

Article

Microwave-Assisted Pyrolysis of Leather Waste

María González-Lucas^{1,2,*}, Manuel Peinado¹ , Juan J. Vaquero^{1,3,4}, Leonor Nozal³, Juan Luis Aguirre^{2,*} 
and Sergio González-Egido^{1,3} 

¹ Environment and Bioproducts Group, Universidad de Alcalá, 28805 Alcalá de Henares, Spain; manuel.peinado@uah.es (M.P.); juanjose.vaquero@uah.es (J.J.V.); sergio.glezegido@uah.es (S.G.-E.)

² Cátedra de Medio Ambiente, FGUA, 28805 Alcalá de Henares, Spain

³ Center of Applied Chemistry and Biotechnology (CQAB), FGUA, Universidad de Alcalá, 28805 Alcalá de Henares, Spain; leonor.nozal@uah.es

⁴ Department of Organic Chemistry and Inorganic Chemistry, Campus Científico-Tecnológico, Chemical Research Institute “Andrés M. del Río” (IQAR), Universidad de Alcalá, 28805 Alcalá de Henares, Spain

* Correspondence: maria.gonzalez@fgua.es (M.G.-L.); juanl.aguirre@uah.es (J.L.A.)

Abstract: The processing of leather into leather is one of the oldest known manufacturing practices. The subsequent refinement of this technique over recent centuries has led to an increase in production, which in turn has led to an increase in waste production. Today, many of the by-products and waste streams from the leather industry have applications in industries such as petfood and in the production of collagen and derivatives, while others, such as waste from trimming and scraping the material, are disposed of in landfills, causing a detrimental environmental impact. For this reason, new alternatives for the treatment of these wastes, such as pyrolysis, are being investigated. The aim of this work is to assess the feasibility of recovering non-recyclable waste from the leather industry by pyrolysis. Waste from the tanning of cowhides with vegetable tannins and tanning with chrome salts, without pre-treatment, were used as raw materials. The operating conditions of the microwave-assisted pyrolysis were analysed by varying the time (15–30 min), the power (600–1000 W) and the dopant (carbon from the pyrolysis itself) in a batch reactor that allows to treat about 30 g of a sample. Three fractions (liquid, solid and gaseous) were obtained from the waste treatment, and the liquid and gaseous fractions were characterised using different analytical techniques. The solid fraction can be used as fuel due to its high calorific value of more than 20 MJ/kg and its low ash content, with the residue containing vegetable tannins giving the best results with a calorific value of up to 28 MJ kg⁻¹. In addition, the solid fraction can be used as activated carbon after activation treatment, which allows for a more technical use, e.g., in the chemical industry. The liquid fraction contains significant amounts of phenolic groups, such as pyrrole and phenol, as well as other derivatives. Pyridine, aniline, cresol and succinimide, among others, were also found. This makes it a valid source of chemical compounds of high added value in the chemical industry. In addition, the heavy liquid fraction has a good heat capacity of more than 21 MJ/kg, which makes it suitable for use as a fuel. The microwave-assisted pyrolysis process results in the possibility of obtaining products from waste that would otherwise be destined for landfill, thereby obtaining a large number of products and bioproducts with the ability to be reintroduced into the value chain quickly and easily.

Keywords: leather waste; microwave-assisted pyrolysis; physical recovery; compound distribution; fraction composition; vegetable tannins; chromium salt tannin; bioproduct



Citation: González-Lucas, M.; Peinado, M.; Vaquero, J.J.; Nozal, L.; Aguirre, J.L.; González-Egido, S. Microwave-Assisted Pyrolysis of Leather Waste. *Energies* **2022**, *15*, 1273. <https://doi.org/10.3390/en15041273>

Academic Editor: Gabriele Di Giacomo

Received: 21 January 2022

Accepted: 7 February 2022

Published: 10 February 2022

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

Leather is mostly produced from animal skin waste from the meat industry [1] and mainly comprises collagen, a natural polymer belonging to the protein group. Tanning dates back to prehistoric times, when skins were already used for protection. This technique cross-links the collagen chains of animal hides and skins, which increases their strength and durability and allows leather to be obtained as a product [2].

A large amount of the waste generated during the tanning process can be treated by introducing sustainable and clean technologies [3]. Some techniques can valorise these wastes and prevent their disposal by giving them a new life [4]. Addressing this option is therefore one of the main challenges for the leather industry [5,6]. The solid waste obtained is mostly unprocessed and processed leather remnants, and around 150,000 metric tons of such waste is thought to be generated per year worldwide [4]. Part of this waste contains different metals and chemicals, such as chromium and titanium salts and oxides, which can be very harmful to the environment. As a consequence, finding alternatives to current management routes is of increasing importance.

The current measures available for the management, reuse and recycling of leather waste are of limited applicability. For example, leather waste is traditionally treated by incineration or open burning, which generates material loss by converting this waste into ash [7,8]. Moreover, the low calorific value of these wastes limits the possibilities for energy recovery [9–13]. As such, one of the most promising treatment alternatives is chemical or tertiary recycling, which consists of transforming post-consumer materials or waste into products with high added value. This type of treatment includes pyrolysis, a technique that is considered highly effective in the treatment of waste from different materials, such as lignocellulosic waste, plastic waste, microalgae waste and ELT waste, amongst others [14–18]. This technique has clear benefits over other techniques such as incineration in waste treatment, as the absence of oxygen in the pyrolysis process drastically reduces CO₂ emissions, thus reducing the greenhouse effect.

The first studies on this field date back to 1982 and were conducted to evaluate the technical and economic viability of a low-temperature pyrolysis process for chromium leather waste [19]. The results showed that pyrolysis of this type of material is profitable, and this led to the awarding of a patent in that same year [20]. A subsequent paper by Caballero et al. (1998) studied the decomposition kinetics of this waste, with gravimetric analyses showing that the pyrolysis process behaves as if the tanned leather waste comprised two different fractions, which decompose independently [21].

Yilmaz et al. (2007) investigated the production of useful by-products from three different types of leather waste, using a fixed-bed reactor in a temperature range between 450 and 600 °C. High percentages of carbonaceous residues were obtained (38–49%) from the three wastes used, and both the liquid and gaseous fractions showed high temperature dependence, with the percentage of liquid fraction decreasing by 4% as the final reaction temperature increased, increasing the percentage of gas generated. This research indicated that the liquid and solid fractions obtained could be used as fuel. In addition, the practicality of activating the solid fraction to produce activated carbon was also studied. In this study, the authors reported that the activated carbon prepared from chromium-containing waste had a higher surface area and could be used as an absorbent [22]. This line was followed by other research groups such as Sethuraman et al. (2013), who studied the treatment of chrome-tanned leather waste by pyrolysis obtaining results similar to those contributed by Yilmaz et al. (2007) [22–24].

In recent years, several studies have been published by the group of Gil et al. (2012). These studies have focused on two main lines of research: the thermal decomposition of vegetable-tanned leather waste, and the thermal decomposition of these wastes after being subjected to a dehairing process [25,26]. In the same year, Marcilla et al. (2012) studied the differences between fast pyrolysis at temperatures below 550 °C versus slow pyrolysis (up to 750 °C) [27]. The results obtained in this research indicated that fast pyrolysis is a more optimal method for obtaining the liquid fraction, while slow pyrolysis favours the solid fraction. These data are in agreement with the literature so far [28–30]. Kluska et al. (2019) studied pyrolysis at a low temperature (below 500 °C) by analysing the mass balances and properties of the different fractions obtained. This study led to the conclusion that the maximum yield of the liquid is obtained at 400 °C, the percentage being above 40%.

There are currently a significant number of publications on the production of activated carbon from tanned leather waste by pyrolysis [31,32].

All these studies offer a technique for obtaining high added value products in an environmentally friendly way. However, the present study aims to demonstrate the technical feasibility of microwave-assisted pyrolysis as a technique for the treatment of leather waste, which has not been fully realised by any research group and therefore the results are unknown. Likewise, this work aims to establish the working conditions and to know, by analysing them, the composition of the liquid fraction and the gas fraction obtained in order to assess their subsequent treatment and application.

2. Materials and Methods

2.1. Feedstock Materials

The leather waste used in this project comes from the leather industry, with all samples being provided by Couro Azul, a Portuguese company with a strong presence in the transport industry. Waste from trimming already tanned leather was used as its waste is easily shredded. Similarly, as mentioned above, two types of waste were used: one of them had been tanned with vegetable tannins, whereas the other came from the tanning process with chromium salts. In both cases, the waste was subjected to previous crushing treatment to obtain better results and to facilitate its handling.

2.2. Pyrolysis Equipment

Chemical recycling of the leather waste was carried out using the pyrolysis technique, i.e., thermal depolymerisation in the absence of oxygen. Treatment of the waste for material evaluation was carried out on a laboratory scale (0.5 kg/h). The plant at which the data were obtained is a microwave heating plant for discontinuous processing with a processing capacity of approximately 100–150 g/h. This installation is equipped with a quartz reactor in which pyrolysis takes place. The solid remains in this reactor after the reaction, whereas the other two gaseous fractions are passed into an ethanol-cooled condensation system ($-5\text{ }^{\circ}\text{C}$), where the liquid fraction is obtained.

2.3. Analysis Methodology

2.3.1. Calorimetry

The heat of combustion was measured using an IKA C200 instrument equipped with kerosene wicks to allow higher temperatures to be reached. The measurements were carried out dynamically and the results are quoted in MJ/kg.

2.3.2. Experimental Design

The pyrolysis prototype consists of a Microsynth microwave oven, a 500 mL quartz flask and a condensation system consisting of three 500 mL flasks with three mouths connected to cooling coils with bridges between them, as shown in Figure 1. All experiments were carried out under an inert atmosphere. Thus, after evacuation using a vacuum pump, the whole system was purged for 10 min. Tests were carried out in triplicate by introducing 30 g of raw material and subjecting it to a radiation of between 600 and 1000 W at intervals of 100 W for times of between 15 and 30 min. Rupture of the bonds in this material generates vapours, which pass into the condensation zone (at $5\text{ }^{\circ}\text{C}$). When passing through the cooling zone, some of the gases condense to give the liquid fraction. The remaining gas was collected in Tesla bags, and the liquid in the flasks and solid fraction were weighed. These weights were used to calculate the mass balance and estimate the product yields.



Figure 1. Pyrolysis prototype.

2.3.3. GC-MS Analysis

The liquid fractions obtained in the pyrolysis of leather waste were analysed using a gas chromatograph (Agilent Technologies 7890A, Santa Clara, CA, USA) coupled to a single quadrupole mass spectrometer (Agilent Technologies 5977A, Santa Clara, CA, USA). A 1 μ L aliquot of each sample was injected into the GC in Split mode (1:50) and a Phenomenex ZB-624 column (30 m; 0.25 mm i.d.; 0.25 μ m film thickness, 6% cyanopropylphenyl/94% dimethylpolysiloxane) was used for chromatographic separation of the analyte. After each injection, the autosampler syringes were rinsed three times with methanol. The chromatographic conditions were as follows: the initial oven temperature of 50 $^{\circ}$ C was maintained for 5 min, then increased at a rate of 20 $^{\circ}$ C/min to 220 $^{\circ}$ C for 5 min. The injector temperature was 225 $^{\circ}$ C. Helium was used as the carrier gas at a constant flow rate of 1 mL/min. The total time for one run of this analysis was 18.5 min. The mass spectrometer was operated in electron ionisation (EI) mode at 70 eV, peak width 2 s, mass range 40–600 amu. Peak identification was carried out using the inverse coincidence factor (RMF) from the NIST library, between the experimental and theoretical mass spectra. This value can be interpreted as a probability of success of more than 80% (RMF values > 700 are generally accepted for tentative identification).

2.3.4. Karl Fischer (KF)

Karl Fischer titration volumetry (KF) was used to determine the water content of the liquid fraction obtained. This analysis was carried out using a Metrohn KF 701 Titrino analyser. Combi titrant 5 (approx. 1 mL per 5 mg H₂O) was used as the titrating reagent. The supplier was Merck KGaA (64271, Darmstadt, Germany) (1.88005.1000).

2.3.5. Elemental Analysis and Calorific Value Determination

Total water content was determined according to ASTM 3302 using a Thermolyne OV35240 oven by performing a weight difference analysis. Ash tests were carried out in a Thermolyne 6000 muffle furnace in accordance with standard UNE 32004. For this purpose, samples were previously air-dried and passed through a 0.2 mm sieve. The value was obtained by difference in weight after calcination of the material in the crucible.

The tests carried out to determine the elemental composition (C, H, N and S content) were performed with respect to the specific standards for each of the elements (ASTM 5375 for C, H and N and ASTM 4239 for sulphur). For C, H and N, Leco CHN600 elemental analysis equipment was used, and for sulphur, sulphur determination equipment of the same brand (model SC 132) was used.

The equipment selected to measure the heat of combustion was an IKA C200, with paraffin wicks, which allow higher temperatures to be reached. Measurements were carried out under dynamic conditions and the results were quoted in MJ/kg.

2.3.6. X-ray Fluorescence Spectrometry

In order to determine the composition in terms of the elements comprising the liquid and solid fractions, a portable energy dispersive X-ray fluorescence (ED-XRF) spectrometer was used, specifically a portable ESPRECTROSCOUT from the brand Spectro Ametek. Analyses were carried out under a nitrogen stream, with a total analysis time of 13 min.

2.3.7. Specific Surface Area Determination

To determine the specific surface area of the solid fraction, the multipoint BET (Brunauer–Emmet–Teller) method was used. The equipment used for this measurement was a Micromeritics ASAP 2020. The sample was pre-treated at 140 °C for two days and then degassed at 250 °C for 18 h.

3. Results

3.1. Raw Material Study

The characterisation of the raw material wastes is shown in Table 1, which lists the values of the elemental analysis on a dry basis. These results show significant differences between the two types of waste from the leather industry. Thus, the vegetable-tannin-tanned leather waste has slightly higher percentages of carbon, hydrogen, sulphur and oxygen and slightly lower percentages of nitrogen. In contrast, the ash and moisture percentages are much lower in the case of vegetable-tannin-tanned leather waste, which means that it has a higher calorific value than leather waste from tanning with chromium salts.

Table 1. Chemical characterisation of the raw material.

	Vegetable Tannins	Chromium Salt
Elemental analysis		
C (%wt)	53.13	44.71
H (%wt)	6.29	5.83
N (%wt)	13.9	17.6
S (%wt)	2.07	1.09
O (%wt)	23.8	23.7
Proximate analysis		
Ash (%wt)	0.79	7.16
Moisture (wt%)	13.3	36.9
Calorific value (MJ kg ⁻¹)	16–17	12–14

The results obtained in the thermogravimetric analysis (TGA) of waste leather scraps tanned with vegetable tannins and with chromium salts are shown in Figures 2 and 3, respectively.

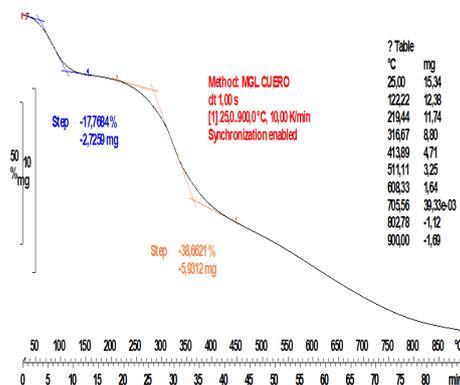


Figure 2. Thermogravimetric analysis of chromium-free tanned leather.

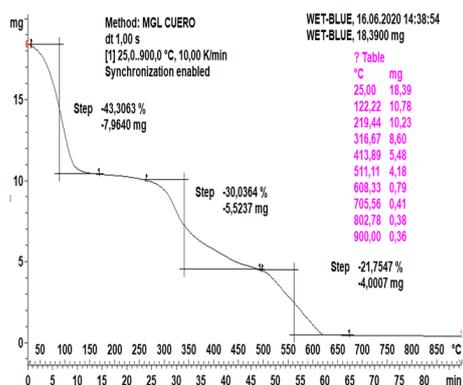


Figure 3. Thermogravimetric analysis of leather tanned with chromium.

In both figures, a very pronounced peak is observed between the onset temperature and 100 °C, which corresponds to the loss of water inherent to the sample and therefore indicates a large amount of moisture. Similarly, the peak at between 300 and 350 °C corresponds to the thermal decomposition of volatile organic compounds in the material.

3.2. Distribution of Pyrolysis Products

Figure 4 shows the influence of radiation power on the yields of the products obtained after the pyrolysis of leather waste tanned with vegetable tannins. The results for this material do not include the values obtained without dopant as these reactions do not give rise to a complete depolymerisation reaction. They are also not collected after 30 min with 1 g of dopant due the observation of some explosive reactions.

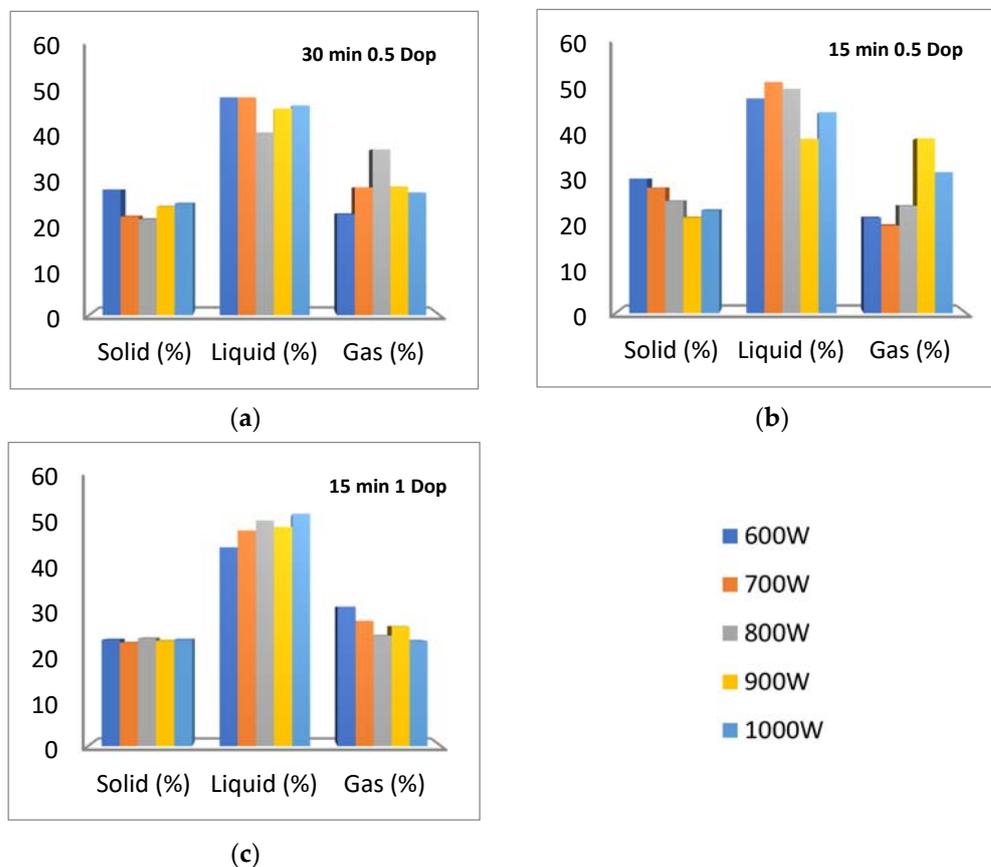


Figure 4. Comparative mass balance for the pyrolysis of leather waste tanned with vegetable tannins: (a) 30 min 0.5 g Dop; (b) 15 min 0.5 g Dop; (c) 15 min 1 g Dop.

In all cases, the liquid fraction is the largest, accounting for between 41% and 55%, with the lowest values being obtained at intermediate powers of 800–900 W in the absence of a high percentage of dopant. The solid fraction does not vary when high dopant quantities are used, while at low dopant quantities, the percentage decreases with increasing power until high powers are reached, where this is reversed.

Figure 5 shows the influence of the powers used in this work on the yields of the products obtained upon the pyrolysis of leather waste tanned with chromium salts.

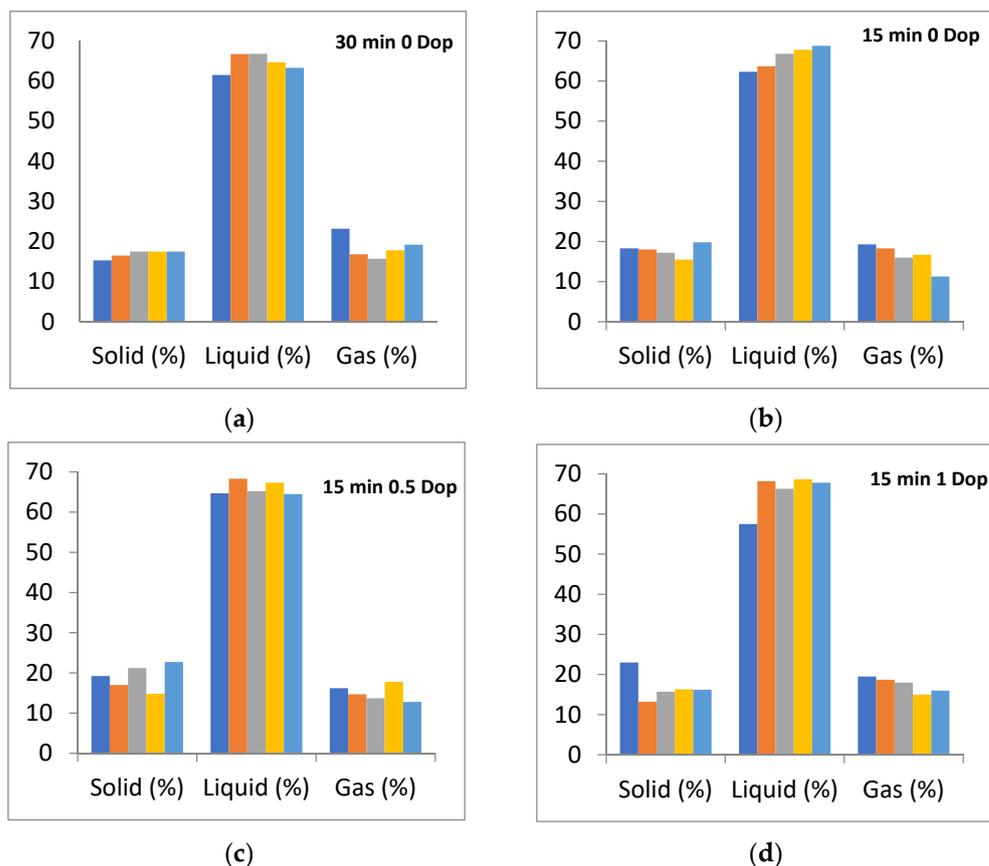


Figure 5. Comparative mass balance for the pyrolysis of waste leather tanned with chromium salts: (a) 30 min 0 g Dop; (b) 15 min 0 g Dop; (c) 15 min 0.5 g Dop; (d) 15 min 1 g Dop.

In the case of leather waste tanned with chromium salts, the mass balances and their comparison show that there is a slight variation when modifying the operating conditions. This variability could be related to the small amount of sample used.

3.3. Characterisation of the Liquid Fraction

The liquid fraction was analysed by Karl Fischer volumetry, combustion calorimetry, gas chromatography coupled to mass spectrometry and X-ray fluorescence spectrometry.

The average moisture content was in the range 48–66% for leather tanned with vegetable tannins and 74–86% for leather tanned with chromium salts. The difference in moisture content between the two types of waste is closely linked to the tanning technique used. A high moisture content implies a low calorific value for the liquid fraction. The calorific value of the liquid fraction from vegetable-tanned leather waste is around 10 MJ/kg (2 MJ/kg for the fraction from leather waste tanned with chromium salts).

The liquid fraction presents two clearly distinguishable phases and is therefore fractionated into a light liquid fraction and a heavy liquid fraction. These two fractions were analysed by combustion calorimetry. In both cases, the heat capacity of the light fraction is negligible. In the case of the heavy fraction, the heat capacity values increase to 26.5 MJ/kg for vegetable-tanned leather and 21.5 MJ/kg for chromium-tanned leather.

Table 2 shows the major compounds in the liquid fraction analysed by gas chromatography coupled to mass spectrometry.

Table 2. Composition of the liquid fraction by CG-MS.

Tanning with Vegetable Tannin					
Light Fraction			Heavy Fraction		
Tr (min)	Compound	Area Sum (%) ^(a)	Tr (min)	Compound	Area Sum (%)
9.25	Pyridine	3.14–12.1	13.33	Phenol	9.86–21.2
10.01	Pyrrole	15.6–38.7	14.00	3-Methylphenol (cresol)	5.16–10.5
13.02	Aniline	15.0–24.1	14.28	<i>m</i> -Cresyl methylcarbamate	3.90–8.44
13.33	Phenol	9.46–26.6	17.56	1 <i>H</i> -Pyrrole-2-carboxamide	4.41–14.6
14.00	3-Methylphenol (cresol)	3.87–12.9	17.93	2,4-Imidazolidinedione, 5,5-dimethyl-	2.05–11.7

Tanning with Chromium Salts		
Tr (min)	Compound	Area Sum (%)
9.25	Pyridine	1.53–6.92
10.01	Pyrrole	18.0–28.1
11.26	3-Methylpyrrol	2.38–6.98
15.94	Succinimide	2.45–7.00
17.56	1 <i>H</i> -Pyrrole-2-carboxamide	3.89–10.3
17.93	2,4-Imidazolidinedione, 5,5-dimethyl-	4.74–8.38

^(a): Qualitative identification.

The liquid fraction from vegetable-tannin-tanned leather waste was studied by X-ray fluorescence spectrometry (ED-XRF) to determine the amount of chromium remaining in the liquid fraction and to compare it with the solid fraction. This analysis showed amounts of 0–68 ppm chromium.

3.4. Characterisation of the Solid Fraction

The solid fraction was analysed by combustion calorimetry, BET surface area studies and X-ray fluorescence spectrometry, giving the results shown in Tables 3 and 4.

Table 3. LHV and BET surface area of solid.

Power (W)	Vegetable Tannins			Chromium Salt		
	600	800	1000	600	800	1000
LHV (MJ/kg)		26–28			20–23	
BET (m ² /g)	0.8–15.3	0.2–104.9	2.0–5.4	0.3–2.4	0.8–119.8	2.9–87.8

The calorific value measured for each of the materials is between 20 and 28 kJ/g, which is considered good enough to be considered a fuel. However, the opposite is true for BET, with the surface area being than expected (between 0.27 and 119.72 m²/g) and larger surface areas being obtained at powers higher than 800 W. In the case of the charcoal tanned with vegetable tannins, the best results were obtained when using 3.5% of dopant. However, for the carbon obtained from leather tanned with chromium salts, the best results were obtained at long times and in the presence of 1.5% dopant.

As for the liquid fraction, the solid fraction was studied by X-ray fluorescence spectrometry (ED-XRF) to determine its chemical composition, which is of great interest because of the amount of chromium it may contain. In general, the solid obtained from vegetable-tanned leather waste contains higher amounts of Al, Si, P and K. However, many elements, such as Zn, Sr, Sn, Sb and I, were found to be present at very similar levels in both residues. The main differences were observed for the Cl and Cr concentrations, the values for which were zero or negligible in the case of vegetable-tanned leathers and very high in the case of those tanned with chromium salts.

Table 4. RD-XRF results.

Element Concentration (ppm)	Vegetable Tannins	Chromium Salt
Al	600–880	170–620
Si	1700–6600	0–310
P	930–1900	118–450
S	1800–3500	3600–7600
Cl	-	11,900–31,600
K	65–90	0–13
Ca	500–630	1000–2100
V	-	18–42
Cr	-	18,000–33,000
Mn	-	80–173
Fe	100–250	395–450
Zn	2–100	1.3–10
Br	0–310	790–5100
Sr	320–610	300–530
Zr	670–1030	310–1900
Sn	0–8	0–7.7
Sb	50–100	20–60
I	38–74	0–53

In the specific case of chromium, the result of this analysis shows that, in the case of vegetable-tanned leather waste, there is no chromium in the solid. However, in the case of the fraction obtained from leather tanned with chromium salts, the amount measured is high. This confirms that most of the chromium from the leather is isolated in the solid fraction. These differences are mainly due to the use of different treatment and tanning agents during the tanning process.

4. Discussion

Pyrolysis is currently receiving increasing attention from a large number of research groups, mainly as a possible means for treating waste that will allow the value of the material itself to be preserved and therefore avoid material loss or waste, as well as all the environmental consequences that this entails.

With regard to the study carried out on the raw material under study, the elemental analysis shows a high carbon content for both residues, in the range of 44–54% on a dry basis, with this being higher in the case of the residue tanned with vegetable tannins. Nitrogen, in turn, is found in the range 14–18%, a value that is in agreement with those reported previously [26,33]. Hydrogen and oxygen are present at around 6% and 24%, respectively. Similarly, sulphur is found in very low quantities (between 1–2%), being slightly higher in the case of the residue cured with vegetable tannins.

From the results obtained in the measurement of ashes, it can be seen that the percentage ash in the case of waste from leather tanned with chromium salts is around 7% on a dry basis. This value is in agreement with the results obtained by Oliveira's group in 2008 [23] and by Roberto Rodriguez in 2013 [26]. In contrast, the residue for leather tanned with vegetable tannins gives an ash value of less than 1% on a dry basis. This agrees with previous studies, which attributed the higher percentage of ash in vegetable tannin tanned residues to the salts used in the tanning process, which remain embedded in the structure.

The heat capacity of the leather wastes studied in this project shows very low values of between 12 and 17 MJ/kg. This value is slightly higher for leather tanned with vegetable

tannins due to the lower amount of minerals in its structure. Even so, it can be considered that the values are low and similar to those found for biomass in general.

With regard to the results obtained upon thermogravimetric analysis, these are in agreement with those found by other researchers, such as Jacek Kluska in 2019 [34]. The highest loss occurs between 100 and 350 °C and is complete at approximately 640 °C. In the case of vegetable-tanned leather, a thermostable mass with a very low loss remains after this temperature.

In 2008, Oliveira's group indicated that leather tanned with chromium salts undergoes complete pyrolysis at 630 °C and above because the chromium present in the material can act as a catalyst, whereas leather tanned with vegetable tannins forms thermally stable compounds during the process, thereby corroborating the analytical findings for the residues used as raw materials herein [23].

In the case of leather waste tanned with vegetable tannins, the percentage weight loss due to the water content was around 20%, whereas in the case of leather waste tanned with chromium salts this percentage is around 40%. This is due to the fact that vegetable-tanned leather waste has already undergone a dyeing process, which helps to dry the fibre, whereas leather tanned with chromium salts must be kept moist for any subsequent treatment, including dyeing.

Analysis of the fractions obtained after treatment by microwave-assisted pyrolysis showed that the main components of the liquid fraction were pyridine, pyrrole and aniline. These compounds are formed during pyrolysis by transformation of the amide groups that form the peptide bonds, which is why they are found in a very high percentage.

Phenol is found in a very representative percentage for this fraction. Phenol is present as it is one of the major components in tanning with vegetable tannins or mixed tannages. It is mainly used in the retanning and dyeing stage as part of the mixture. The same occurs for 3-methylphenol or cresol, although their use is less widespread and the percentages used in the blends are generally lower [2].

The variation of the majority components depends on both the power and the time and amount of dopant used. In the case of a power of 600 W, the variation with respect to time is not particularly pronounced, whereas a considerable variation is observed as the amount of dopant increases, increasing in almost all cases, except in the case of aniline, which decreases as the percentage of dopant increases. At a power of 800 W, a decrease in aniline, phenol and cresol is observed at short times and low dopant percentages. However, as the amount of dopant increases, these percentages increase considerably. The behaviour of pyridine and pyrrole is completely opposite to that of the other three compounds. At 1000 W, the variation coincides with that observed at 800 W, but in a much less pronounced manner. However, pyrrole behaves in an opposite manner.

Phenol was the compound found in the highest percentage in the heavy fraction of the liquid from the pyrolysis of leather waste tanned with vegetable tannins. The values for this compound were similar at 600 and 1000 W, although its behaviour varied at intermediate powers such as 800 W. The highest percentage of this compound was found at long reaction times (30 min) with a dopant concentration of 1.6% (0.5 g per 30 g of material). The rest of the majority compounds varied markedly depending on the experimental conditions, therefore each case would have to be studied individually.

Many of the major components of the liquid fraction from chromium-tanned leather waste were the same as those found in the liquid fractions of vegetable-tanned leather waste, thus indicating that these types of compounds mainly arise due to the composition of the leather or from the initial stages of leather preparation. 3-Methylpyrrole and succinimide do not appear as major components in the composition of vegetable tannins. This is due to the fact that these compounds are formed when tanning leather with chromium salts. Among the compounds selected as the major components, pyrrole was found in a percentage of more than 15% in all cases, reaching values above 25% in some cases. The remaining compounds are found in a percentage of 10% or lower, with small variations with respect to the working parameters.

With all this, it can be indicated that the liquid fractions obtained from the pyrolysis process of these wastes are rich in nitrogenous and oxygenated compounds. The high content of nitrogen compounds results in the capacity of application of these fractions as nitrogen fertilisers, as already pointed out by the Marcilla research group in 2012 [27]. Furthermore, this fraction has pyrrole and its derivatives as the main compound, which makes it a fraction with the capacity to provide high added value compounds useful in different chemical industries such as pharmaceuticals, the dye industry, the generation of agri-food products and even the perfume industry [27,35].

In addition to pyrrole, this fraction contains nitrogen compounds that are highly valued in the adhesives and lubricants industry for industrial use, a fact that has already been collected by other research groups [8,36].

This suggests that this fraction is a good source of high added value chemicals that, after proper treatment, will allow the recovery of the fraction creating a very positive economic and environmental impact. Another possible use for the heavy liquid fraction is as fuel because it has a high calorific value of more than 20 MJ/kg, which is higher than that of some fuels such as wood and agricultural waste (16.0–19.0 MJ/kg) and pine/spruce wood (16.4–17.6 MJ/kg) [37]. The use as fuel is only possible after treatment of this heavy fraction by some cracking, hydrogenation or Fischer–Tropsch synthesis process, which will achieve optimal quality and comply with legislation [22].

In the case of the solid fraction, analysis of the calorific value indicates that both solid products can be considered to be good fuels, with higher values than for biomass of around 16.5–19.0 MJ/kg, which is in line with carbonaceous fuels such as hard coal and anthracite (24–29 MJ/kg) [38]. This makes them cheap fuels that can be used pure or mixed with other carbonaceous fuels [22], within their possible uses as fuels they are ideal for introduction in the metallurgical sector, partly replacing traditional coals. This is possible because the metallurgical sector requires a calorific value of more than 20.8 MJ/kg, a figure that coal from leather waste exceeds [39].

The decrease in the calorific value of the solid obtained from leather waste tanned with chromium salts is mainly due to the higher quantity of mineral salts from the tanning process.

The values obtained from the BET surface area analysis indicate that the surface area is very low when compared with those reported previously, with values in the range 300–2000 m²/g, although it should be noted that, in these publications, the raw material or charcoal itself were treated to obtain a charcoal with a higher surface area [1,40,41]. This is why, by means of a simple carbon activation treatment prior to pyrolysis or post-pyrolysis, a carbon with a greater BET surface area can be obtained and therefore, with the capacity to be used as an active carbon in different industries such as the pharmaceutical and environmental industries [22] or the leather tanning industry itself in the treatment of wastewater and the elimination of Cr(III) from these waters [42,43]. This type of biochar, once activated, can be used as an absorbent for dyes in aqueous solutions, which allows for its use in wastewater treatment plants and textile industries [44]. Furthermore, the transformation of chrome-tanned leather into a high quality biochar allows the stabilisation of chromium within the carbonaceous structure as chromium carbide, allowing chromium control and serving as a method of soil remediation and carbon sequestration [45]. Some research groups, such as that of Martínez Castillas in 2018, are studying the use of biochar from leather waste for application in supercapacitors [46], which provides a new commercial outlet for this material obtained from waste.

This indicates that the pyrolysis of body waste is a good alternative for its valorisation, reducing the environmental impact and giving rise to high added value compounds with the capacity to be reintroduced into different value chains.

The practical implications of this study provide a new treatment route for leather wastes from the tanning industry, which are currently a serious environmental problem, especially those tanned with chromium salts, which are potentially hazardous to the environment. This project marks the first step towards the development of microwave-

assisted pyrolysis technology at an industrial level to enable the treatment of these wastes, taking into account the concept of circular economy and the need for the technique to be versatile and reusable. Obtaining high added value products from waste generates great interest at an industrial level, however, one of the challenges faced by this project is that there are fewer and fewer leather tanning factories, so the industrialisation of the technology is decreasing, this gives rise to future research in which different waste streams can be treated, such as those from biomass together with leather waste, thus achieving a technological boost.

5. Conclusions

Although leather is one of the oldest natural polymers, large quantities of waste leather are still disposed of in landfill. This study has shown that the microwave-assisted pyrolysis technique may be a good alternative for the treatment and recovery of such waste.

Analysis of the raw materials studied shows that leather tanned with vegetable tannins is richer in C, H, N and S, and its ash content is much lower than leather tanned with chromium salts. In addition, the former has a lower water content and higher calorific value.

Analysis of the mass balances shows non-linear variations for each fraction with the treatment conditions. As such, depending on the fraction of interest, the most appropriate conditions must be chosen.

The liquid fraction mainly comprises pyridine, pyrrole, aniline, phenol and cresol, in the case of leather waste tanned with vegetable tannins, and pyridine, pyrrole, 3-methylpyrrol and succinimide, in the case of leather waste tanned with chromium salts. In both cases, this properly treated fraction can be used in the chemical industry as a precursor for different chemical compounds, as a fertiliser thanks to its high content of nitrogen compounds and as a fuel thanks to the good calorific capacity of the heavy fraction.

The solid fraction shows a high calorific value of between 20 and 28 MJ/kg, values similar to those for carbonaceous fuels. The BET surface analyses show values of less than 105 m²/g, thus indicating that a pre- or post-treatment is required for use as activated carbon. Furthermore, according to the ED-XRF results, chromium from the tanning process (in the case of leather tanned with chromium salts) mostly remains in the solid fraction. The application for this fraction is very varied. It can be used as a fuel due to its high calorific value; in the case of leather waste tanned with vegetable tannins, it can be applied directly to the soil like biochar from lignocellulosic resources. Moreover, this fraction can easily increase its specific BET surface area, resulting in an activated carbon that can be used as adsorbent for different wastes for different industries, including leather tanning, as well as in the chemical industry and as technical activated carbon. Additionally, the transformation of tanned leather waste with chromium salts allows the chromium to be stabilised within the carbonaceous structure avoiding a great environmental impact.

Author Contributions: Conceptualisation, S.G.-E. and M.G.-L.; methodology, S.G.-E. and M.G.-L.; software, S.G.-E. and M.G.-L.; validation, J.J.V., J.L.A., M.P., S.G.-E. and M.G.-L.; formal analysis, L.N. and M.G.-L.; investigation, M.G.-L.; resources, S.G.-E. and M.G.-L.; data curation, S.G.-E. and M.G.-L.; writing—original draft preparation, M.G.-L.; writing—review and editing, J.J.V., J.L.A., M.P., S.G.-E. and M.G.-L.; visualisation, J.J.V., J.L.A., M.P., S.G.-E. and M.G.-L.; supervision, J.J.V., J.L.A., M.P., S.G.-E. and M.G.-L.; project administration, J.J.V., M.P. and S.G.-E.; funding acquisition, S.G.-E. and M.G.-L. All authors have read and agreed to the published version of the manuscript.

Funding: This research was supported by the call for industrial doctoral grants (2017) from the Comunidad de Madrid (IND2017/AMB-7848) and by project European funds LIGNOBIOLIFE, LIFE 17 CCM/ES/000051 (www.lignobiolife.com). This publication reflects the views only of the authors and the Commission is not responsible for any use that may be made of the information contained therein.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Data can be requested from author S.G.-E. and M.G.-L.

Acknowledgments: We are grateful to Eco al Cuadrado S.L. Couro Azul, the University of Alcalá (UAH), the Centre for Applied Chemistry and Biotechnology (CQAB) and the Government of the Community of Madrid (grant for A.R., Ref.: IND2017/AMB-7848) for their support. We are also grateful to Couro Azul for providing the leather waste and for their technical support.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Gil, R.R. Aprovechamiento Integral de Residuos Sólidos de Curtición. Implicaciones Medioambient. 2014. Available online: <https://dialnet.unirioja.es/servlet/tesis?codigo=89768> (accessed on 6 February 2022).
2. Engineers, N.B.C. *Leather Processing & Tanning Technology Handbook*; NIIR Projeet Consultancy Services: Delhi, Indonesia, 2011; ISBN 9788190568593.
3. Kanagaraj, J.; Senthilvelan, T.; Panda, R.C.; Kavitha, S. Eco-friendly waste management strategies for greener environment towards sustainable development in leather industry: A comprehensive review. *J. Clean. Prod.* **2015**, *89*, 1–17. [[CrossRef](#)]
4. Bermúdez, J.; Dominguez, P.; Arenillas, A.; Cot, J.; Weber, J.; Luque, R. CO₂ separation and capture properties of porous carbonaceous materials from leather residues. *Materials* **2013**, *6*, 4641–4653. [[CrossRef](#)] [[PubMed](#)]
5. Cabeza, L.F.; Taylor, M.M.; DiMaio, G.L.; Brown, E.M.; Marmer, W.N.; Carrio, R.; Celma, P.J.; Cot, J. Processing of leather waste: Pilot scale studies on chrome shavings. Isolation of potentially valuable protein products and chromium. *Waste Manag.* **1998**, *18*, 211–218. [[CrossRef](#)]
6. Rao, J.R.; Thanikaivelan, P.; Sreeram, K.J.; Nair, B.U. Green route for the utilization of chrome shavings (chromium-containing solid waste) in tanning industry. *Environ. Sci. Technol.* **2002**, *36*, 1372–1376. [[CrossRef](#)] [[PubMed](#)]
7. Aylón, E.; Fernández-Colino, A.; Murillo, R.; Navarro, M.V.; García, T.; Mastral, A.M. Valorisation of waste tyre by pyrolysis in a moving bed reactor. *Waste Manag.* **2010**, *30*, 1220–1224. [[CrossRef](#)] [[PubMed](#)]
8. Van Rensburg, M.L.; Mkhize, N.M. Characterization and pyrolysis of post-consumer leather shoe waste for the recovery of valuable chemicals. *Detritus* **2021**, *14*, 92. [[CrossRef](#)]
9. López, L.A.; De Becerra, J.O.; Sánchez, M.A.M.; Palacios, J.F.; Alicante, E. Combustión limpia de residuos de piel. *CIEMAT INESCOP* **2008**, 1–23.
10. Alptekin, E.; Canakci, M.; Sanli, H. Evaluation of leather industry wastes as a feedstock for biodiesel production. *Fuel* **2012**, *95*, 214–220. [[CrossRef](#)]
11. Özgünay, H.; Çolak, S.; Zengin, G.; Sari, Ö.; Sarikahya, H.; Yüceer, L. Performance and emission study of biodiesel from leather industry pre-fleshings. *Waste Manag.* **2007**, *27*, 1897–1901. [[CrossRef](#)]
12. Luis, M.; Damaris, C. Estudio mecánico del asfalto modificado con polímeros y cueros que son utilizados en la elaboración del calzado. *Rev. L'Estrit Ingénieurs* **2014**, *5*.
13. El-Sabbagh, S.H.; Mohamed, O.A. Recycling of chrome-tanned leather waste in acrylonitrile butadiene rubber. *J. Appl. Polym. Sci.* **2011**, *121*, 979–988. [[CrossRef](#)]
14. Baena-González, J.; Santamaria-Echart, A.; Aguirre, J.L.; González, S. Chemical recycling of plastic waste: Bitumen, solvents, and polystyrene from pyrolysis oil. *Waste Manag.* **2020**, *118*, 139–149. [[CrossRef](#)] [[PubMed](#)]
15. Foong, S.Y.; Liew, R.K.; Yang, Y.; Cheng, Y.W.; Yek, P.N.Y.; Mahari, W.A.W.; Lee, X.Y.; Han, C.S.; Vo, D.-V.N.; Van Le, Q. Valorization of biomass waste to engineered activated biochar by microwave pyrolysis: Progress, challenges, and future directions. *Chem. Eng. J.* **2020**, *389*, 124401. [[CrossRef](#)]
16. Martínez, J.D.; Puy, N.; Murillo, R.; García, T.; Navarro, M.V.; Mastral, A.M. Waste tyre pyrolysis—A review. *Renew. Sustain. Energy Rev.* **2013**, *23*, 179–213. [[CrossRef](#)]
17. Huang, Z.; Zhang, J.; Pan, M.; Hao, Y.; Hu, R.; Xiao, W.; Li, G.; Lyu, T. Valorisation of microalgae residues after lipid extraction: Pyrolysis characteristics for biofuel production. *Biochem. Eng. J.* **2021**, *179*, 108330. [[CrossRef](#)]
18. Li, G.; Bai, X.; Huo, S.; Huang, Z. Fast pyrolysis of LERDADEs for renewable biofuels. *IET Renew. Power Gener.* **2020**, *14*, 959–967. [[CrossRef](#)]
19. Muralidhara, H.S.; Maggin, B.; Phipps, H., Jr. Conversion of tannery waste to useful products. *Resour. Conserv.* **1982**, *8*, 43–59. [[CrossRef](#)]
20. Muralidhara, H.S. Recovery of Potential Energy and Chromium Values from Leather Tannery Wastes. U.S. Patent No 4,332,584, 1982.
21. Font, R.; Caballero, J.A.; Esperanza, M.M.; Fullana, A. Pyrolytic products from tannery wastes. *J. Anal. Appl. Pyrolysis* **1999**, *49*, 243–256. [[CrossRef](#)]
22. Yılmaz, O.; Kantarli, I.C.; Yuksel, M.; Saglam, M.; Yanik, J. Conversion of leather wastes to useful products. *Resour. Conserv. Recycl.* **2007**, *49*, 436–448. [[CrossRef](#)]
23. Oliveira, L.C.A.; Guerreiro, M.C.; Gonçalves, M.; Oliveira, D.Q.L.; Costa, L.C.M. Preparation of activated carbon from leather waste: A new material containing small particle of chromium oxide. *Mater. Lett.* **2008**, *62*, 3710–3712. [[CrossRef](#)]
24. Sethuraman, C.; Srinivas, K.; Sekaran, G. Double pyrolysis of chrome tanned leather solid waste for safe disposal and products recovery. *Int. J. Sci. Eng. Res.* **2013**, *4*, 61–67.

25. Gil, R.R.; Girón, R.P.; Lozano, M.S.; Ruiz, B.; Fuente, E. Pyrolysis of biocollagenic wastes of vegetable tanning. Optimization and kinetic study. *J. Anal. Appl. Pyrolysis* **2012**, *98*, 129–136. [CrossRef]
26. Gil, R.R.; Ruiz, B.; Lozano, M.S.; Fuente, E. The role of crosslinking treatment on the pore structure and water transmission of biocollagenic materials. *J. Appl. Polym. Sci.* **2013**, *130*, 1812–1822. [CrossRef]
27. Marcilla, A.; León, M.; García, A.N.; Bañón, E.; Martínez, P. Upgrading of tannery wastes under fast and slow pyrolysis conditions. *Ind. Eng. Chem. Res.* **2012**, *51*, 3246–3255. [CrossRef]
28. Gürel, K.; Magalhães, D.; Kazanç, F. The effect of torrefaction, slow, and fast pyrolysis on the single particle combustion of agricultural biomass and lignite coal at high heating rates. *Fuel* **2022**, *308*, 122054. [CrossRef]
29. Ronsse, F.; Van Hecke, S.; Dickinson, D.; Prins, W. Production and characterization of slow pyrolysis biochar: Influence of feedstock type and pyrolysis conditions. *Gcb Bioenergy* **2013**, *5*, 104–115. [CrossRef]
30. Al Arni, S. Comparison of slow and fast pyrolysis for converting biomass into fuel. *Renew. Energy* **2018**, *124*, 197–201. [CrossRef]
31. Amdouni, S.; Trabelsi, A.B.H.; Elasm, A.M.; Chagtmi, R.; Haddad, K.; Jamaoui, F.; Khedhira, H.; Chérif, C. Tannery fleshing wastes conversion into high value-added biofuels and biochars using pyrolysis process. *Fuel* **2021**, *294*, 120423. [CrossRef]
32. El-Hout, S.I.; Attia, S.Y.; Mohamed, S.G.; Abdelbasir, S.M. From waste to value-added products: Evaluation of activated carbon generated from leather waste for supercapacitor applications. *J. Environ. Manag.* **2022**, *304*, 114222. [CrossRef]
33. Oliveira, L.C.A.; Coura, C.V.Z.; Guimarães, I.R.; Gonçalves, M. Removal of organic dyes using Cr-containing activated carbon prepared from leather waste. *J. Hazard. Mater.* **2011**, *192*, 1094–1099. [CrossRef]
34. Kluska, J.; Ochnio, M.; Kardaś, D.; Heda, Ł. The influence of temperature on the physicochemical properties of products of pyrolysis of leather-tannery waste. *Waste Manag.* **2019**, *88*, 248–256. [CrossRef]
35. Kaur, R.; Rani, V.; Abbot, V. Recent synthetic and medicinal perspectives of pyrroles: An overview. *J. Pharm. Chem. Chem. Sci.* **2017**, *1*, 17–32.
36. Getachew, P.; Getachew, M.; Joo, J.; Choi, Y.S.; Hwang, D.S.; Hong, Y.-K. The slip agents oleamide and erucamide reduce biofouling by marine benthic organisms (diatoms, biofilms and abalones). *Toxicol. Environ. Health Sci.* **2016**, *8*, 341–348. [CrossRef]
37. Chiamonti, D.; Oasma, A.; Solantausta, Y. Power generation using fast pyrolysis liquids from biomass. *Renew. Sustain. Energy Rev.* **2007**, *11*, 1056–1086. [CrossRef]
38. Francescato, V.; Antonini, E.; Bergomi, L.Z. Manual de Combustibles de Madera Producción Requisitos de Calidad Comercialización. AIEL Italian Agriforestry Energy Association. 2008. Available online: <https://docplayer.es/11944307-Manual-de-combustibles-de-madera-produccion-requisitos-de-calidad-comercializacion.html> (accessed on 6 February 2022).
39. Tórres Filho, A.; Lange, L.C.; de Melo, G.C.B.; Praes, G.E. Pyrolysis of chromium rich tanning industrial wastes and utilization of carbonized wastes in metallurgical process. *Waste Manag.* **2016**, *48*, 448–456. [CrossRef]
40. Konikkara, N.; Kennedy, L.J.; Vijaya, J.J. Preparation and characterization of hierarchical porous carbons derived from solid leather waste for supercapacitor applications. *J. Hazard. Mater.* **2016**, *318*, 173–185. [CrossRef]
41. Kong, J.; Yue, Q.; Wang, B.; Huang, L.; Gao, B.; Wang, Y.; Li, Q. Preparation and characterization of activated carbon from leather waste microwave-induced pyrophosphoric acid activation. *J. Anal. Appl. Pyrolysis* **2013**, *104*, 710–713. [CrossRef]
42. Choudhury, T.R.; Naher, U.H.B.; Akter, S.; Begum, B.A.; Rahman, M.S. Chromium (III) Removal from Synthetic Wastewater Using Biochar Produced from Vegetable Tanned Leather Shaving Dust. *J. Sci. Res. Rep.* **2020**, *26*, 68–80. [CrossRef]
43. Qiao, K.; Tian, W.; Bai, J.; Zhao, J.; Du, Z.; Song, T.; Chu, M.; Wang, L.; Xie, W. Synthesis of floatable magnetic iron/biochar beads for the removal of chromium from aqueous solutions. *Environ. Technol. Innov.* **2020**, *19*, 100907. [CrossRef]
44. Huang, X.; Yu, F.; Peng, Q.; Huang, Y. Superb adsorption capacity of biochar derived from leather shavings for Congo red. *RSC Adv.* **2018**, *8*, 29781–29788. [CrossRef]
45. Wells, H.C.; Sizeland, K.H.; Edmonds, R.L.; Aitkenhead, W.; Kappen, P.; Glover, C.; Johannessen, B.; Haverkamp, R.G. Stabilizing chromium from leather waste in biochar. *ACS Sustain. Chem. Eng.* **2014**, *2*, 1864–1870. [CrossRef]
46. Martínez-Casillas, D.C.; Alonso-Lemus, I.L.; Mascorro-Gutiérrez, I.; Cuentas-Gallegos, A.K. Leather waste-derived biochar with high performance for supercapacitors. *J. Electrochem. Soc.* **2018**, *165*, A2061. [CrossRef]