Outline of a Process for the Hydrothermal Liquefaction of a Tannery Sludge for Biofuel Production

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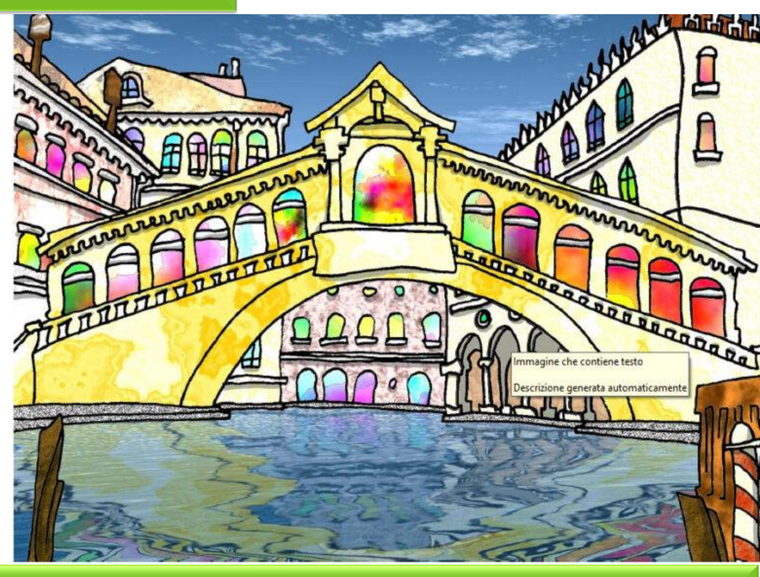


▪ Introduction

The growing interest in renewable energies due to climate change concerns have led research towards liquid fuels production from renewable energy resources. The civil/industrial sludge conversion into bio-crude via hydrothermal liquefaction (HTL) can simultaneously provide a replacement to non-renewable crude-oil while dealing with waste disposal issues. HTL takes advantage of liquid water's interesting properties at high temperatures near the critical point, which facilitate the break down and reformation of biomass into a more energy dense bio-oil.

Aim of the work

In this work a tannery sludge has been characterised by several techniques to preliminary assess the sludge composition and properties prior to its energetic valorisation via HTL. Moreover, a lab-scale plant consisting in a batch autoclave was designed, also with the aim to elucidate the reaction pathways of the HTL process so to identify optimal operating conditions for obtaining a high-yield bio-crude with more attractive energy properties. Finally, to investigate the relationships between HTL operating conditions and yield/quality of the sludge-derived bio-fuels, an original elaboration of literature data was performed.

▪ Characterisation of a tannery sludge

Proximate/ultimate analysis and higher heating value

	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

Excellent candidate for HTL process, where water acts as a solvent and catalyst in the bio-oil production process.

Good potentiality to act as energy vector in the HTL process.

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	3886.68	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, which also take part in the step of leather production.

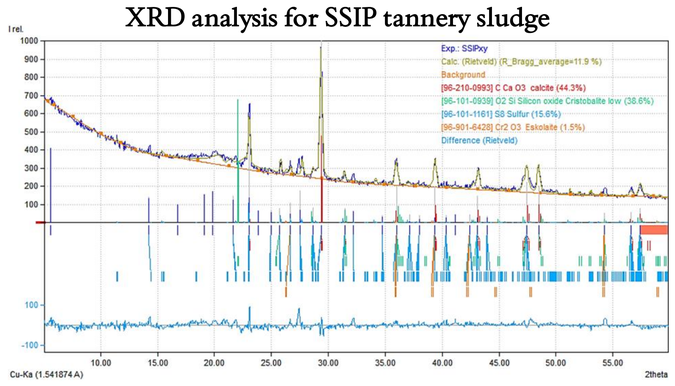
The spectrophotometric technique did not detect the presence of highly harmful Cr(VI) in the solution containing the sludge.

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 for SSIP tannery sludge



The 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 apparatus for HTL

Legend

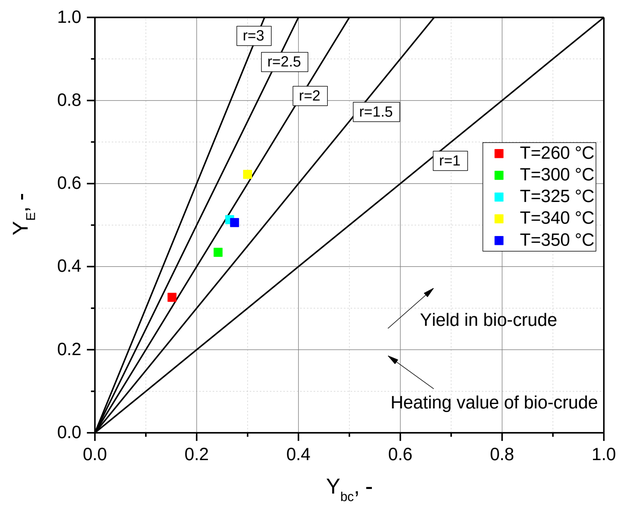
A.P. = aqueous phase	E.H. = electric heater	S.C. = gas sampling cylinder
B.C. = bio-crude	I.R. = infrared analyser	S.R. = solid residue
B.R. = batch reactor	M = pressure gauge	T = thermocouple
G.P. = gas phase	P.I.D = temperature controller P.I.D.	V = valve

Layout of the lab-scale apparatus for the execution of HTL tests

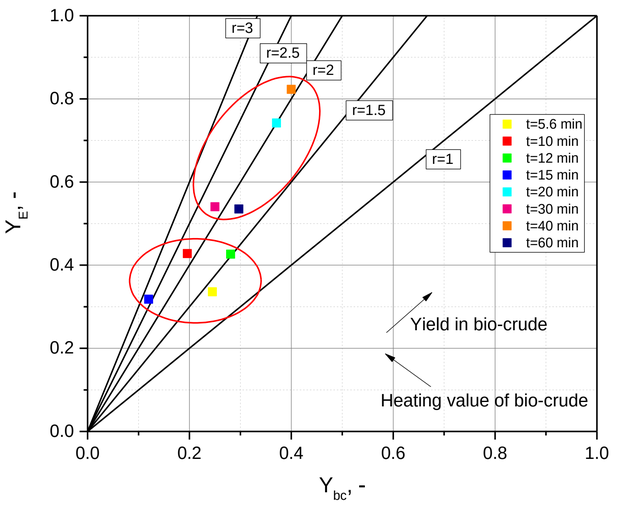
Hard reaction environment → choice of a metal alloy nikel-chromium-molybdenum (Hastelloy C-276)

▪ Role of operating parameters on the performances of HTL

Energy yield as a function of the bio-crude yield for HTL of sludges treated at different temperatures.



Energy yield as a function of the bio-crude yield for HTL of sludges treated at different reactions time.



Data show an increase in the energy and mass yield of the bio-crude in the range 260–340°C:

Y_E → increases from 0.33 at 260 °C (Y_{bc}=0.15) to 0.62 at 340 °C (Y_{bc}=0.30)

decrease to 0.51 at 350 °C (Y_{bc}= 0.27)

Data analysis enables to identify two main "clouds" in which data gather:

Short times → Y_E =0.32–0.43 Y_{bc} =0.12–0.28 (6–15 min)

Long times → Y_E =0.58–0.82 Y_{bc} =0.25–0.40 (20–60 min)

Results suggest that a temperature of ca. 340 °C and reaction times of about 20 min can provide satisfactorily values of both energy and mass yield of sludges-derived bio-crude.

▪ Conclusions

According to the characterisation of the tannery sludge and the elaboration of the optimal experimental conditions, a deeper experimental campaign will be performed in the designed lab-scale apparatus to consolidate the highlighted trends, also for the treated tannery sludge.