

Valorisation of Leather Wastes from the Footwear Industry via Pyrolysis: Product Yields and Characterisation



F. Silva , D. Direito , R. Pilão , and A. M. Ribeiro 

Abstract The footwear industry, although contributing positively to the Portuguese economy, generates a lot of residues including chromium tanned leather wastes. This study presents results on the slow pyrolysis of these residues at particle sizes between 5 and 6.3 mm and temperatures inside the reactor ranging from 444 to 875 °C. For this range of temperatures, char yield decreased from 36.2 to 28.1% and gas yield increased between 33.2 and 47.6%. The liquid phase yield was highest at 444 °C (30.6%) and then decreased to 24.3% at 875 °C. As the operating temperature increased, there was an increase in the ash content (15.8 to 21.6%) and a decrease in volatiles content (20.9–3.7%) of biochars. The higher heating values (HHV) of the chars were between 21.9 and 23.1 MJ/kg. Preliminary results show that an increase in particle size leads to a rise in char yield. The infrared analysis of the liquid phase indicated the presence of water, alcohols, phenols, carboxylic acids, alkanes, alkenes, and aromatics. The liquid phases had an average water content of 43%, densities between 1110 and 1120 kg/m³ and the HHV between 12.7 and 15.1 MJ/kg. The gases produced were analysed by gas chromatography. For 538 °C, the production of H₂, CO, CH₄ and CO₂ was, respectively, 1.00, 0.37, 0.18 and 1.37 mol/kg of leather. At 875 °C, H₂ was the most produced gas (2.74 mol/kg leather), followed by CO, CO₂ and CH₄ with quantities of 1.40, 1.26 and 0.42 mol/kg leather.

Keywords Chromium tanned leather wastes · Pyrolysis · Biochar · Bio-oil

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1 Introduction

In Portugal, a prominent industry that highly contributes to the national economy is the shoe manufacturing industry. In 2017, 83.3 billion pairs of shoes were exported, generating around 1.96 billion euros. Furthermore, 87% of these exports correspond to leather footwear [1]. Nonetheless, the leather shoe industry is very pollutant, since it generates around 70.5 tonnes of residues per day, 53–67 tonnes of which correspond to chromium tanned leather wastes [2]. These are normally disposed in landfills without any treatment, which causes the release of chromium(III) into water streams, with consequent water contamination and pollution of the surrounding environment [3]. So, it is of the utmost importance to find efficient and low carbon footprint waste management techniques to deal with these toxic residues. One of those techniques and the focus of this study is pyrolysis. In this process, waste is thermally decomposed in an inert atmosphere at temperatures ranging from 400 to 1000 °C. The obtained products are biochar (the solid phase), bio-oil (the liquid phase) and the non-condensable gases mainly composed of carbon monoxide (CO), hydrogen (H₂), carbon dioxide (CO₂), methane (CH₄) and other gases in minor percentages [3]. All of these are value-added products that can be used as energy sources by other industries, thus contributing to a circular economy.

Several authors investigated the pyrolysis of leather wastes. Yilmaz et al. [4] studied the pyrolysis of various tanned wastes at temperatures of 450 and 600 °C. Marcilla et al. [5] investigated the fast and slow pyrolysis of chromium tanned leather wastes. Simioni et al. [6] used a fluidized bed reactor for the pyrolysis of chromed leather shavings at temperatures of 500 and 600 °C. Kluska et al. [7] and Fang et al. [8] studied the influence of temperature on the pyrolysis of chrome tanned leather residues. Van Rensburg et al. [9] investigated the pyrolysis of post-consumer leather shoe wastes. González-Lucas [10] studied the microwave-assisted pyrolysis of vegetable and chromium tanned leather residues.

In this work, the influence of temperature on the pyrolysis of leather trimmings from the footwear industry was investigated. Also, some preliminary results of the influence of particle size on char yield are presented. Biochars were characterised in terms of proximate analysis and higher heating value, HHV. The liquid phases were analysed by infrared spectroscopy (FTIR) with attenuated total reflectance (ATR) module. Density, water content and HHV of the liquid phases were also determined. The gas produced was analysed by gas chromatography (GC).

2 Experimental

2.1 Leather Waste Characterisation

The leather wastes used in this work come from a Portuguese footwear manufacture. The leather trimmings were characterised in terms of proximate analysis, namely, moisture (EN14774), ash (EN 15,148) and volatiles contents (EN 14,775). Chromium content was determined by standard ASTM D6714—01. The ultimate analysis was carried out according to standard CENT/TS 15,104. The HHV of the feed material, biochars and bio-oils produced during pyrolysis was measured using a Parr calorimeter 1451.

2.2 Experimental Apparatus and Procedure

Pyrolysis of the leather waste was performed in a refractory steel reactor, 78 cm in height and 9.7 cm in internal diameter. The pyrolyser was equipped with a vertical split furnace linked to a control system and with two thermocouples, one, the set-point control placed on the oven, and another located inside the reactor.

For each experiment a wire mesh basket was filled with a 100 g of pre-dried leather, which was then placed in the heating zone of the reactor. The carrier gas was nitrogen, fed at the top of the reactor at a flow rate of 0.105 kg/h.

The volatiles exiting the reactor flowed through a vertical double pipe heat exchanger, with water as cooling fluid, and a set of two trapping bottles immersed in an iced bath where the liquid phase was collected. After, the non-condensable gas flowed through a silica gel fixed bed to remove traces of water. During each experiment various samples of the gas phase were collected in Tedlar bags for further analysis by GC.

When each experiment ended, the heating system was switched off and the carrier gas was left to run for another two hours. After the system was cooled, the mass of biochar in the basket and the bio-oil collected in the trapping bottles were weighted. The amount of gas produced was determined by performing mass balances.

Pyrolysis experiments were carried at set point temperatures (T_{set}) in the range of 565–1030 °C (corresponding to final inside temperatures, T_i , in the range of 444 to 875 °C), with leather residues having a particle size between 5.3 and 6 mm. Also, some preliminary experiments were done to verify the effect of particle size on char yield. These were performed using leather squares with 10 mm side length, for $T_i =$ of 444 and 630 °C.

2.3 Characterisation of Solid, Liquid and Gas Phases

The biochar was characterised in terms of its proximate analysis (moisture, volatiles, ash, and fixed carbon contents) and HHV using the methods described in Sect. 2.1.

Samples of the liquid phase were analysed by FTIR with ATR module. The infrared spectra were collected in the 4000–400 cm^{-1} region, with a resolution of 4 cm^{-1} . The HHV of the liquid phases was measured using the Parr calorimeter. The bio-oil density was determined with a 10 mL glass pycnometer at 20 °C (ASTM D 1298). The water content was determined using a Karl Fisher apparatus. The gas fraction was analysed in a Dani 1000 DPC gas chromatograph equipped with an OPT333 injector, a 60/80 Carbonex 1000 column and a thermal conductivity detector TCD OPT266. Argon was used as the carrier gas and the gases identified were CO_2 , CO, H_2 , CH_4 , O_2 and N_2 .

3 Results and Discussion

3.1 Properties of Leather Waste

The moisture content, proximate and ultimate analysis on a dry basis (db), chromium oxide content and HHV on a dry basis of the leather wastes used in this work, together with data provided by Fang et al. [8] for chrome tanned leather shavings, and by González-Lucas et al. [10] for chrome leather trimmings, are listed in Table 1.

Table 1 Proximate and ultimate analysis, chromium oxide content and HHV of the residues

	This work	Fang et al. [8]	González-Lucas et al. [10]
Moisture (wt%)	12.3	9.2	36.9
<i>Proximate analysis (db—wt%)</i>			
Ash	6.4	10.32	7.16
Volatiles	73.1	74.60	–
Fixed carbon	20.5	15.08	–
<i>Ultimate analysis (db—wt%)</i>			
C	48.9	42.13	44.71
H	6.4	5.52	5.83
N	11.4	13.41	17.6
O	33.3	27.18	23.7
S	–	1.44	1.09
Chromium oxide (wt%)	2.5	2.18	–
HHV (MJ/kg)	20.3 (db)	17.2	12–14

105 The proximate analysis shows that this leather waste has a high value of volatiles
106 (73.1%), close to the 74.6% presented by [8]. The volatile content is related to the
107 production of bio-oil and non-condensable gas during the pyrolysis process. The ash
108 content was 6.4%, lower than the data obtained by [8] and [10]. The percentage of
109 chromium oxide (2.5%) is close to the value determined by [8] (2.18%). The fixed
110 carbon content of leather waste was 20.5%, and the amount of fixed carbon content
111 is positively correlated with biochar yield during pyrolysis process [11].

112 The mass percentage of carbon (C), hydrogen (H), nitrogen (N) and oxygen (O)
113 in the present leather residues was of 48.9, 6.4, 11.4 and 33.3%, respectively. For C,
114 H and O, these values are slightly higher than the data presented by [8] and [10], but
115 the N content was lower. The nitrogen is derived from the protein, which is one of
116 the main components of leather [12].

117 The higher heating value was 20.3 MJ/kg, higher than the values of 17.2 and
118 12–14 MJ/kg determined, respectively, by [8] and [10]. This difference could be
119 due to the type of leather waste or to the moisture content of the raw materials. The
120 HHV of the leather trimmings of this work was close to values presented by some
121 lignocellulosic biomass, such as olive stones, 21.1 MJ/kg [13], and almond shells,
122 19.72 MJ/kg [14].

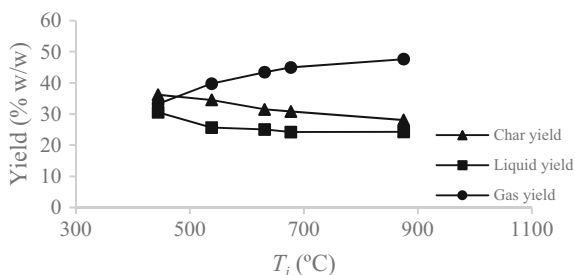
123 3.2 Effect of Parameters on Pyrolysis Product Yields

124 **Effect of pyrolysis temperature.** As mentioned before, pyrolysis experiments were
125 carried at T_{set} in the range of 565 to 1030 °C, corresponding to T_i of 444 to 875 °C,
126 respectively, using a particle size between 5.3 and 6 mm.

127 Figure 1 shows the trend of the yields of the char, liquid phase, and non-
128 condensable gas as a function of T_i . In general, as T_i rose from 444 to 875 °C,
129 char yield decreased from 36.2 to 28.1% and the gas yields increased from 33.2 to
130 47.6%. The highest liquid yield, 30.6%, was obtained at a temperature of 444 °C and
131 then decreased to 24.3% at 875 °C.

132 Similar behaviour was reported by other researchers. Marcilla et al. [5] using fast
133 pyrolysis and for temperatures of 450, 500 and 550 °C, obtained char yields of 38.5,
134 30.4 and 31%, respectively. Gas yields increased from 20.5 to 26.6% as the pyrolysis

Fig. 1 Yields of solid, liquid and gas phases as a function of T_i



temperature was rose. Liquid yield presented a maximum of 44.5% at 500 °C. Kluska et al. [7] performed pyrolysis experiments in the range of 300 to 500 °C. The solid yield was about 33% in the range of 300 to 450 °C and 29% at 500 °C. For the liquid phase, the yield increased from 21 to 40%, presenting a maximum of 42% at 400 °C. The decrease in liquid yield at high temperatures could be related to the gas phase secondary cracking reactions that contribute to the release of low molecular weight compounds.

Effect of particle size on char. Some preliminary results were carried out to determine the influence of particle size on char yield using particle sizes of $d_p = 5\text{--}6.3$ mm and squares with a side length $l = 10$ mm. When changing from one particle type to the other at $T_i = 444$ °C, char yield increased from 36.2 to 39.4% and at $T_i = 630$ °C, the increase was from 31.5 to 32.9%. Similar behaviour was found by Somerville and Deev [15] when working with the pyrolysis of radiata pine wood, with nitrogen as the carrier gas. As particle size was increased from 0.5 to 1 mm to 67.5 mm, char yield rose from 16.6 to 25%. Ogunkanmi et al. [16], working with the pyrolysis of palm kernel shells at 550 °C, found a change in char yield from 19.33 to 70.67% as the particle size rose from 1.18 to 5 mm. Larger particles offer more resistance to the escape of condensable gases, leading to secondary cracking which results in an increase in solid yield [17].

3.3 Analysis of Solid, Liquid, and Gaseous Products

Proximate analysis and high heating value of solid products. The proximate analysis (db) and HHV of chars obtained during the pyrolysis experiments was carried out. Table 2 shows the results obtained for $T_i = 444, 631$ and 875 °C. As temperature was rose the ash content increased from 15.8 to 21.6%, volatiles decreased from 20.9 to 3.7% and the fixed carbon increased from 63.3 to 74.7%. Yilmaz et al. [4] obtained chars from chromium tanned leather with ash concentrations of 19.5 and 22.6%, at temperatures of 450 and 600 °C. Biochars produced by Gorshkov et al. [18] during the pyrolysis of several nuts at temperatures of 400 to 600 °C, showed an increase in the ash content and a decrease in the volatiles as the temperature was rose.

The HHV was of 21.9 MJ/kg for chars obtained at $T_i = 444$ and 630 °C and 23.2 MJ/kg for the char at $T_i = 875$ °C. The HHV of chars was higher than for the raw material (20.3 MJ/kg). Kluska et al. [7] produced chars from the pyrolysis of leather

Table 2 Proximate analysis (db) and HHV of chars

T_{set} (°C)	T_i (°C)	Ash (% w/w)	Volatile matter (% w/w)	Fixed carbon (% w/w)	HHV (MJ/kg)
565	444	15.8	20.9	63.3	21.9
765	630	18.8	9.4	71.8	21.9
1030	875	21.6	3.7	74.7	23.1

167 wastes at 300 to 500 °C, which presented HHV between of 18.55 to 21.50 MJ/kg.
 168 Van Rensburg et al. [9] found an HHV = 25.55 MJ/kg for chars obtained from used
 169 leather footwear at temperatures in the range of 409 to 690 °C. According to [9], the
 170 chars from leather wastes can be used in the metallurgical industry, as a fuel, in the
 171 production of activated carbon and as an adsorbent.

172 **FTIR analysis, density, water content and HHV of liquid products.** The liquid
 173 phases were analysed by FTIR-ATR, a technique which allows the identification of
 174 functional groups. As all the samples analysed presented similar curves, only the
 175 data obtained for the bio-oil from the pyrolysis experiment at $T_i = 444$ °C is shown
 176 in Fig. 2. Table 3 presents the peaks identified, the characteristic wavelength of each
 177 functional group and compounds associated: water, alcohols, phenols, carboxylic
 178 acids, alkanes, alkenes, and aromatics [19, 20].

179 The presence of these substances in bio-oils from the pyrolysis of chromium
 180 leather wastes was confirmed by Marcilla et al. [5], Simioni et al. [6] and Van
 181 Rensburg et al. [9], using gas chromatography-mass spectrometry (GC-MS) analysis.

Fig. 2 FTIR spectrum of the liquid phase obtained at $T_i = 444$ °C

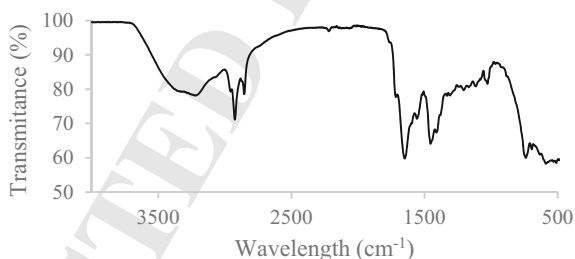


Table 3 Results obtained from the FTIR-ATR analysis at $T_i = 444$ °C

Peak wavelength (cm ⁻¹)	Wavelength (cm ⁻¹)	Functional group	Compounds
3388	3200–3700	O–H stretching vibrations	Water, alcohols, phenol, or carboxylic acids
2933	2800–3000	C–H stretching vibrations	Alkanes
2855			
1710	1550–1750	C = C stretching vibrations	Alkenes, carboxylic groups
1612			
1515	1600–1430	C = C stretching vibrations	Aromatics
1463			
1364	1350–1500	C–H deformation vibrations	Alkanes
1215	1275–1000	C–H deformation vibrations	Aromatics
1110			
1021			

Table 4 Density and heating values of the liquid phases

T_{set} (°C)	T_i (°C)	Density (kg/m ³)	HHV (MJ/kg)
565	444	1110	12.7
765	630	1120	13.2
1030	875	1120	15.1

Density and HHV of the liquid phase produced at $T_i = 444, 630$ and 875 °C are shown in Table 4. The density of the liquid phase varied between 1110 and 1120 kg/m³ and was slightly higher than the value of 997 kg/m³, reported by Amdouni et al. [21] for bio-oil from the pyrolysis of tannery fleshing. For lignocellulosic biomass, Shah et al. [22] compiled densities in the range of 951–1190 kg/m³. The liquid phases exhibited an average water content of 43% (w/w). The presence of water in the liquid phase has a positive impact in lowering its viscosity (increases the fluidity), but a negative influence on the heating value. As the water content increases, there is a decrease in the HHV, and the possibility of phase separation rises [23]. According to Yilmaz et al. [4], the condensed phase produced by the pyrolysis of chromium-tanned leather had a water content of 65.9 and 67.5%, at temperatures of 450 and 600 °C, respectively.

The HHV of the condensed phases ranged from 12.7 to 15.1 MJ/kg (Table 4). These values are lower than the HHV of 33.6 MJ/kg for bio-oil from the pyrolysis of used leather shoe residues at 550 °C, reported by [9], and 39.36 MJ/kg for bio-oil coming from the pyrolysis of tannery fleshing wastes at 600 °C [21]. These differences could be due to the amount of water present in the bio-oils. For the liquid phase obtained from microwave pyrolysis of chromium tanned leather wastes, González-Lucas et al. [10] reported an HHV of 2 MJ/kg and for the respective heavy fraction, the HHV increased to 21.5 MJ/kg. The bio-oils obtained from pyrolysis could be used for energy production, as they can be fired in boilers and furnaces, as a source for obtaining chemicals or as a transport fuel after proper treatment [17].

Gas chromatography analysis. The non condensable gases produced during the pyrolysis of the leather residues were analysed by GC. Figure 3 shows the variation of the volumetric percentage of the different gases produced (CO₂, CO, CH₄ and H₂) with time, for $T_i = 875$ °C. For this temperature, the most released gas was H₂ with a maximum volumetric fraction of 15.2% at $t = 2940$ s and at a temperature of 600 °C. CO presented a maximum concentration of 8.5% at $t = 2760$ s and 502 °C, followed by CO₂ with a maximum volumetric fraction of 5.8% ($t = 2250$ s and 256 °C). The lowest maximum concentration, 2.9%, was presented by CH₄ at $t = 2760$ s and 502 °C. For the pyrolysis experiment run at $T_i = 538$ °C, the gas with the highest concentration was CO₂, with a maximum volumetric fraction of 6.8% at $t = 2040$ s and at 250 °C, followed by H₂ with maximum concentration of 5.5%, at $t = 2760$ s and 447 °C. The maximum volumetric fraction of CO was 2.2%, at $t = 2040$ s and at 250 °C. Finally, CH₄ presented the lowest maximum concentration of 1.0%, at $t = 2760$ and at 447 °C.

Table 5 lists the amount of H₂, CO, CH₄ and CO₂, in mol/kg of leather, released during the pyrolysis experiments at $T_i = 536$ and 875 °C and the HHV of the produced

Fig. 3 Variation of the concentrations of CO₂, CO, CH₄ and H₂ with time, for $T_i = 875\text{ }^\circ\text{C}$

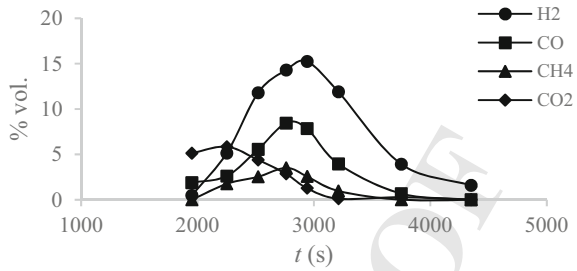


Table 5 Total amount of H₂, CO, CH₄ and CO₂ produced during the experiments at $T_i = 538$ and $875\text{ }^\circ\text{C}$ and HHV of the gas mixture

T_i (°C)	Gas production (mol/kg of leather)				HHV (kJ/Nm ³)
	H ₂	CO	CH ₄	CO ₂	
538	1.00	0.37	0.18	1.37	279.3
875	2.74	1.40	0.42	1.26	731.5

220 gas (in kJ/Nm³), calculated according to Eq. (1) [17]:

222
$$\text{HHV} = 10 \times (12.74 \times \%H_2 + 12.63 \times \%CO + 39.82 \times \%CH_4) \quad (1)$$

223 The total production of each individual gas was determined by considering the
 224 area under the curve of the function, molar flow rate of the gas versus time, and a
 225 constant mass flow of nitrogen equal to 0.105 kg/h. The HHV of the produced gas
 226 increased from 279.3 to 731.5 kJ/Nm³ as the temperature rose from $T_i = 538$ to 875
 227 °C. The presence of H₂, CO₂, CO and CH₄ in the produced gas was also reported by
 228 [7] and [8].

229 **4 Conclusions**

230 This study presents results on the pyrolysis of waste leather trimmings from the
 231 footwear industry, on a fixed bed reactor. The effect of operating temperature on
 232 product yields was studied for T_i ranging from 444 to 875 °C and using leather with
 233 particle size $d_p = 5\text{--}6.3$ mm. As the temperature was rose, char yield decreased from
 234 36.2 to 28.1%, gas yield increased from 33.2 to 47.6% and the liquid phase yield was
 235 highest at 444 °C (30.6%) and then decreased to 24.3% at 875 °C. Preliminary results
 236 showing the influence of particle size on char yield were carried out for T_i equal to
 237 444 and 630 °C and for particle sizes of $d_p = 5\text{--}6.3$ mm and squares with $l = 10$
 238 mm. For $T_i = 444\text{ }^\circ\text{C}$, char yield changed from 36.2 to 39.4%, and for $T_i = 630\text{ }^\circ\text{C}$,
 239 the increase in char yield was from 31.5 to 32.9%, as the particle size increased from
 240 $d_p = 5.3\text{--}6.0$ mm to squares with $l = 10$ mm. The proximate analysis of the produced

biochars showed that, as the operating temperature increased, there was an increment on the ash content (15.8 to 21.6%) and a decrease in the percentage of volatiles (20.9 to 3.7%). The HHV of the chars was between 21.9 and 23.1 MJ/kg. The FTIR-ATR analysis of the liquid phase indicated the presence of water, alcohols, phenols, carboxylic acids, alkanes, alkenes, and aromatics. The liquid phases presented an average water content of 43%, their density was between 1110 and 1120 kg/m³ and the HHV varied between 12.7 and 15.1 MJ/kg. The gas produced was analysed in terms of CO₂, CO, CH₄ and H₂ by CG. For $T_i = 538$ °C, the production of H₂, CO, CH₄ and CO₂ was, respectively, 1.00, 0.37, 0.18 and 1.37 mol/kg of leather. At $T_i = 875$ °C, H₂ was the most produced gas (2.74 mol/ kg of leather), followed by CO, CO₂ and CH₄ with quantities of 1.40, 1.26 and 0.42 mol/kg of leather, respectively.

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References

1. APPICAPS Homepage, <https://www.apiccaps.pt/getfilev2/download.aspx?f=/2018-facts--numbers.pdf>, last accessed 2023/01/22.
2. CTCP Homepage, <https://www.ctcp.pt/detalhe-publicacao/valorizacao-de-residuos-de-couro-curtido-com-cromiocalcado/373.html>, last accessed 2023/01/22.
3. Jadhav, N.C., Jadhav, A.C.: Waste and 3R's in Footwear and Leather Sectors. In: Muthu, S. (eds): *Leather and Footwear Sustainability*. Textile Science and Clothing Technology. 1st ed. Springer, Singapore (2020).
4. Yılmaz, O., Kantarli, I.C., Yuksel, M., Saglam, M., Yanik, J. "Conversion of leather wastes to useful products," *Resources, Conservation and Recycling* 49(4), 436–448 (2007).
5. Marcilla, A., León, M., García, Á, N., Bañón, E., Martínez, P.: Upgrading of Tannery Wastes under Fast and Slow Pyrolysis Conditions. *Industrial & Engineering Chemistry Research* 51(8), 3246–3255 (2012).
6. Simioni, T., Matos, E., Bacca, E., Perondi, D., Godinho, M., Dettmer, A.: Pyrolysis of chrome leather waste shavings in fluidized bed. *Journal of the American Leather Chemists Association* 109, 342–352 (2014).
7. Kluska, J., Ochnio, M., Kardaś, D., Heda, L.: The influence of temperature on the physico-chemical properties of products of pyrolysis of leather-tannery waste. *Waste Management* 88, 248–256 (2019).
8. Fang, C., Jiang, X., Lv, G., Yan, J., Lin, X., Song, H., Cao, J.: Pyrolysis characteristics and Cr speciation of chrome-tanned leather shavings: influence of pyrolysis temperature. *Energy Sources, Part A: Recovery, Utilization, and Environmental Effects* 41(7), 881–891 (2019).
9. Van Rensburg, M., Nkomo, S., Mkhize, N.: Characterization and pyrolysis of post-consumer leather shoe waste for the recovery of valuable chemicals. *Detritus* 14, 92–107 (2021).
10. González-Lucas, M., Peinado, M., Vaquero, J., Nozal, L., Aguirre, J., González-Egido, S.: Microwave-assisted pyrolysis of leather waste. *Energies* 15, 1273 (2022).
11. Zaman, C., Pal, K., Yehye, W., Sagadevan, S., Shah, S., Adebisi, G., Marlina, E., Rafique, R., Johan, R.: Pyrolysis: A Sustainable Way to Generate Energy from Waste. In Samer, M. (eds): *Pyrolysis*, 1st edn. InTech (2017).
12. Cabeza, L., Taylor, M., DiMaio, G., Brown, E., Marmer, W., Carrió, R., Celma, P., Cot, J.: Processing of leather waste: pilot scale studies on chrome shavings. Isolation of potentially valuable protein products and chromium. *Waste Management* 18(3), 211–218 (1998).

- 286 13. Sanchez, F., San Miguel, G.: Improved fuel properties of whole table olive stones via pyrolytic
287 processing. *Biomass and Bioenergy* 92, 1–11 (2016).
- 288 14. Din, M., Amanat, A., Hussain, Z., Khalid, R., Rauf, A.: Pyrolysis of almond shell biomass:
289 effect of temperature and catalyst on product yield. *International Journal of Environmental*
290 *Analytical Chemistry*, 1–12 (2021).
- 291 15. Somerville, M., Deev, A.: The effect of heating rate, particle size and gas flow on the yield of
292 charcoal during the pyrolysis of radiata pine wood. *Renewable Energy* 151, 419–425 (2020).
- 293 16. Ogunkanmi, J., Kulla, D., Omisanya, N., Sumaila, M., Obada, D., Dodoo-Arhin, D.: Extraction
294 of bio-oil during pyrolysis of locally sourced palm kernel shells: Effect of process parameters.
295 *Case Studies in Thermal Engineering* 12, 711–716 (2018).
- 296 17. Basu, P.: *Biomass Gasification, Pyrolysis and Torrefaction. Practical Design and Theory*. 3rd
297 edn. Elsevier Inc., London (2018).
- 298 18. Gorshkov, A., Berezikov, N., Kaltaev, A., Yankovsky, S., Slyusarsky, K., Tabakaev, R., Lari-
299 onov, K.: Analysis of the physicochemical characteristics of biochar obtained by slow pyrolysis
300 of nut shells in a nitrogen atmosphere. *Energies* 14(23), 8085 (2021).
- 301 19. Stuart, B.: *Infrared Spectroscopy: Fundamentals and Applications*. John Wiley and Sons, Ltd.
302 (2004).
- 303 20. González, F., Ramiro, A., González-García, C., Gáñan, J., Encinar, J., Sabio, E., Rubiales,
304 J.: Pyrolysis of almond shells. Energy applications of fractions. *Industrial & Engineering*
305 *Chemistry Research* 44, 3003–3012 (2005).
- 306 21. Amdouni, S., Hassen, A., Asmi, A., Chagtmi, R., Haddad, K., Jamaoui, F., Khedhira, H.,
307 Chérif, C.: Tannery fleshing wastes conversion into high value-added biofuels and biochars
308 using pyrolysis process. *Fuel* 294(7), 120423, (2021).
- 309 22. Shah, M., Khan, N., Kumar, V., Qurashi, A.: Pyrolysis of walnut residues in a fixed bed
310 reactor: effects of process parameters, chemical and functional properties of bio-oil. *Journal*
311 *of Environmental Chemical Engineering* 9(4), 105564, (2021).
- 312 23. Bardalai, M., Mahanta, D.: A review of physical properties of biomass pyrolysis oil.
313 *International Journal of Renewable Energy Research* 5(1), 277–286 (2015).