Bio-crude production and inorganics elements distribution during the hydrothermal liquefaction of tannery sludge

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Abstract
Tannery sludge (TS) is the major waste in leather industry. The wastewater treatment of tanning plants produces large amounts of sludge contaminated with chromium, which disposal is a hard issue to deal. In this context, hydrothermal liquefaction (HTL) is an innovative thermochemical process to convert contaminated biomasses into bio-fuels. In this study, a tannery sludge was chosen as substrate to perform the HTL process. The HTL tests were carried out in a 500 mL batch reactor for different reaction times (0–10 min) and temperatures (250°C, 275°C, 300°C and 350°C). Results proved that under the best operating conditions (350ºC and 10 min) it is possible to obtain a bio-crude yield (on dry and ash-free basis) of 29.5% with an associated energy recovery of 44.1% (higher heating value of 36.1 MJ/kg). ICP-MS analysis of the three HTL products (bio-crude, aqueous phase and solid residue), showed that the inorganic elements are mainly concentrated in the solid residue. Finally, UV-vis analysis of Cr showed that it is present in reaction products in its trivalent form, thus demonstrated that HTL, in this study at least, avoids the undesired oxidation of Cr(III) to Cr(VI).

Introduction
About 6.9 Gt/year of raw leathers are produced worldwide [1], with a considerable release into the environment of hazardous sewage sludge, contaminated by heavy metals. In particular, basic chromium (III) sulphate salt is used as a tanning agent. However, only 60% of the total amount of chromium is effectively used during the tanning process, binding with animal skin collagen. The rest of chromium remains in the tanning bath and is subsequently discharged into the wastewater, whose treatment produces the tannery sludge [2]. Therefore, new routes for the valorization

of these contaminated waste must be identified to achieve a more sustainable production of leathers. In this context, hydrothermal liquefaction (HTL) represents an emerging process for the energy valorization of tannery sludge, by converting it into liquid bio-fuels and avoiding the high-energy demanding dehydration step commonly associated with conventional thermochemical processes [3]. Indeed, HTL is generally carried out in a hot, pressurised water environment (200–375°C and 40–200 bar) for sufficient time to convert the organic matter of the tannery sludge (TS) into bio-crude as target product, together with gas and aqueous phases, and a solid residue as co-products [4]. Moreover, not aiming at the complete oxidation of the organic component, HTL process potentially limits the oxidation of Cr in its more harmful hexavalent form. In this study, a tannery sludge was adopted as substrate for the HTL process to produce bio-crude. HTL tests were carried out in a 500 mL batch apparatus for reaction times ranging from 0 to 60 min and temperatures of 250, 275, 300°C and 350°C, also to assess the possible formation of bio-crude during the thermal transients. Bio-crude samples obtained under the best operating conditions, were also chemically and energetically characterized by proximate and ultimate analysis and Mahler bomb calorimeter. Moreover, the distribution of inorganic elements (with particular reference to heavy metals) in the different HTL products was assessed by ICP-MS analysis. Lastly, the distribution and speciation of chromium in the HTL products was studied by UV-vis analysis.

Tannery sludge

Chromium-rich industrial sludge from a tanning wastewater treatment plant was used as a substrate to perform HTL tests. By proximate analysis, TS consists of 18.46% moisture, 50.13% volatile material and 31.41% ash, while no fixed carbon was detected. Moreover, a total C content of 33.61% was detected by ultimate analysis, along with 5.10% H, 2.44% N and 4.07% S, and a Cl content equal to 0.35% on dry basis. The high percentage of S is due to high amount of sulfates used in the tanning process (about five times higher on dry basis than S content of a municipal sludge, as reported in [5]). Regarding the energy properties of TS, on a dry basis, the average value of higher heating value HHV is 14.90 MJ/ kg. Lastly, the metal content of TS, on dry basis, was obtained by inductively coupled plasma-mass spectrometry (ICP-MS), according to which Ca is the most abundant metal, with a concentration of 49.64 g/kg, followed by Fe (24.77 g/kg), Cr (22.52 g/kg), Si (8.74 g/kg), Al (4.77 g/kg), Na (4.32 g/kg), Zn (1.16 g/kg) and Mg (1.01 g/kg). The Cr(total) content obtained by atomic absorption spectroscopy is about 25.38 g/kg on dry basis, while no Cr(VI) was detected in the sludge by UV-vis analysis.

Experimental apparatus for HTL and products separation procedure

The HTL tests were performed in a 500 mL batch autoclave reactor [6] equipped with a pressure measurement and control system, an internal loop coil to ensure the fast cooling of the system, a magnetic stirrer, a tubular electric heater surrounding the reactor coupled with a thermocouple and PID systems for the temperature setting and measurement. A layer of rock wool and a band heater, respectively on the top and the bottom of the reactor, were used to optimize the thermal transient. More details on reactor configuration are reported in our previous work [7]. Briefly, the reactor was loaded with a slurry of 10%$_{wt}$ biomass content, consisting of 30 g (on dry basis) of parent sludge, together with distillated water, after which the head space of reactor was purged with N_2. Then, the system is pressurized to obtain a pressure of about 200 bar at the temperature selected for the reaction. HTL tests were conducted at temperatures (*T*) of 300 °C and 350 °C, and for isothermal residence times (*t*) ranging from 10 to 60 min. Moreover, the possible formation of bio-crude during the thermal transients was assessed by stopping heating as soon as the reactor reached a temperature of 250°C, 275°C, 300°C and 350°C. After the HTL test, the solid-liquid mixture recovered from the reactor was filtered on a Büchner under vacuum. The solid phase was subjected to a Soxhlet extraction with dichloromethane (DCM) to recover the bio-crude from the pores of solid, and then oven-dried at 105°C for 24 h. The bio-crude fraction extracted from DCM was recovered for subsequent distillation. The liquid fraction was separated into bio-crude and aqueous phase by centrifugation for 10 min at 4000 rpm using a NEYA BASIC ventilated apparatus. The bio-oil was recovered using 20 g of DCM and mixed with the bio-crude fraction extracted from DCM by Soxhlet procedure. Finally, the bio-crude was distilled under vacuum distillation at 0.4 bar to get the evaporation of the solvent. Finally, the yield of the products was calculated as the mass of product obtained compared to that of sludge loaded (on a dry basis). Moreover, after the separation protocol, the bio-crude samples were subjected to a Mahler bomb calorimeter for the HHV determination, and the energy recovery (*ER*) was estimated according to the following equation:

$$ER = \frac{\mathrm{HHV}_{bio-crude}}{\mathrm{HHV}_{biomass}} Y_{bio-crude}^{db}$$

Results and discussion

Figure 1 shows the yields on dry basis of bio-crude (a), water-soluble compounds (b), solid residue (c) and gas phase (d) at different reaction times as a function of the operating temperature. For both the temperatures investigated of 300°C and 350°C, the yield of HTL products remains almost constant, showing that the effect of the isothermal reaction time is negligible. In detail, for the test carried out at 350ºC, the bio-crude yield slightly increases from 0 to 10 min (18.2%), remains about constant until 40 min and then decreases to 60 min (15.8%), probably due to the reactions of polymerization/cracking of the bio-crude for long reaction times with the consequent increase in the yields of the solid residue and gas phase from 40 to 60 min. A similar trend, shifted to longer times, was obtained for tests carried out at 300°C. The yield of bio-crude slightly increases from 0 to 30 min (17.1%), remains constant up to 50 min and then decreases to 60 min (15.4%). In addition, the yield of the solid residue between 0 and 60 min decreases slightly from 61.18% to 56.77% and from 54.70% to 52.91%, respectively at 300 and 350°C. Lastly, the yield of the gas phase does not follow a clear, with a slight increasing trend from 1.6% to 6.5% at 300°C and from

3.9% to 8.1% at 350°C. The bio-crude samples with the maximum yield, (29.5% at 350°C–10min and 27.8% at 300°C–30min on dry and ash-free basis), were chemically and energetically characterized. Similar HHV values were obtained for both samples (36.1 MJ/kg at 350°C and 35.5 MJ/kg at 300°C); while the slight difference in *ER* (44.1% at 350°C and 41% at 300°C) is determined by the slightly higher yield of the bio-crude obtained at 350°C. About the chemical composition, Cl content of samples is one order of magnitude lower than its concentration in the starting biomass (0.001% at 350°C and 0.028% at 300°C, on dry basis). The S content in the bio-crude is similar to the one detected in the parent sludge (3.32% at 350°C and 3.34% at 300°C, on dry basis). The high S content in the bio-crude can be ascribed to the presence of basic chromium sulphates which are used in tanning process.

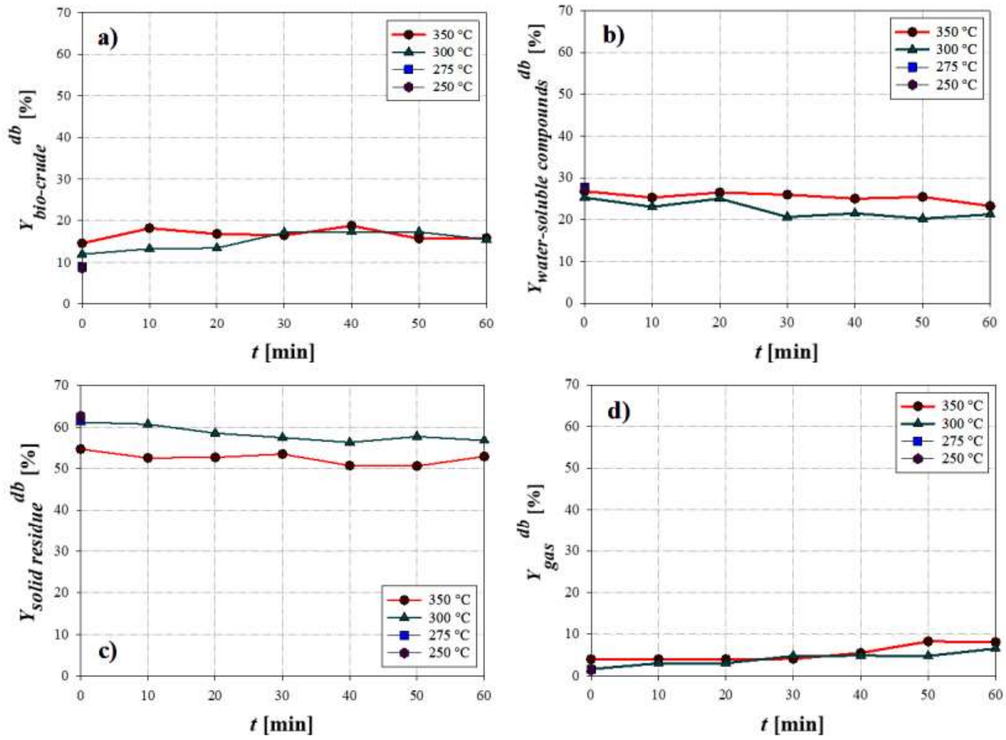

Fig. 1. Yield of a) bio-crude b) water-soluble compounds c) solid residue and d) gas yields as a function of time and for different temperature.

Table 1 shows the distribution of inorganic elements in the three HTL products. The investigated elements are mainly concentrated in the solid residue, while some of them are found in traces in the bio-crude and in the aqueous phase. In detail, Ca is the most abundant in the solid residue, followed by Fe and Cr. About the Cr distribution in the HTL products, solid residue has a Cr content of 29.0 g/kg at 300°C and 45.87 g/kg at 350°C, and it is almost all the Cr of the parent sludge. Cr in the solid residue is two orders of magnitude higher than that of the bio-crude (0.15 g/kg at 300°C and 0.14 g/kg at 350°C) and four orders of magnitude higher than that of the aqueous phase (0.004 g/kg at 300°C and 0.00044 g/kg at 350°C). However, even if at very low concentration, the presence of Cr, as well as of Fe, found in both bio-crude samples could require additional metals removal techniques. The speciation of

Cr during the HTL process was assessed by UV-vis analysis of the HTL products for the best operating condition in terms of bio-crude yield (350°C–10min). Results show that, the Cr(VI) content was not detected by UV-vis analysis in all HTL products. This result confirms the potential use of TS in the HTL process, avoiding the problem of Cr oxidation found in other thermochemical processes (i.e. combustion, gasification).

Table 1. ICP-MS analysis for solid residue (SR), bio-crude (BC) and aqueous phase (AP) obtained in TS hydrothermal liquefaction tests, (not detection, n.d.).

Element	SR-300-30 [g/kg]	SR-350-10 [g/kg]	BC-300-30 [g/kg]	BC-350-10 [g/kg]	AP-300-30 [g/kg]	AP-350-10 [g/kg]
B	0.012	n.d.	n.d.	n.d.	n.d.	n.d.
Na	1.50	1.61	n.d.	0.041	0.84	1.06
Mg	3.71	2.70	n.d.	n.d.	n.d.	0.0058
Al	13.53	24.29	0.027	0.48	0.0017	0.00051
P	17.23	7.96	0.0027	0.012	0.021	0.0014
K	0.68	0.23	n.d.	n.d.	0.14	0.050
Ca	92.86	78.49	0.050	0.049	0.25	0.032
Ti	0.003	0.004	n.d.	n.d.	n.d.	n.d.
V	0.030	0.037	0.0062	0.0067	0.00054	0.00054
Cr	29.00	45.87	0.15	0.14	0.0040	0.00044
Mn	0.28	0.015	n.d.	n.d.	n.d.	n.d.
Fe	40.92	54.15	1.12	1.18	0.00049	n.d.
Co	0.010	0.012	0.00002	n.d.	n.d.	n.d.
Ni	0.099	0.051	0.0064	n.d.	n.d.	n.d.
Cu	0.20	0.13	n.d.	n.d.	n.d.	n.d.
Zn	1.18	3.58	n.d.	n.d.	n.d.	n.d.
As	0.054	0.012	0.0022	n.d.	0.00040	0.00012
Zr	0.0001	0.0021	n.d.	n.d.	n.d.	n.d.
Mo	0.0004	0.0032	n.d.	n.d.	n.d.	n.d.
Ba	0.57	0.067	0.00023	0.0012	0.00055	0.00032
Pb	0.043	0.045	n.d.	n.d.	n.d.	n.d.

Conclusion

Tanning industry annually produces a large amount of sludge, contaminated mainly with chromium compounds. The disposal of this hazardous waste in landfill leads to high management costs and secondary pollution issues. A sustainable development means the identification of new technologies for the valorization of the heavy metals contaminated biomasses, as tannery sludge. To this end, the hydrothermal liquefaction process was applied to a tannery sludge to produce an energy vector. The HTL tests were carried out in a 500 mL batch reactor for different reaction times and temperatures, proving that in the best operating conditions (350ºC and 10 min) it is possible to obtain a bio-crude yield (on a dry and ash-free basis) of 29.5% with an associated energy recovery of 44.1% (HHV of 36.1 MJ/kg). The distribution of inorganic elements in the three HTL products, obtained through ICP-MS analysis, showed that the elements are mainly concentrated in the solid residue, with values up to 4 orders of magnitude higher than those shown in the bio-crude and aqueous phase. Finally, UV-vis analysis of Cr showed that it is present in reaction products in its trivalent form, demonstrating that HTL under the adopted conditions did not oxidize Cr(III) in its more harmful hexavalent state.

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