. 1069/2009), that is recovered by tanneries, thus avoiding the disposal of such material in landfills as waste.

2) Its use is an alternative to synthetic, fossil-derived, non-renewable, and poorly biodegradable materials.

3) It is a pure 'bio-based' material by nature, consisting of at least 85% collagen, a 100% biodegradable organic material.

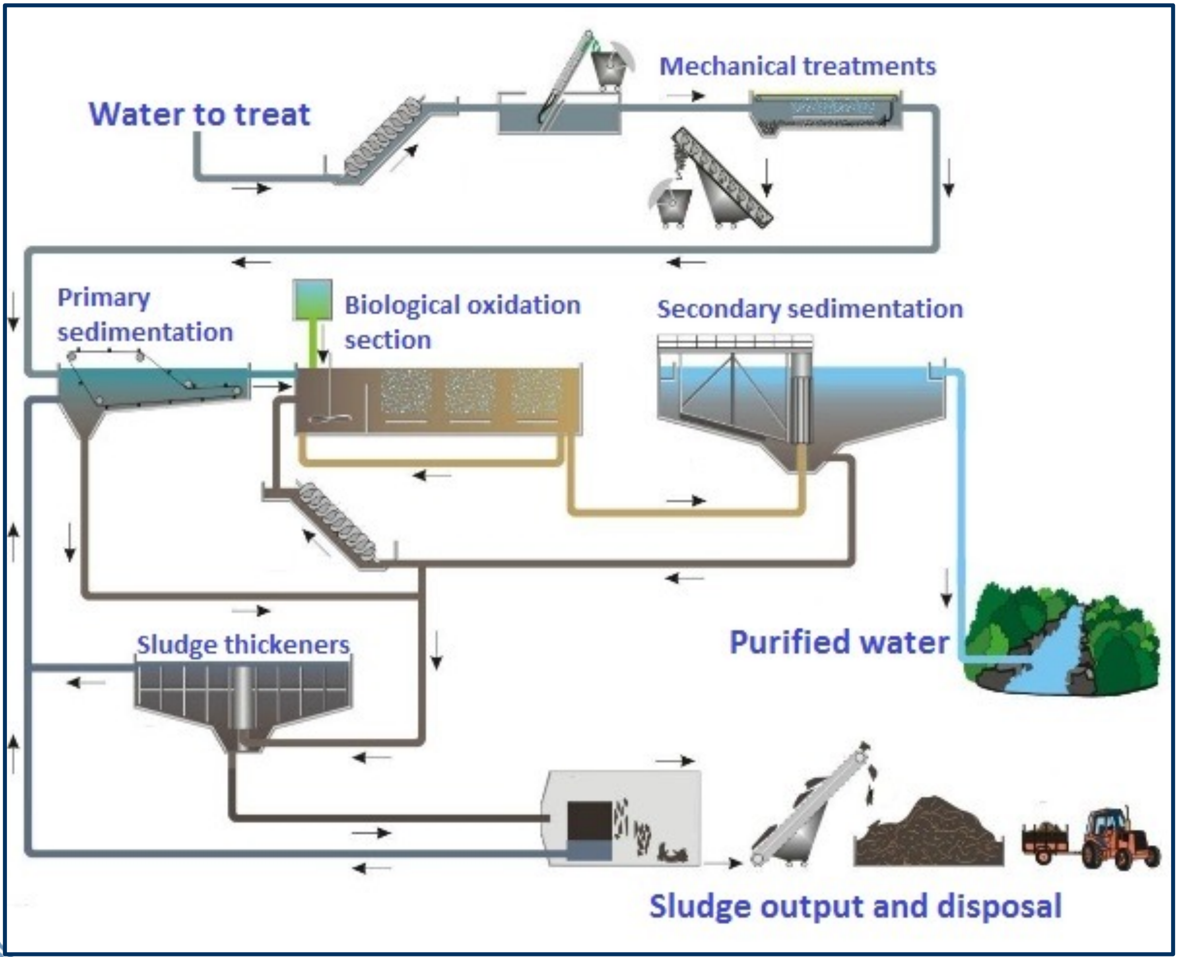
Leather manufacturing process



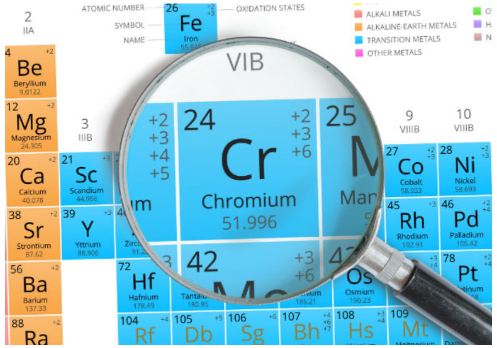
*Kocaoba, S., Cetin, G. & Akcin, G. Chromium removal from tannery wastewaters with a strong cation exchange resin and species analysis of chromium by MINEQL+ . *Sci Rep* 12, 9618 (2022).

Wastewater treatment plant

Tannery sludge is the residual material deriving from the treatment of tanning wastewaters



The purification process of this industrial wastewater, produces a tannery sludge with high concentration of Cr(III), generally stored in authorised landfills.



Due to the high content of Cr(III) in tannery sludge, special attention must be paid to limit/avoid the oxidation of Cr(III) to Cr(VI), extremely harmful for the environment and human health.

Sludge management

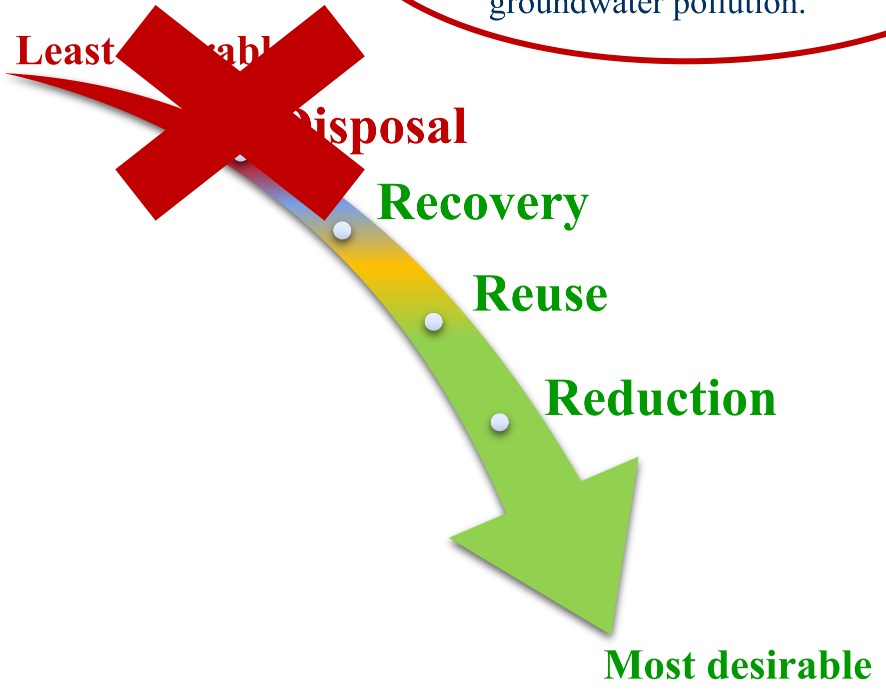
E.W.C. CODE

Sewage sludge is a waste regulated in Italy by the **Legislative Decree 152/06** including all the related disposal, treatment and transport activities.

E.W.C. code	Description of the E.W.C. code
190805	Sludges from treatment of urban wastewater
190811*	Sludges containing hazardous substances from biological treatment of industrial wastewater
190812	Sludges from biological treatment of industrial wastewater other than those mentioned in 190811
190813*	Sludges containing hazardous substances from other treatment of industrial wastewater
190814	Sludges from other treatment of industrial wastewater other than those mentioned in 190813

Article 1(a) of Directive 75/442/EEC on waste and Article 1(4) of Directive 91/689/EEC on hazardous waste. Hazardous wastes are marked with *.

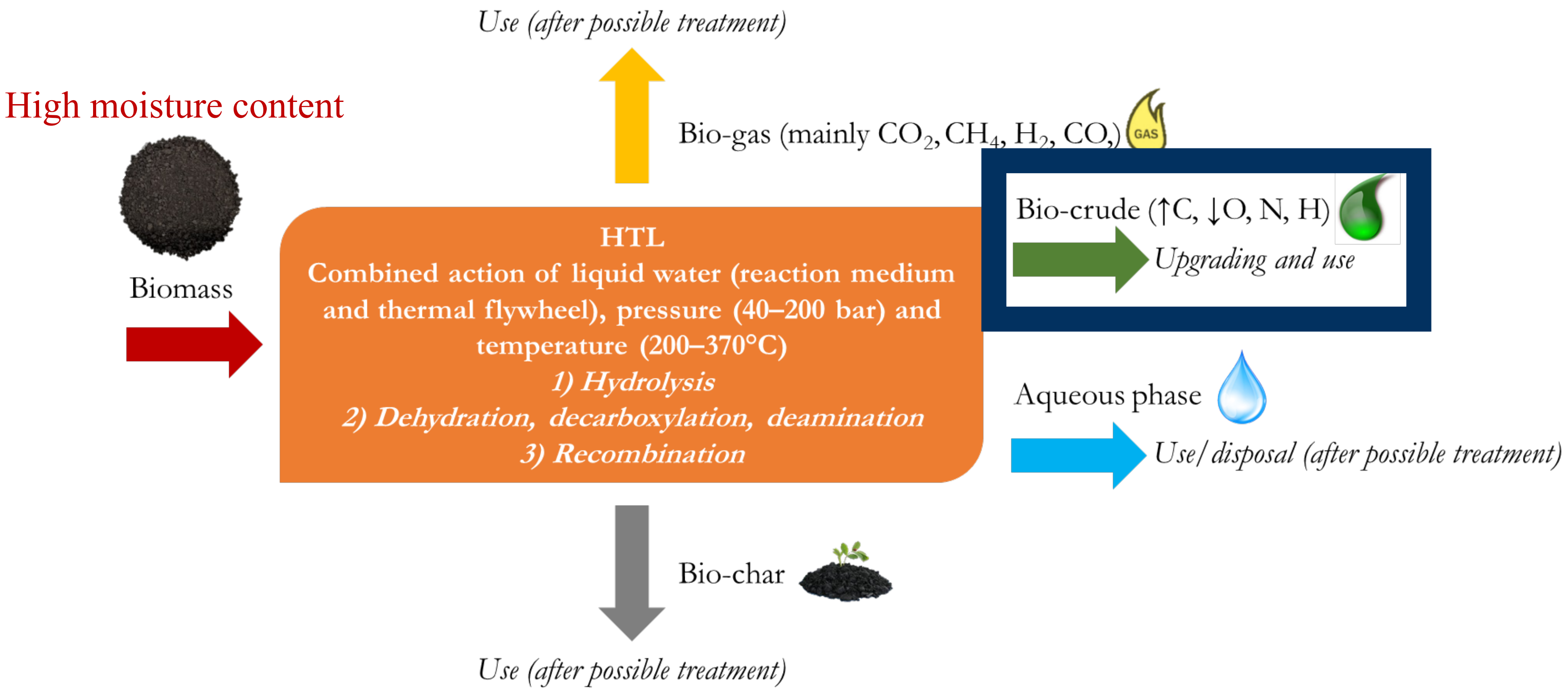
- High operating costs (ca. 90-200 € ton^{-1}),
- Decline in available land space,
- Potential risk of soil and groundwater pollution.



In the circular economy perspective, the valorisation of the organic content of TS to produce energy vectors is a promising strategy to overcome the abovementioned issues (“Sludge-to-Energy (StE)” strategy).

Hydrothermal liquefaction process (HTL)

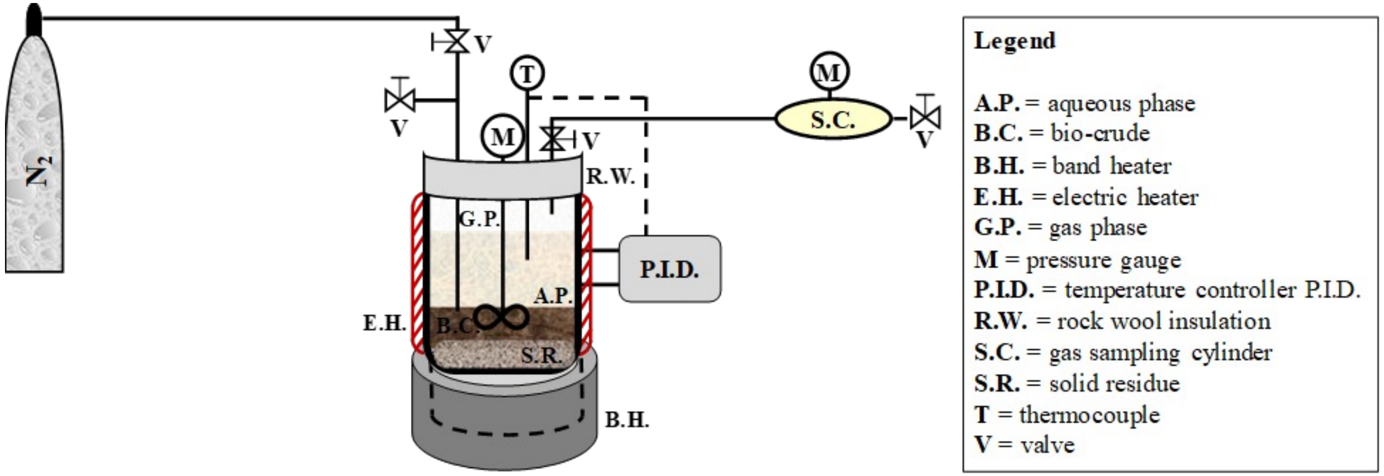
Valorisation of tannery sludge is evaluated through the hydrothermal liquefaction (HTL) process



Direct combustion, gasification and anaerobic digestion risk releasing heavy metals back into the environment. Alternatively, thermochemical conversions such as pyrolysis or hydrothermal liquefaction offer significant advantages in terms of the segregation of metals into a relatively inert and compact solid phase while producing a bio-crude for bioenergy production.

Lab-scale apparatus for HTL tests

500 mL batch reactor



Heating rate → **8°C/min**

Cooling rate → **30°C/min**

Drying and grinding of sludge → **Injection of sludge/water slurry** → **N_2 purging** → **Pressurization/ heating** → **HTL test**

Pressure 200bar; T=250-350°C; reaction time under isothermal conditions 0-60min

Tannery sludge properties

- ***Proximate analysis*** →by TGA701 LECO thermobalance (UNI 9903/ASTM D5142 references standards)
- ***Ultimate analysis*** → by element analyser LECO CHN628 (ASTM reference standard D5373)
- ***Higher heating value (HHV)*** →by Mahler bomb using ASTM D5865
- ***Metal determination*** →by Inductively Coupled Plasma Mass Spectrometry ICP-MS (EPA 3052 reference standard)
- ***Total Cr content*** →by atomic absorption spectroscopy (AAS)
- ***Cr(VI) content*** →by UV-Vis spectrophotometric method (EPA 3060A reference method)

	Tannery sludge [$\%_{wt.}$] dry basis	Tannery sludge [$\%_{wt.}$] wet basis
C	33.61	27.41
H	5.10	4.16
N	2.44	1.99
S	4.07	3.32
Cl	0.35	0.29
Ash	38.52	31.41
Moisture	---	18.46
Organic matter	61.47	50.13
O (by difference)	15.91	12.96

Tannery sludge	*HHV* [MJ/kg]		14.90 ± 0.31
	LHV [MJ/kg]	value calculated from *HHV**	13.62

$*LHV = HHV \cdot n\Delta H$

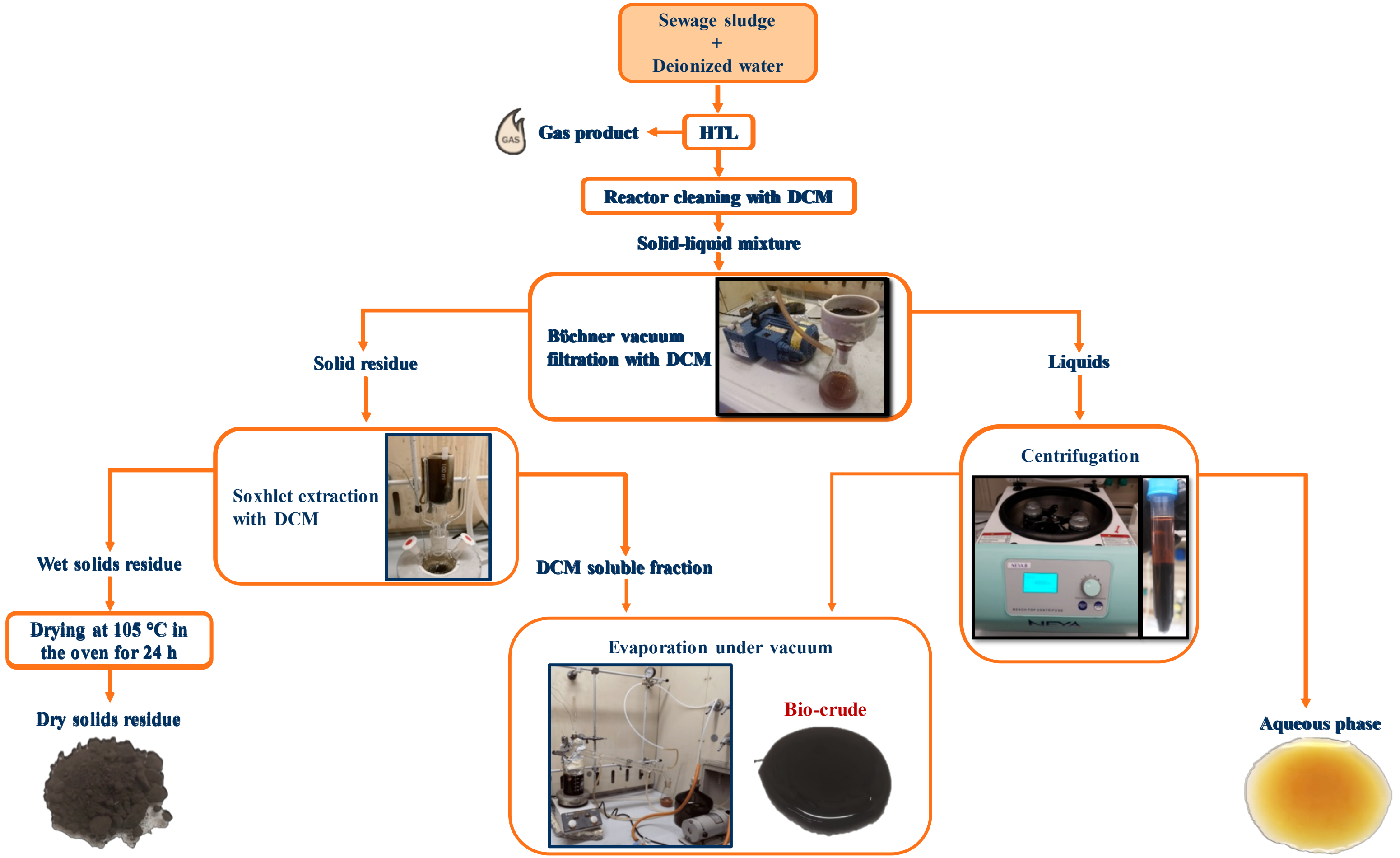
where *n* represents the kg of water produced on kg of fuel, while Δ*H* is the latent heat of evaporation of H_2O, approx. 2.5 MJ/kg.

Metal	Tannery sludge [g/kg]
Na	4.32 ± 0.06
Mg	1.01 ± 0.03
Al	4.77 ± 0.17
Si	8.74 ± 0.22
P	0.46 ± 0.02
Ca	49.64 ± 1.89
K	0.46 ± 0.02
Ti	0.72 ± 0.07
Cr	22.52 ± 0.12
Mn	0.081 ± 0.001
Fe	24.77 ± 0.06
Cu	0.072 ± 0.002
Zn	1.16 ± 0.03
Pb	0.024 ± 0.001

	Dry basis [g/kg]
Cr_{tot}	25.38±0.15
Cr(VI)	n.d.

≤ 2 ppm, if present

HTL products separation



Bio-crude and acqueous phase characterisation techniques:

- Higher heating value by Mahler bomb calorimeter
- Speciation of bio-oil and aqueous phase by H-NMR
- Speciation of metal content in the HTL products by ICP-MS and AAS

$$Y_{bio-crude}^{db} = \frac{m_{bio-crude}}{m_{biomass,db}} \cdot 100 \; or \; Y_{biocrude}^{dafb} = \frac{m_{bio-crude}}{m_{biomass,dafb}}$$

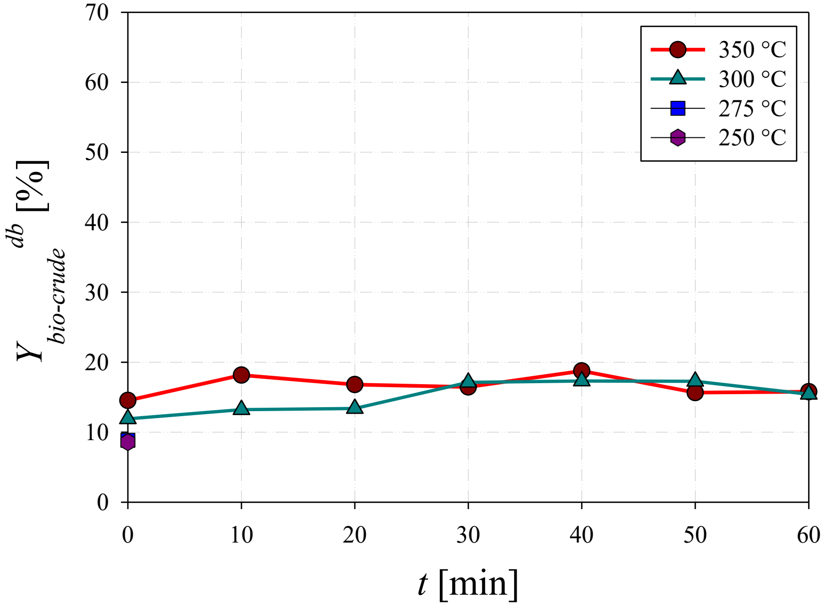
$$Y_{solid\ residue}^{db} = \frac{m_{solid\ residue_{db}}}{m_{biomass,db}} \cdot 100$$

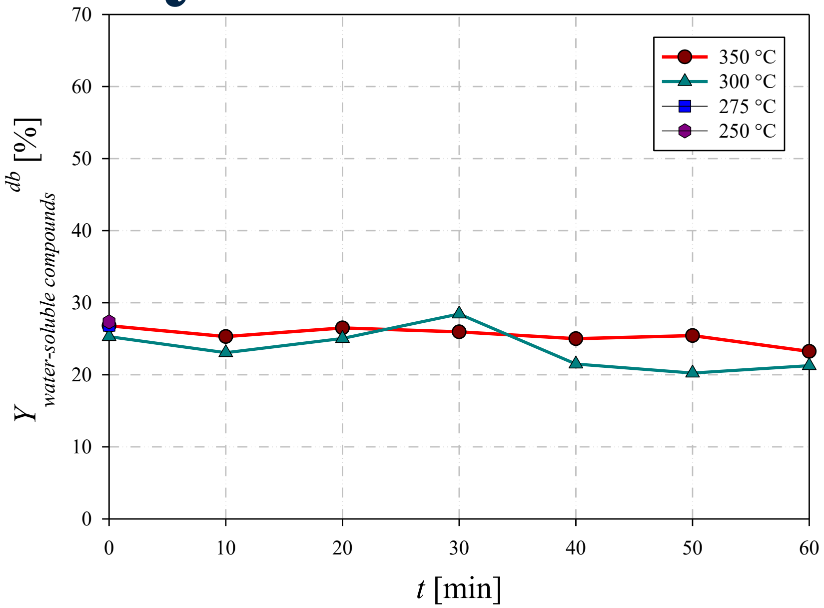
$$Y_{gas}^{db} = \frac{m_{CO_2}}{m_{biomass,db}} \cdot 100 \text{ or } Y_{gas}^{dafb} = \frac{m_{CO_2}}{m_{biomass,dafb}} \cdot 100$$

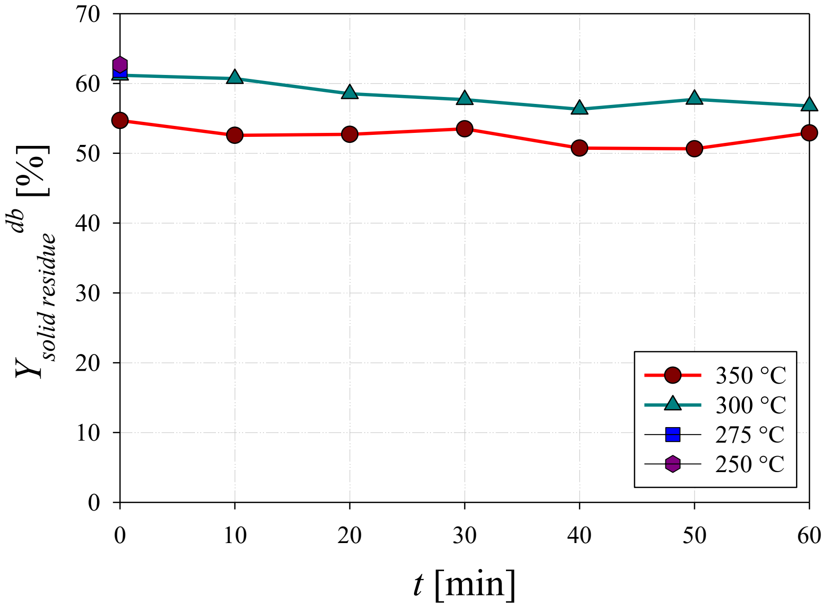
$$Y_{water-soluble\ compaunds}^{db} = 100 - (Y_{bio-crude} + Y_{solid\ residue} + Y_{gas})$$

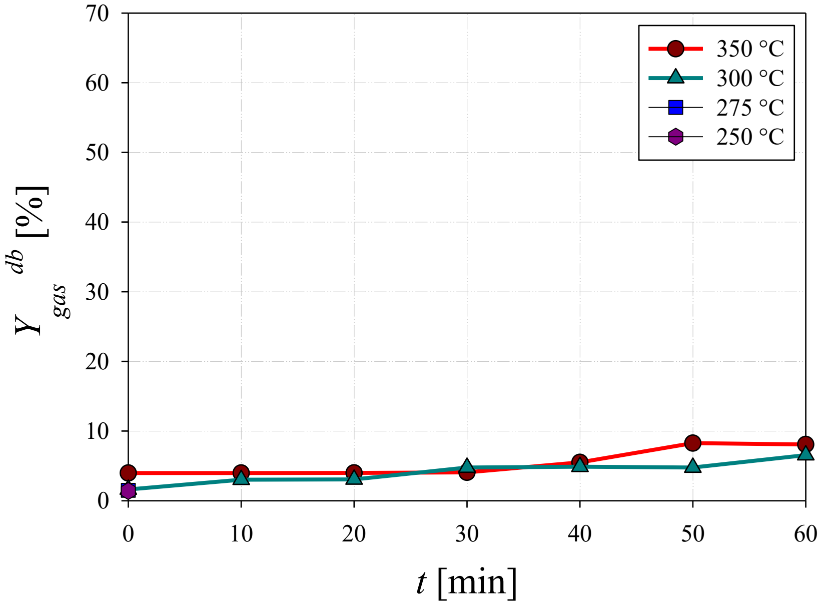
$$ER = \frac{HHV_{bio-crude} \cdot Y_{bio-crude}^{db}}{HHV_0}$$

HTL Products yield









Bio-crude properties

Test	$Y_{bio\text{-}crude}^{dafb}$ ($Y_{bio\text{-}crude}^{db}$) [%]	HHV [MJ/kg]	ER [%]	Cl content [%]	S content [%]
Cen-300-30	27.8 (17.2)	35.5	41.0	0.010 ± 0.001	3.32 ± 0.72
Cen-350-10	29.5 (18.2)	36.1	44.1	0.028 ± 0.003	3.34 ± 0.53

Advantages:

- The obtained bio-crude has an HHV higher 2.9 times the tannery sludge
- Through the HTL process a good energy recovery is achieved

Drawback:

- The issue is linked to the high sulphur content present in the bio-crude

Products characterisation by ^{1}H-NMR

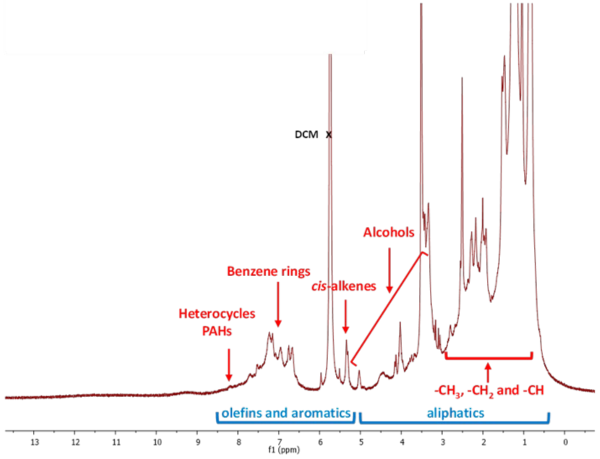
For both analysed bio-crude samples (A e B):

- Major contribution aliphatic protons
- Minor contribution of aromatic compounds and amines and alcohols protons.

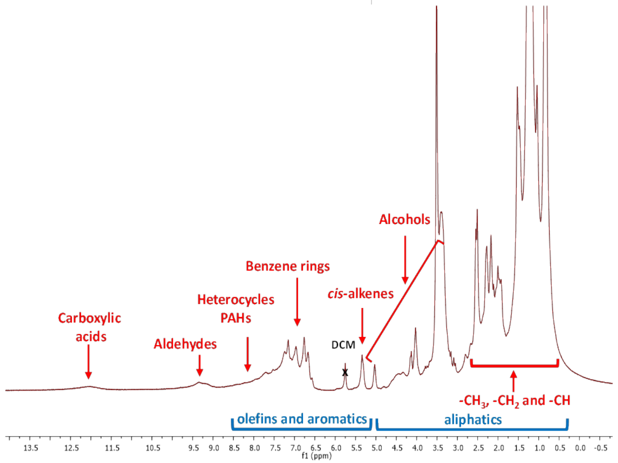
For both analysed aqueous phase samples (C e D):

- Major contribution of aliphatic protons but an increasing of amines and alcohols protons

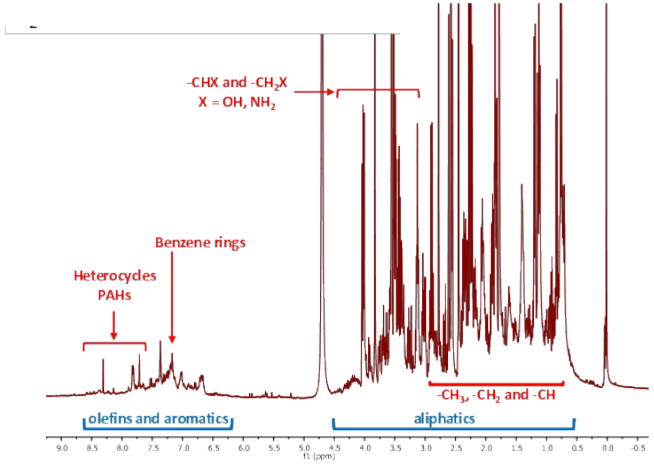
A) Bio-crude at 300°C and 30 min



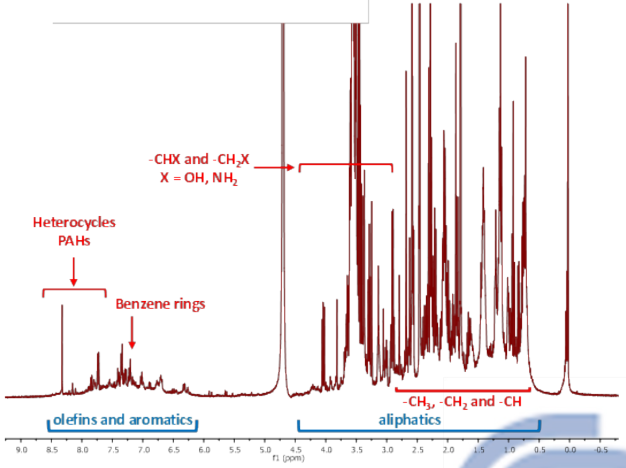
B) Bio-crude at 350°C and 10 min



C) Aqueous phase at 300°C and 30 min



D) Aqueous phase at 350°C and 10 min



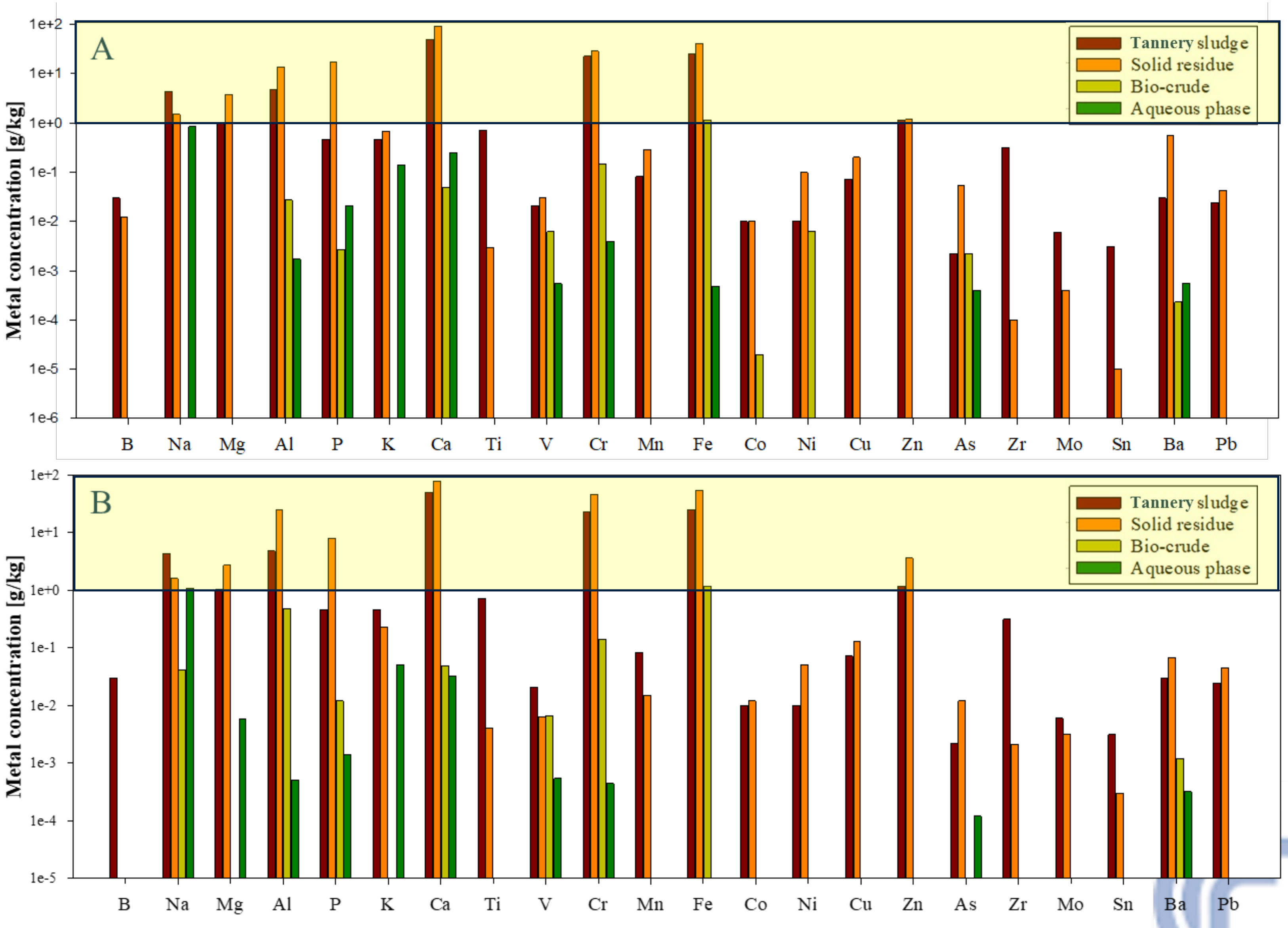
Products characterisation by ICP-MS analysis

Legend:

A) Bio-crude at 300°C and 30 min

B) Bio-crude at 350°C and 10 min

Tannery sludge
Solid residue
Bio-crude
Aqueous phase



Inorganic elements after the HTL process are concentrated in the solid residue, with values in the bio-crude that is up to about 3 orders of magnitude lower with respect to the solid residue.

Chromium distribution in HTL products

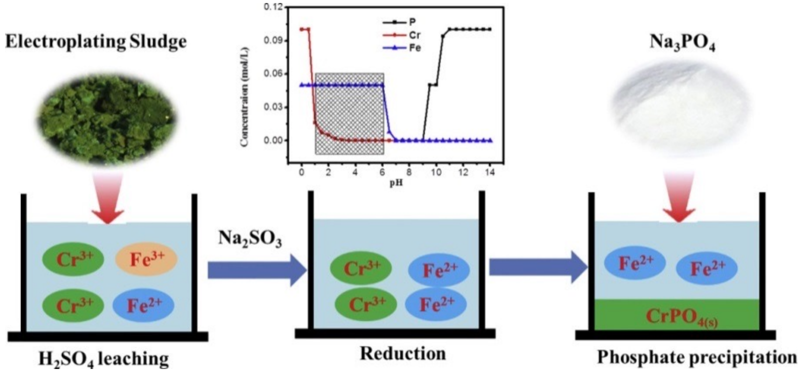
	Tannery Sludge	Solid Residue	Bio-crude	Aqueous Phase
Cr [g/kg]	25.38	47.35	0.23	0.0005
Cr [g]	0.76	0.75	0.001	0.00013
Cr(VI)	n.d.	n.d.	n.d.	n.d.
Cr recovery [%]		98.3		

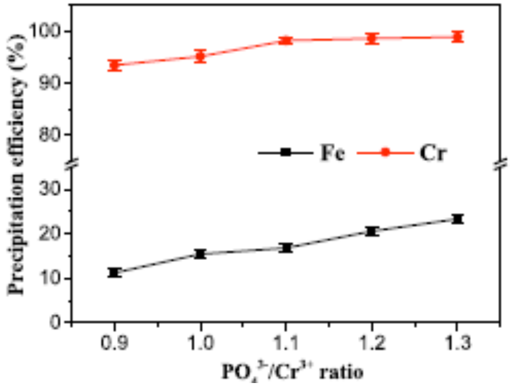
If present, the Cr(VI) content in the solid residue, bio-crude and aqueous phase produced during HTL test would not exceed 0.5 ppm.

At 350 °C and 10 min, more than 98% of Cr was found in its trivalent form in the solid residue, allowing us to obtain clean biofuels

Valorisation of Cr-rich solid residue

Possible options could include leaching with acid solutions or extraction with solvents followed by chemical precipitation for selective recovery of Cr in the form of basic chromium sulphate, a valuable product for the tanning process.





Cr present in the solid residue could represent a substitute for the chromite ore, which is a raw material essential to produce HC-ferrochrome alloy

Chemical composition of the slag from the production of the HC-FeCr alloy.

Chemical composition (%, w/w)	Slag from HC-FeCr production	
	Simulation	Experiment
SiO_2	43.90	41.75
CaO	37.35	36.38
Al_2O_3	18.66	11.88
MgO	–	5.53
MnO	–	0.08
FeO	–	0.31
Cr_2O_3	–	0.30
P_2O_5	–	0.02

Elemental analysis of the HC-FeCr alloy obtained by carbothermal reduction of the ashes from leather shaving incineration (ALSI).

Element (%, w/w)	HC-FeCr alloy		
	Simulation	Experiment	Specification
Cr	55.20	50.31	>50
C	7.96	7.63	6–9
Si	8.11	2.50	<5
S	–	0.04	<0.03
P	–	0.03	<0.04

In Alves et al. 2012 it was produced, per each 100 g of leather ashes 58.5 g of HC-FeCr alloy and 56.3 g of slag. The metallurgical recovery of chromium as HC-FeCr alloy in relation to the initial chromium concentration was 99.1%

Yan, K., Liu, Z., Li, Z., Y, R., Guo, F., Xu, Z. Selective separation of chromium from sulphuric acid leaching solutions of mixed electroplating sludge using phosphate precipitation. *Hydrometallurgy* 2019, 186, 42–49.

Alves, C. R.; Keglevich de Buzin, P. J. W.; Heck, N. C.; Schneider, I. A. H. Utilization of ashes obtained from leather shaving incineration as a source of chromium for the production of HC-FeCr alloy. *Miner. Eng.* 2012, *29*, 124−126.

Operating conditions:

Reaction time = 0–60 min
Reaction temperature = 300°C and 350°C
Reaction pressure = 200 bar

	Bio-crude yield (dry and free ash basis)	**Bio-crude chemical composition**	**Metal speciation**	**Cr oxidation**
HTL on sewage sludge in a 500mL batch reactor	$Y^{dafb}_{bio\text{-}crude}$ = 29.5% (10 min – 350°C) *ER*= 44.1% (HHV=30 MJ/kg)	Mainly composed by aliphatic compounds and in minor percentage of amines, alcohols and aromatic compounds Reduced concentration of inorganic elements	Inorganic elements concentrated in the solid residue, with values in the bio-crude up to about 3 orders of magnitude lower with respect to the other co-products.	**Prevented**

Thank you for your kind attention

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