

Tannery Sludge Gasification in a Fluidized Bed for Its Energetic Valorization

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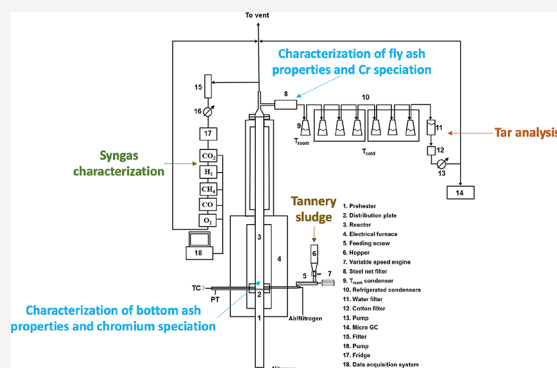
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ABSTRACT: The present article deals with the valorization of the organic content of tannery sludges to produce energy vectors. In this scenario, gasification is a viable option to obtain a flexible gaseous stream (syngas) of interesting energetic value, under operating conditions that do not favor the oxidation of Cr(III) (typically found in tannery sludges) to the more harmful Cr(VI) state. To this end, an industrial tannery sludge was characterized through proximate/ultimate analyses and determination of the heating value, showing its capability to act as a solid fuel in a gasification process, and metal analyses, showing that its Cr(VI) content was below the detection limit (2 ppm). The material was subjected to gasification tests in a lab-scale fluidized bed (FB) reactor. The reactor, with a 41 mm inside diameter and a 1 m height, was electrically kept at an operating temperature of 850 °C. The fluidization velocity was 0.30 m/s at 850 °C, i.e., 7.5 times the value of the minimum fluidization velocity. The gasifying stream was composed by O₂ (3% vol.) diluted in N₂. The adopted oxidant equivalence ratio (ER) levels were 0.15 and 0.24, to ensure substoichiometric (i.e., reducing) conditions in the FB atmosphere. Under the most reducing operating conditions, it was possible to produce syngas with a lower heating value of 12.0 MJ/N m³ (dry and N₂-free basis). It contained, under these conditions, about 42% H₂, 36% CO, and 4% CH₄, plus 16% CO₂ and other components. The tar produced from the process, fully characterized by gas chromatography–mass spectrometry, showed a favorably low concentration of about 25 g/N m³. FB bottom and fly ashes were analyzed for their carbon and metal contents. In bottom ash, the total Cr concentration resulted in the range of 8–12 g/kg, with a Cr(VI) concentration between 8 and 10 ppm. In the elutriated stream, the total Cr concentration was about 55 g/kg, with a Cr(VI) concentration between 4 and 7 ppm. The Cr(VI) concentration was higher when higher values of the ER were used, but it resulted in 3–4 orders of magnitude lower than the total Cr concentration, showing the appropriateness of the process to produce syngas with very limited oxidation of chromium in the solid residues.



1. INTRODUCTION

The Italian leather industry comprises about 1200 companies. Italy, in 2019, produced 128 millions of m² of finished leathers for a production value of 4.9 billion euros, of which 3.6 billion euros account for export. The tannery districts are nowadays using advanced treatment plants that are reaching high levels of specialization for tannery discharges.¹ The obtained sludge is rich in chromium (the removal of chromium by wastewater is greater than 99.4%). The huge volume of sludges generated by the leather industry, with a yearly global production of solid wastes derived from the tanning process estimated to be on the order of 1 ton per ton of raw leather, poses economic and environmental issues associated with their landfilling, mainly due to the relevant amount of chemicals adopted in the tanning process (on average, 2 kg of chemicals are used to produce 1 m² of leather). In the circular economy perspective, the valorization of the organic content of tannery sludge to produce energy

vectors is a promising strategy to overcome the abovementioned issues (“sludge-to-energy (StE)” strategy).²

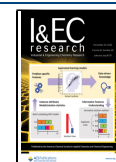
Among currently available StE technologies, the thermochemical treatments such as combustion, pyrolysis, and gasification appear to be particularly promising due to both the possibility of fixing harmful metals in the solid residues and the high conversion efficiency of organic compounds, the latter being generally greater than 80%.³ Thermochemical processing of sludges has also the advantage of characteristic reaction times (from seconds to minutes) much shorter than those required in

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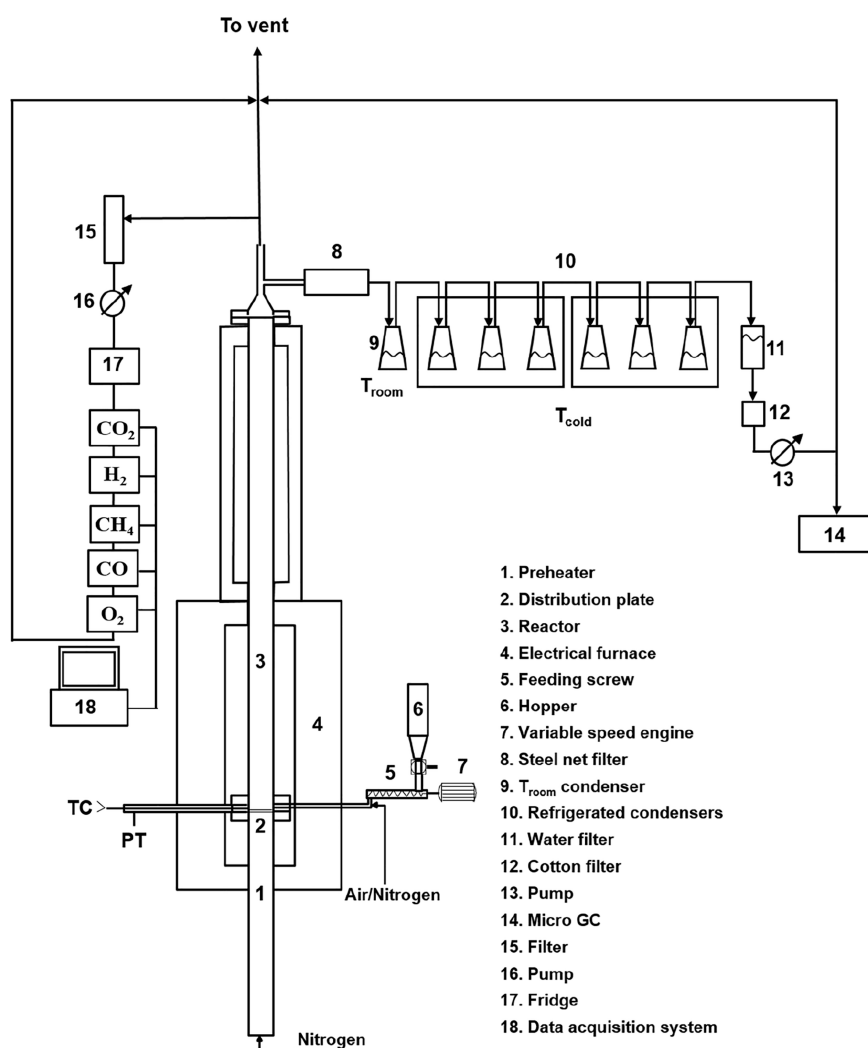


Figure 1. Scheme of the fluidized bed apparatus for gasification tests.

biochemical conversion routes such as anaerobic digestion (in the order of days/weeks), where the converted organic fraction does not exceed 60%.⁴ While the direct combustion of several types of sludges is a common practice, gasification and pyrolysis processes are still limitedly explored for the valorization of this residue.⁵

Among the abovementioned thermal processes, the direct combustion of a tannery sludge suffers critical environmental issues that limit its applicability, as the full oxidizing conditions that are realized in the combustion chamber would unavoidably lead to the oxidation of Cr(III) (typically found in tannery sludges) to the more harmful Cr(VI) state.⁶ Several studies have been carried out to limit undesired chromium release from sludge combustion, such as pretreatment with hydroxyapatite to reduce heavy-metal volatilization along incineration⁷ or postcombustion stabilization of Cr-rich ashes through vitrification with SiO₂, Na₂O, and CaO.⁸

Gasification, instead, is an StE process carried out under partially oxidizing conditions and allows to produce syngas (that can be flexibly used as an energy source also in places/times different from those of production) together with the reduction of the amount of sludge to be landfilled and has the potential to reuse ashes (obtained as a coproduct, in the construction materials industry^{9–11} or as adsorbents for fluid stream purification^{12,13}), with an eye to the principles of circularity.

Furthermore, the substoichiometric oxygen conditions adopted in gasification could reduce the production of Cr(VI). For example, a gasifier equipped with a multipoint hot-air injection system to treat leather solid waste was used, and only Cr(III) oxide was found in bottom ashes.¹⁴ Similarly, it was demonstrated that the chromium species, obtained after gasification of tannery sludge in a downdraft reactor process, remain in the solid residue and mainly in their trivalent form.³

In this context, fluidized bed (FB) reactors are widely known to be appropriate as gasifiers due to the very good mass and heat transfer coefficients ensured by FB fluid dynamics and to the possibility of controlling emissions through proper design of the gasifier and its operating conditions.^{15–17}

By also considering the relatively limited literature on this specific topic,¹⁸ this research article reports on lab-scale FB gasification carried out on an industrial tannery sludge. After a complete chemical characterization of the material by a combination of techniques, gasification was carried out under two different reducing operating conditions, according to literature indications. Syngas, tar, and bottom and fly ash streams were analyzed, and their characteristics were critically discussed in relation to the parent sludge properties and the gasification conditions.

2. MATERIALS, EQUIPMENT, AND EXPERIMENTAL PROCEDURES

The raw material (an industrial tannery sludge coming from a plant located in southern Italy) was characterized by means of the following:

- (i) proximate analysis (TGA701 LECO thermobalance, UNI 9903/ASTM D5142 standard procedures);
- (ii) ultimate analysis (LECO CHN628 analyzer with the ASTM D5373 standard procedure for C, H, and N determination; LECO SC-144DR analyzer with the UNI 7584 standard procedure for S determination);
- (iii) evaluation of the higher heating value (HHV), in a Parr 6200 calorimeter (ASTM D5865 standard procedure), followed by determination of the chlorine content by ionic chromatography (883 Basic IC plus Metrohm, UNI 9903 standard procedure);
- (iv) determination of the content of Cr(total) and Cr(VI), according to a procedure developed by IRSA-CNR, through atomic absorption spectrometry (by dissolving 0.5 g of sludge with 10 mL of 65wt % HNO₃ and 5 mL of H₂O₂) and UV–visible spectrophotometry (Cr(VI) was solubilized in sulfuric acid, and its concentration was determined by a colorimetric reaction with diphenylcarbazide), respectively. The adopted spectrophotometers were an Agilent UV–vis Cary 5000 and an Agilent UV–vis Varian Cary 50.
- (v) X-ray diffraction (XRD) analysis was carried out in a D8 Bruker diffractometer, by scanning the 5–60° 2θ range of diffraction angles at a velocity of 0.05° 2θ/s.

The bench-scale FB gasifier (electrically heated at a controlled temperature) is illustrated in Figure 1. It consisted of a stainless-steel (AISI 310) fluidization column (inner diameter = 41 mm; height = 1 m), with a distributor plate (made of a series of stainless-steel nets) that separates the gas inlet chamber/preheater (600 mm height) from the fluidization column. The reactor was equipped with a steel net filter, located downstream the reactor, for the capture of elutriated fines (fly ash stream). The material was fed at the bottom of the bed through a combination of pneumatic and mechanical conveying devices.

The operating conditions of the gasification tests (carried out at 850 °C) are illustrated in Table 1. The bed inert material was

Table 1. Operating Conditions of FB Gasification Tests of Industrial Tannery Sludge

	test 1	test 2
bed inert material	silica sand, 300–400 μm, inventory = 180 g	
gasification temperature	850 °C	
minimum fluidization velocity	0.04 m/s (@850 °C)	
fluidizing gas	300 NL/h N ₂ + 50 NL/h air (3% O ₂ ; 97% N ₂)	
fluidization velocity	0.30 m/s (@850 °C)	
flow rate of <1 mm sludge	99 g/h	63 g/h
air-to-fuel ER	0.15	0.24

silica sand, 300–400 μm (inventory = 180 g). The fluidizing gas was composed by the sum of a stream of 300 NL/h of N₂ and a stream of 50 NL/h of air. This resulted in a fluidizing gas composed by 3% O₂ (rest N₂), with a fluidization velocity of 0.30 m/s (expressed at 850 °C; the minimum fluidization velocity for this system was 0.04 m/s). After sieving the sludge to a size finer than 1 mm, two tests were carried out: “test 1” and “test 2”, with

sludge flow rates of 99 and 63 g/h, respectively. Once the characteristics of the sludge were known, these two values resulted in air/fuel equivalence ratios (ER) of 15 and 24% of the stoichiometric value for tests 1 and 2, respectively, ensuring that operating conditions were well far from ER = 100% and able to favor the desired gasification (rather than combustion) kinetic patterns. These ER values were in line with literature reviews on the topic.¹⁹ The total duration of each test, after reaching stationary conditions in the bench-scale apparatus, was 1 h. The gas obtained from the process, after filtration and water condensation, was sent to a system of online IR gas analyzers and to a condensation train (composed of one flask at room temperature and six flasks at –12 °C) to collect the produced tar compounds and then measured and analyzed by means of gas chromatography (Agilent 7890A) equipped with mass spectrometry (5975C-VLMSD) (GC–MS). The gasification tests were carried out under semibatch conditions: at the end of each test, the FB was cooled down in N₂ flux, and then, the bed material (sand + bottom ash) was withdrawn. Sand was separated by bottom ash through a combination of sieving and density-based procedures. Finally, bottom and fly ashes were characterized by proximate and ultimate analyses, and their chromium (Cr(total) and Cr(VI)) content was determined.

3. RESULTS AND DISCUSSION

3.1. Properties of the Industrial Tannery Sludge. Table 2 reports the main characteristics of the sludge. Moisture and

Table 2. Results of the Analyses on the Industrial Tannery Sludge with Tests Carried Out in Triplicates (Standard Deviation Reported)

proximate analysis (% by weight)	
moisture	18.46 ± 0.26
volatiles	50.13 ± 0.05
fixed carbon	n.d.
ash	31.41 ± 0.30
ultimate analysis (% by weight; dry basis)	
C	33.61 ± 0.12
H	5.10 ± 0.16
N	2.44 ± 0.05
S	4.07 ± 0.02
HHV [MJ/kg] (dry basis) = 14.90 ± 0.26	

volatiles accounted for, respectively, 18.46 and 50.13%, while an ash content of 31.41% was detected. A total C content of 33.61% was revealed by ultimate analysis (dry basis), together with 5.10% H, 2.44% N, and 4.07% S. The quite high C content is positive in view of the further energetic valorization process. Moreover, HHV = 14.90 MJ/kg for the sludge at hand, a value in line with data commonly reported for sludges and, more generally, biomasses. Finally, a Cl content of 0.35% was detected. Table 3 synoptically illustrates the contents of the main elements (including O, calculated by difference), along with those of ashes and moisture, both on a dry and wet basis.

The concentration of Cr(total) in the parent sludge resulted in equal to 20.65 ± 0.05 g/kg (wet basis, corresponding to 25.32 ± 0.06 g/kg dry basis). No Cr(VI) was detected by UV–visible spectrophotometry. The detection limit of this technique was 2 mg/kg of Cr(VI); thus, if present, the Cr(VI) concentration in the tannery sludge was not higher than 2 ppm, and the concentration of Cr(total) substantially coincided with that of Cr(III).

Table 3. Synoptic List of Main Tannery Sludge Properties (Average % by Weight)

	dry basis	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
O (by difference)	15.91	12.96

Figure 2 reports the XRD spectrum for the dried sludge. The degree of crystallinity of the sample resulted in 7.90% only, to highlight its prevailing amorphous nature. Within the crystalline phase, we found the presence of Ca (as calcite CaCO_3), Si (as cristobalite SiO_2), S, and Cr (as eskolaite Cr_2O_3). The presence of the latter species was expected on the one hand due to the sludge nature; on the other hand, it is interesting to observe that Cr in eskolaite was present as Cr(III), to confirm the chromium analysis above discussed.

3.2. Outcomes of Fluidized Bed Gasification Tests.

Table 4 reports the main outcomes of the FB gasification tests. On a dry and N_2 -free basis, for test 1 (ER = 0.15), syngas was mostly composed of CO (35.49% by vol.), H_2 (41.58%), CH_4 (3.67%), and C_2H_4 (2.89%), the rest being CO_2 . H_2/CO and CH_4/H_2 ratios of 1.17 and 0.09, respectively, were obtained. The tar concentration in syngas was 26.4 g/ N m^3 , and a fly ash flow rate of 7.57 g/h was collected. For test 2 (less reducing conditions, ER = 0.24), syngas was mostly composed of CO (27.05% by vol.), H_2 (32.69%), CH_4 (5.15%), and C_2H_4 (4.66%), the rest being CO_2 . H_2/CO and CH_4/H_2 ratios of 1.21 and 0.16, respectively, were obtained. The tar concentration in syngas was 22.3 g/ N m^3 , and a fly ash flow rate of 4.24 g/h was collected.

The more severe reducing conditions of test 1 allowed to obtain an amount of the two main gasification species (CO +

Table 4. Main Outcomes of the FB Gasification Tests

	test 1 (ER = 0.15)	test 2 (ER = 0.24)
Syngas composition (dry and N_2 -free basis)		
CO [% vol.]	35.49	27.05
H_2 [% vol.]	41.58	32.69
CH_4 [% vol.]	3.67	5.15
C_2H_4 [% vol.]	2.89	4.66
C_2H_6 [% vol.]	0.09	0.09
CO_2 [% vol.]	16.16	30.10
Total [% vol.]	99.88	99.74
SO_2 [ppm]	193	137
H_2/CO [vol./vol.]	1.17	1.21
CH_4/H_2 [vol./vol.]	0.09	0.16
HHV (dry and N_2 -free basis) [MJ/ N m^3]	13.1	12.6
LHV (dry and N_2 -free basis) [MJ/ N m^3]	12.0	11.6
tar concentration in syngas [g/ N m^3]	26.4	22.3
elutriated stream flow rate (fly ash) [g/h]	7.57	4.24

H_2) of 77.07%, which is 22% more than what we observed during test 2 ($\text{CO} + \text{H}_2 = 59.74\%$). Correspondingly, the CO_2 content obtained in the syngas from test 1 (16.16%) was far lower than what was observed in test 2 ($\text{CO}_2 = 30.10\%$). It is here obviously recalled that CO_2 does not contribute to the syngas heating value and that its formation is favored by less reducing conditions as those experienced in test 2.

The evaluation of both the HHV and the lower heating value (LHV) of the syngas was carried out based on its chemical composition: in test 1, it had LHV = 12.0 and HHV = 13.1 MJ/ N m^3 , while values were lower in test 2 (LHV = 11.6 and HHV = 12.6 MJ/ N m^3). They fall within the range reported by NETL-DOE, USA,²⁰ where data from industrial gasifiers to produce syngas as an energetic vector are reported (LHV = 8.3–13.0 MJ/ N m^3 on a dry and N_2 -free basis).

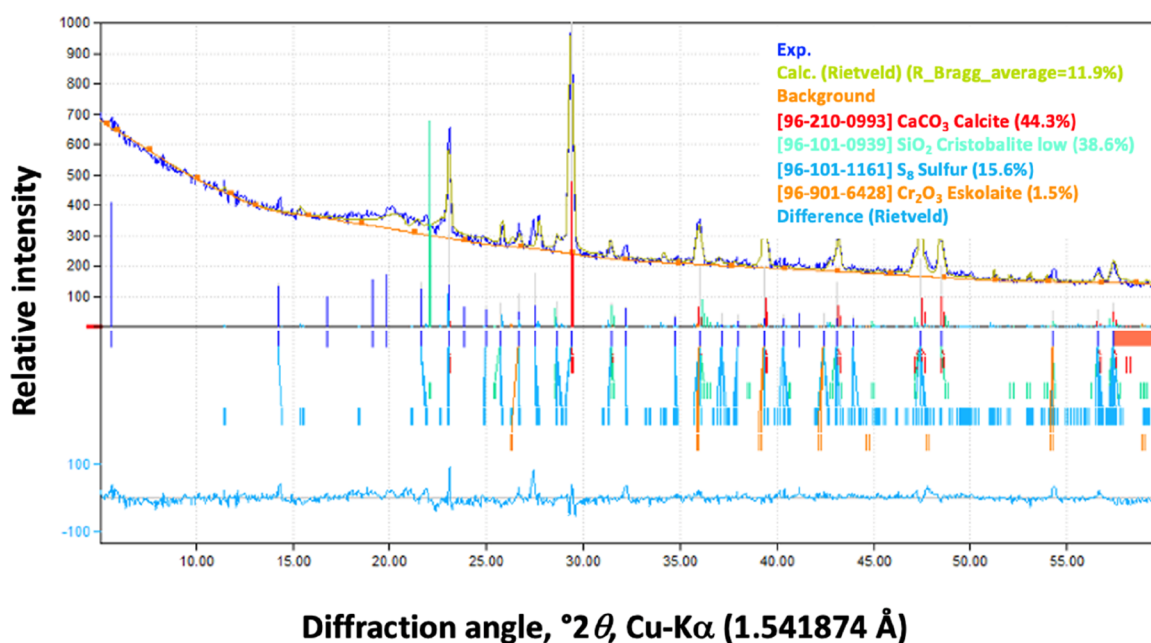
**Figure 2.** XRD spectrum for dried sludge (as received), with indication of the main identified peaks.

Table 5. GC–MS Results on the Characterization of Tar Compounds Collected during Gasification Test 1, at Room Temperature and at $-12\text{ }^{\circ}\text{C}^a$

retention time	peak-normalized area, %	compound	CAS no.	match quality	retention time	peak-normalized area, %	compound	CAS no.	match quality
Test 1, tar collected at room temperature					Test 1, tar collected at $-12\text{ }^{\circ}\text{C}$ (stage I)				
65.848	35.85	anthracene (C ₁₄ H ₁₀)	120-12-7	95	65.864	2.93	phenanthrene (C ₁₄ H ₁₀)	85-01-8	96
39.402	13.20	naphthalene (C ₁₀ H ₈)	91-20-3	95	52.470	1.90	acenaphthylene (C ₁₂ H ₈ S)	208-96-8	90
64.776	12.74	dibenzothiophene (C ₁₂ H ₈ S)	132-65-0	97	13.956	1.89	pyridine (C ₅ H ₅ N)	110-86-1	97
66.212	5.97	phenanthrene (C ₁₄ H ₁₀)	85-01-8	96	32.474	1.71	phenol (C ₆ H ₆ O)	108-95-2	94
52.47	5.54	acenaphthylene (C ₁₂ H ₈)	208-96-8	90	48.485	1.40	biphenyl (C ₁₂ H ₁₀)	92-52-4	95
78.942	5.07	fluoranthene (C ₁₆ H ₁₀)	206-44-0	94	44.830	1.19	1-methylnaphthalene (C ₁₁ H ₁₀)	90-12-0	95
48.485	4.43	biphenyl (C ₁₂ H ₁₀)	92-52-4	95	64.788	0.90	dibenzothiophene (C ₁₂ H ₈ S)	132-65-0	96
57.826	4.43	fluorene (C ₁₃ H ₁₀)	86-73-7	94	55.022	0.87	dibenzofuran (C ₁₂ H ₈ O)	132-64-9	93
82.346	3.31	pyrene (C ₁₆ H ₁₀)	129-00-0	94	57.838	0.79	fluorene (C ₁₃ H ₁₀)	86-73-7	90
55.015	2.98	dibenzofuran (C ₁₂ H ₈ O)	132-64-9	91	29.584	0.78	aniline (C ₆ H ₇ N)	62-53-3	94
45.655	1.53	1-methylnaphthalene (C ₁₁ H ₁₀)	90-12-0	94	47.945	0.60	indole (C ₈ H ₇ N)	120-72-9	95
44.826	1.16	2-methylnaphthalene (C ₁₁ H ₁₀)	91-57-6	93	31.399	0.44	indene (C ₉ H ₈)	95-13-6	91
72.930	0.97	2-phenylnaphthalene (C ₁₆ H ₁₂)	612-94-2	93	8.734	0.36	benzene (C ₆ H ₆)	71-43-2	94
72.948	0.80	1-phenylnaphthalene (C ₁₆ H ₁₂)	605-02-7	90	66.238	0.34	anthracene (C ₁₄ H ₁₀)	120-12-7	76
47.937	0.61	indole (C ₈ H ₇ N)	120-72-9	94	51.131	0.30	2-vinylnaphthalene (C ₁₂ H ₁₀)	827-54-3	81
32.478	0.57	phenol (C ₆ H ₆ O)	108-95-2	87	45.662	0.26	2-methylnaphthalene (C ₁₁ H ₁₀)	91-57-6	97
13.994	0.48	pyridine (C ₅ H ₅ N)	110-86-1	94	42.761	0.14	quinoline (C ₉ H ₇ N)	91-22-5	94
67.685	0.37	dibenzo[<i>a,e</i>]cyclooctene (C ₁₆ H ₁₂)	262-89-5	94	29.798	0.12	benzonitrile (C ₇ H ₅ N)	100-47-0	87
Test 1, tar collected at $-12\text{ }^{\circ}\text{C}$ (stage I)					42.712	0.07	isoquinoline (C ₉ H ₇ N)	119-65-3	81
39.413	80.00	naphthalene (C ₁₀ H ₈)	91-20-3	95	8.742	54.40	benzene (C ₆ H ₆)	71-43-2	90
39.945	3.00	benzo[<i>c</i>]thiophene (C ₈ H ₆ S)	270-82-6	97	6.178	45.60	2-methylfuran (C ₅ H ₆ O)	534-22-5	81

^aCompounds are listed in order of relevance of the peak-normalized area. Database: NIST 11.

3.3. Tar Characterization. Tar concentration values listed in Table 4 are in line with values reported in the literature.²¹ The detailed speciation of the tar compound content in the syngas from tests 1 and 2 is illustrated in Table 5/ Figure 3 and Table 6/ Figure 4, respectively. In both cases, tar species were mostly made up of polycyclic aromatic hydrocarbons (PAH), with the number of C atoms variable between 5 and 16, and in some cases also in the presence of heteroatoms (N, S, and O). More oxidizing conditions (test 2) determined a larger relative contribution of 2-, 3-, and 4-ring PAH not containing heteroatoms. Moreover, the following compounds were also identified:

- compounds with a simple structure (benzene);
- PAH without heteroatoms, having 2 (naphthalene, methylnaphthalene, indene, biphenyl, and vinylnaphthalene), 3 (anthracene, fluorene, phenanthrene, acenaphthylene, phenylnaphthalene, and methylanthracene), and 4 (fluoranthene and pyrene) rings;
- compounds containing N, with a simple structure (pyridine, aniline, and benzonitrile) or having 2 rings (indole and quinoline);
- compounds containing S, with 2 (benzothiophene) and 3 (dibenzothiophene and naphthothiophene) rings;
- compounds containing O, with a simple structure (phenol and methylfuran) or having 3 rings (dibenzofuran).

The chemical nature of the detected tar species is consistent with literature indications for sludges, at least from the qualitative viewpoint (a quantitative comparison cannot be performed, as data specifically referred to tannery sludge are hard to be found). For example, Phuphuakrat and colleagues²¹ detected, as main tar compounds from sewage sludge fixed bed gasification, benzene, phenol, indene, and naphthalene. Among biomass tar species discussed by Pio et al.,²² naphthalene, heterocyclic compounds, and two-/three-/four-ring aromatic hydrocarbons were present.

3.4. Bottom and Fly Ash Characterization with Chromium Speciation. Bottom ash from both FB gasification tests 1 and 2 was mostly composed by inorganic ash (Table 7), to confirm the almost complete conversion of volatiles and C under both ER values. As a matter of fact, from ultimate analysis, C contents not higher than 0.2% were observed. On the other hand (Table 8), the elutriated fly ash, having experienced a mean residence time in the FB gasifier that is much shorter than for the case of bottom ash, contained about 14–17% of volatiles and 3–4% of fixed carbon (i.e., the gasification burn-off degree for this stream is lower than 1).

In both bottom and fly ash, the concentration of the harmful Cr(VI) species was, as expected, higher when a higher ER value was adopted (9.6 vs 8.2 ppm in bottom ash, 7.1 vs 4.1 ppm in fly ash), but the gasifier operating conditions indeed guarantee that these values are 3–4 orders of magnitude lower than the

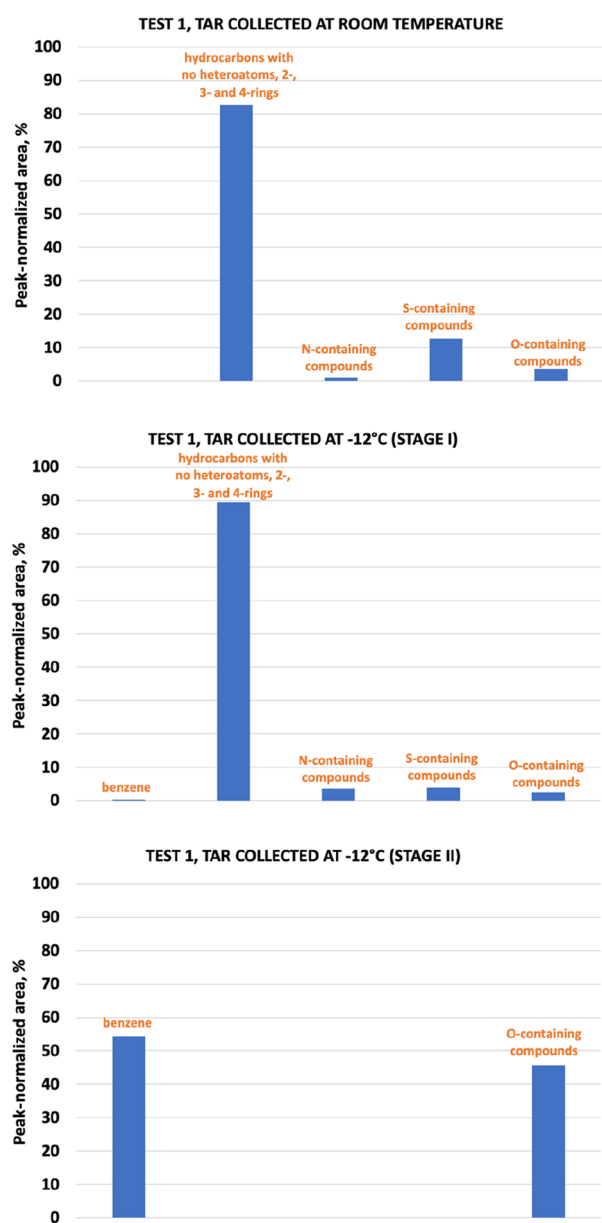


Figure 3. Speciation of tar collected from gasification test 1 based on the peak-normalized area.

concentration of total chromium, which remains in the preferred form of Cr(III) and tends to concentrate in elutriated fly rather than bottom ash. While the (although) limited oxygen presence in the FB gasifier was able to promote the chromium oxidation to Cr(VI), the degree of conversion in bottom ash was 0.069 (ER = 0.15) and 0.12% (ER = 0.24) only. The shorter mean residence time of fly ash in the gasifier has, in this respect, a positive consequence, i.e., chromium has less time to enter in contact with oxygen. As a matter of fact, the degree of chromium oxidation to Cr(VI) was 0.008 (ER = 0.15) and 0.013% (ER = 0.24), i.e., 1.6–1.7 times smaller than for bottom ash.

In the circular economy perspective, an interesting route lies on the possibility of chromium removal (in particular, in its trivalent state) from ashes in order to recirculate the metal in the tanning process. Contextually, 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 sulfate, a valuable product for the tanning

Table 6. GC–MS Results on the Characterization of Tar Compounds Collected during Gasification Test 2, at Room Temperature and at $-12\text{ }^{\circ}\text{C}$ ^a

retention time	peak-normalized area, %	compound	CAS no.	match quality
Test 2, tar collected at room temperature				
65.834	53.87	phenanthrene (C ₁₄ H ₁₀)	85-01-8	96
64.761	12.30	dibenzothiophene (C ₁₂ H ₈ S)	132-65-0	97
66.205	8.95	anthracene (C ₁₄ H ₁₀)	120-12-7	93
78.916	8.58	fluoranthene (C ₁₆ H ₁₀)	206-44-0	96
82.316	4.87	pyrene (C ₁₆ H ₁₀)	129-00-0	93
52.458	2.43	acenaphthylene (C ₁₂ H ₈)	208-96-8	91
57.823	2.38	fluorene (C ₁₃ H ₁₀)	86-73-7	93
72.911	2.31	2-phenylnaphthalene (C ₁₆ H ₁₂)	612-94-2	92
48.466	1.38	biphenyl (C ₁₂ H ₁₀)	92-52-4	94
55.004	1.22	dibenzofuran (C ₁₂ H ₈ O)	132-64-9	81
39.394	0.85	naphthalene (C ₁₀ H ₈)	91-20-3	94
70.272	0.50	2-methylanthracene (C ₁₃ H ₁₂)	613-12-7	83
51.109	0.35	2-vinylnaphthalene (C ₁₂ H ₁₀)	827-54-3	86
Test 2, tar collected at $-12\text{ }^{\circ}\text{C}$ (stage I)				
39.394	91.75	naphthalene (C ₁₀ H ₈)	91-20-3	95
39.934	2.03	benzo[<i>c</i>]thiophene (C ₈ H ₆ S)	270-82-6	97
32.474	1.07	phenol (C ₆ H ₆ O)	108-95-2	91
65.860	0.95	phenanthrene (C ₁₄ H ₁₀)	85-01-8	95
13.967	0.92	pyridine (C ₅ H ₅ N)	110-86-1	97
52.466	0.71	acenaphthylene (C ₁₂ H ₈)	208-96-8	91
48.470	0.55	biphenyl (C ₁₂ H ₁₀)	92-52-4	91
29.580	0.46	aniline (C ₆ H ₇ N)	62-53-3	93
44.815	0.44	1-methylnaphthalene (C ₁₁ H ₁₀)	90-12-0	83
54.985	0.27	dibenzofuran (C ₁₂ H ₈ O)	132-64-9	76
8.730	0.24	benzene (C ₆ H ₆)	71-43-2	94
47.937	0.21	indole (C ₈ H ₇ N)	120-72-9	76
31.372	0.17	3-ethynyltoluene (C ₉ H ₈)	766-82-5	91
64.761	0.16	dibenzothiophene (C ₁₂ H ₈ S)	132-65-0	70
57.819	0.05	fluorene (C ₁₃ H ₁₀)	86-73-7	90
Test 2, tar collected at $-12\text{ }^{\circ}\text{C}$ (stage II)				
65.841	49.98	phenanthrene (C ₁₄ H ₁₀)	85-01-8	94
8.738	13.64	benzene (C ₆ H ₆)	71-43-2	94
6.174	10.44	2-methylfuran (C ₅ H ₆ O)	534-22-5	81
64.776	9.40	naphtho[1,2- <i>b</i>]thiophene (C ₁₂ H ₈ S)	234-41-3	81
52.447	8.75	acenaphthylene (C ₁₂ H ₈)	208-96-8	74
66.205	4.33	9-methylidene fluorene (C ₁₄ H ₁₀)	4425-82-5	76
52.477	3.45	biphenylene (C ₁₂ H ₈)	259-79-0	70

^aCompounds are listed in order of relevance of the peak-normalized area. Database: NIST 11.

process. Moreover, Cr present in the solid residue could represent a substitute for the chromite ore, which is a raw

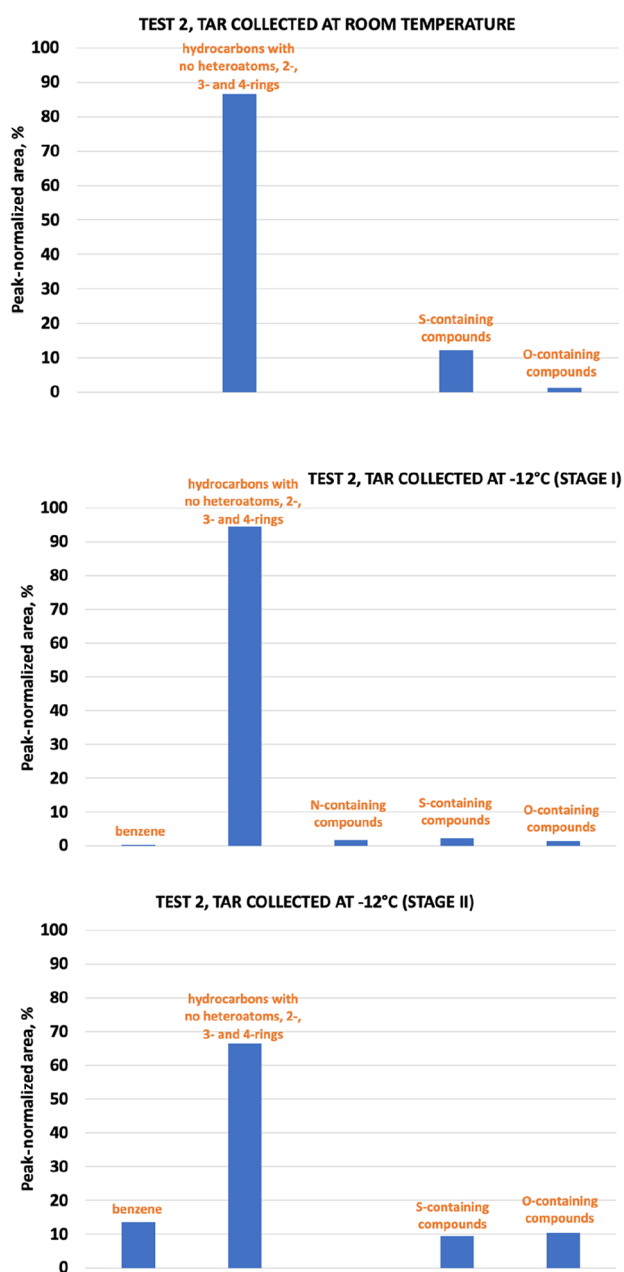


Figure 4. Speciation of tar collected from gasification test 2 based on the peak-normalized area.

material essential to produce ferro-chromium, the substrate for the manufacture of stainless steel. In fact, chromium is the main element that provides the high corrosion resistance of stainless steel. To this end, the possibility of recycling Cr contained in the ash resulting from thermal processes on the leather residues was studied by reduction in carbon at a temperature of 1600 °C to produce a commercial high-carbon ferrochrome alloy.²³ This process is particularly suitable for tannery ashes that contain high concentrations of both chromium and iron, which also have a role in leather production.

4. CONCLUSIONS

In this preliminary research campaign, a tannery sludge of industrial origin was taken into consideration. With its 34% carbon content (dry basis), the material can be considered appropriate for energetic valorization. The selected process was

Table 7. Results of the Analyses on Bottom Ash from FB Gasification of Tannery Sludge

	proximate analysis (% by weight)	
	test 1 (ER = 0.15)	test 2 (ER = 0.24)
moisture	n.d.	n.d.
volatiles	n.d.	n.d.
fixed carbon	n.d.	n.d.
ash	100.00	100.00
	ultimate analysis (% by weight; dry basis)	
	test 1 (ER = 0.15)	test 2 (ER = 0.24)
C	0.18	0.12
H	n.d.	n.d.
N	0.29	0.30
	chromium speciation	
	test 1 (ER = 0.15)	test 2 (ER = 0.24)
Cr(total)	11.8 g/kg	8.0 g/kg
Cr(VI)	8.2 mg/kg	9.6 mg/kg
conversion to Cr(VI)	0.069%	0.120%

Table 8. Results of the Analyses on Fly Ash from FB Gasification of Tannery Sludge

	proximate analysis (% by weight)	
	test 1 (ER = 0.15)	test 2 (ER = 0.24)
moisture	1.54	1.31
volatiles	13.84	17.10
fixed carbon	3.17	3.97
ash	81.45	77.62
	ultimate analysis (% by weight; dry basis)	
	test 1 (ER = 0.15)	test 2 (ER = 0.24)
C	9.54	7.99
H	n.d.	n.d.
N	0.68	0.62
	chromium speciation	
	test 1 (ER = 0.15)	test 2 (ER = 0.24)
Cr(total)	53.3 g/kg	56.4 g/kg
Cr(VI)	4.1 mg/kg	7.1 mg/kg
conversion to Cr(VI)	0.008%	0.013%

the sludge gasification in a fluidized bed reactor, to produce syngas. Since the sludge came from the tannery industry, particularly relevant was its chromium content. In the parent material, we did not observe the harmful hexavalent Cr species. Under the best adopted operating conditions, a syngas with 42% H₂ (dry and N₂-free basis) and a lower heating value of 12 MJ/kg was obtained, with a limited tar concentration and the production of bottom ash whose gasification degree was, for all practical purposes, complete. The Cr(VI) concentration in bottom and fly ashes was not higher than 10 mg/kg, while the Cr(total) concentration was 3–4 orders of magnitude greater, showing the right choice of operating conditions that did not promote the oxidation of Cr(III) to Cr(VI) at a relevant extent. The evaluation of the energetic yield of the process, along with the investigation of possible recycle routes for gasification ash (f.i.: as an adsorbent material, or in the materials construction industry), will help to increase the circularity of the proposed process, with clear financial and environmental advantages accompanying the production of an energy vector from an industrial residue. Of course, the reuse of ashes should not end up into additional contaminations of water bodies. So, leaching

of Cr(VI) needs to be carefully evaluated for a proper risk analysis and compliance with environmental regulations. To give examples, nowadays, the Italian limit for total chromium is 200 mg per kg of dry solid if the sludge is meant to be utilized in agriculture, and that for Cr(VI) is 2 (or 100) mg per kg of dry solid for agricultural use (or simple disposal). Stabilization of chromium in ashes by means of vitrification or encapsulation is a possible means to reduce the risk related to their reuse.

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Notes

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