

Pyrolysis of Leather Trimmings in a Fixed Bed Reactor

by

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Abstract

The leather industry, in spite of using by-products of the meat industry, is also a potential pollutant, as it generates solid and liquid wastes. In the traditional manufacturing process, chromium may be present in a large part of such wastes. A lot of research has been made in order to find ways to valorize these wastes, although for crust and finishing leather trimmings more work is needed to show their potential. The aim of the present investigation is to create useful products through the pyrolysis of waste leather trimmings. The experiments were performed in a vertical semi-batch reactor with ID of 9.7 cm. The influence of operating temperature (490 – 800°C) and heating rate on the composition and distribution of the different phases (solid, liquid and gas) was studied. The gas and the liquid fractions were analyzed by gas chromatography and FTIR, respectively. The char obtained was characterized in terms of its higher heating value and proximate analysis. In addition, the thermal degradation of the leather waste was followed using thermogravimetric analysis.

As the temperature increased, the yields of char and gas phase decreased and increased, respectively. The yield of the liquid phase was almost constant for 490 and 610°C, and decreased for higher temperatures. The effect of heating rate on the yields of pyrolysis products was almost negligible. The amount of chromium oxide in the char tended to increase with increasing temperatures. The FTIR analysis of bio-oils indicated the presence of phenols and alcohols, alkanes, aldehydes, ketones, carboxylic acids and aromatic compounds. GC analysis of the gas phase indicated that CO₂ was the most abundant gas at 490°C, while hydrogen presented higher concentrations at bed temperatures of 610, 700 and 800°C.

Introduction

In some ways the leather industry may be considered environmentally friendly as it uses cowhides, by-products of the meat industry, as its raw material. On the other hand, the industry is also a pollutant as it produces significant quantities of organic wastes and uses large amounts of water in the traditional manufacturing process. Data by Buljan *et al.*¹ showed that, for every 1750 kg of cattle hide entering a tannery (when applying conventional technologies), 195 kg of shoe upper leather and 60 kg of split leather are obtained, 400 kg of non-tanned solid waste are produced and 237 kg of tanned waste. The same data showed that from the total Cr₂O₃ used in the tanning process, 45% remains in the final leather obtained, 30% is discharged as solid waste and 25% as effluents. In recent years a lot of research has been performed in order to find alternatives to the disposal of solid tanning wastes in landfills, including: fat recovery from fleshings, biopolymers from non-tanned solid waste, leatherboard from chromium shavings, and chromium and protein recovery from chromium shavings, amongst others.¹ Leather trimmings from the finishing process step and from footwear have not yet been shown to constitute a viable alternative. One of the available solutions for the disposal of crust or finished leather trimming solid wastes is the use of pyrolysis, which offers a good alternative to disposal in landfills.² According to Caballero *et al.*,³ pyrolysis has the advantage of concentrating the Cr³⁺ ion in the carbonaceous residue, which in turn prevents the chromium from being leached into the environment. Work by Aitkenhead and Edmonds⁴ showed that biochars produced by pyrolysis at temperatures higher than 600°C did not leach when in contact with an acid solution, thus allowing them to be safely disposed of in landfills.

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Pyrolysis refers to the thermochemical decomposition of organic waste or other organic matter at high temperatures, and in the absence of oxygen. The products resulting from pyrolysis can be classified into three main types: a solid phase (carbonized char), a liquid phase (tar, heavy hydrocarbons and water) and a gas phase composed basically of CO₂, H₂O, CO, H₂, CH₄, C₂H₂, C₂H₄, C₂H₆, and C₆H₆.⁵ The char may be used as a solid fuel or for the production of activated carbon. The liquid phase can be further refined and used as a fuel or as a source for extracting other chemicals. The gas phase is often used as a fuel source to sustain the pyrolysis process itself, but also has applications in heat production and power generation.^{6,7}

The nature of the products obtained from pyrolysis depends upon various factors: temperature, heating rate, particle size, flow rate of the carrier gas, and so on.

Temperature has a significant effect on the yields of char, liquid and gas phases. As the temperature rises, there is an increase in the gas phase and a decrease in the solid phase. Experiments performed by Encinar *et al.*⁶ in the fast pyrolysis regime (isothermal), using grape bagasse as a raw material, showed a decrease in the amount of solid phase produced as the temperature was increased. The quantity of gas increased with the temperature, and the liquid yield reached a maximum at 600°C. Studies by González *et al.*⁷ using isothermal pyrolysis of cherry stones demonstrated that the percentage of char decreased from 56.8 to 20.1% while the gas phase increased from 8.8 to 47.6% when the temperature was increased from 300 to 800°C. The liquid phase attained a maximum value of 54.7% at 400°C. The investigation performed by Becidan *et al.*⁸ for isothermal pyrolysis (temperatures in the range of 600 to 900°C) using coffee waste, brewer spent grains and fiberboard, showed that a rise in temperature resulted in an increase in gas yield and a decrease in the char and liquid yields. Yilmaz *et al.*⁹ investigated the slow pyrolysis of chromium-tanned leather for maximum temperatures of 450 and 600°C. They found that as the temperature was raised, there was a corresponding decrease in the solid and liquid yields and an increase in the gas yield. Experiments on flash pyrolysis of chromium-tanned leather (bovine split leather) by Marcilla *et al.*,¹⁰ showed that increasing temperature (from 450 to 550°C) led to a decrease in the char yield (from 38.5 to 31%) and an increase in gas production (from 20.5 to 26.6%). The maximum in the liquid phase yield (44.5%) was obtained at 500°C.

Several studies have been performed which included investigation of the effects of heating ramp (HR) on the production of char, gas and liquid (González *et al.*,⁷ Katyal *et al.*,¹¹ Ayllón *et al.*¹² and Morali and Şensöz¹³). Despite the use of a wide range of very different raw materials, including cherry stones, coffee and brewer waste, meat and bone meal, and hornbeam shell, the results all showed that the HR had little or no effect on the final yields of the pyrolysis end products.

Few studies have been published in the literature concerning the pyrolysis of tannery wastes. Caballero *et al.*³ performed a kinetic study of the thermal degradation of tanned cowhide using thermogravimetric analysis. Font *et al.*¹⁴ studied the pyrolytic products resulting from the thermal degradation of chromium tanned cow hide using a Pyroprobe 1000 connected to a secondary tubular reactor heated by a furnace. In addition, some experiments were done in two different horizontal quartz reactors: one permitting a low cracking degree and another, where a high cracking degree was achieved. Yilmaz *et al.*⁹ investigated the obtainment of useful products by slow pyrolysis of chromium and vegetable tanned leather and buffing dust. Marcilla *et al.*¹⁵ studied the thermal decomposition of bovine leather wastes and collagen using two techniques: thermogravimetric analysis and flash pyrolysis with a Pyroprobe connected to a gas chromatograph with a mass spectrometer. Marcilla *et al.*¹⁰ investigated the flash and the slow pyrolysis of chromium-tanned waste leather in a vertical lab scale reactor. The resultant gases and the liquid phase were analyzed by gas chromatography and by gas chromatography with mass spectrometry, respectively. The solid residue was characterized in terms of its low heating value and using X-ray photoelectron spectroscopy. Simioni *et al.*¹⁶ studied the pyrolysis of chrome leather waste shavings in a fluidized bed reactor. The effect of the operating temperature on the distribution of pyrolysis products was presented, and the liquid phase was analyzed by FTIR and gas chromatography with mass spectrometry. Wells *et al.*¹⁷ studied the production of biochar through the pyrolysis of chrome-tanned leather waste, as an alternative way to dispose of leather waste. Filho *et al.*¹⁸ investigated the pyrolysis of leather wastes from the chromium tanning process and their utilization in metallurgical processes, such as for the production of iron ore pellets.

This paper presents new results on the slow pyrolysis of leather trimmings in a vertical semi-batch reactor with ID of 9.7 cm. The influence of operating temperature and heating rate on the composition and distribution of the different phases was studied. The gas fraction and bio-oil were analyzed using gas chromatography and FTIR, respectively. The char obtained was characterized in terms of its higher heating value and proximate analysis. In addition, the thermal degradation of the leather waste was followed using thermogravimetric analysis.

Experimental

Materials

Before being pyrolyzed, the leather trimmings were subjected to grinding in order to reduce their particle size. The raw material was characterized in terms of its proximate (moisture, volatiles, ash and fixed carbon) and ultimate (C, H, N and O) analyses, chromium oxide content, and by its higher heating value (HHV).

Moisture content was determined according to standard EN14774, the ash content in terms of EN 15148, and standard EN14775 was used for quantifying the volatiles. The fixed carbon was calculated by mass difference. The ultimate analysis of the leather waste was performed by LNEG (“Laboratório Nacional de Engenharia e Geologia”) according to standard CENT/TS 15104. The measurement of the HHV of the feed material, and of the chars obtained after pyrolysis, was performed using a Parr calorimeter composed of three interconnected units: a 1341 Oxygen Bomb Calorimeter, an 1108 Oxygen Combustion Bomb and a 6772 Calorimetric Thermometer. The chromium oxide of the raw material and chars was measured according to standard BS1309-1974.

Data about the proximate and elemental analyses, chromium oxide (Cr_2O_3) content and higher heating value of the leather waste trimmings are listed in Table I.

The characterization of chromium leather waste shavings presented by Simioni *et al.*¹⁶ showed a percentage of chromium oxide (Cr_2O_3) of 3.0% and an ash content of 7.4%. The results of the current experiments showed a chromium oxide content of 2.1%, less than the 2.5% minimum recommended for footwear. The leather trimmings were collected from a Portuguese tannery and it is quite possible that they were not tanned by a pure chromium tanning process.

Thermogravimetric Analysis

The thermal degradation characteristics of the leather trimmings were studied under a nitrogen inert atmosphere using a thermal analyzer type Netzsch STA 449 F3 Jupiter. During the experiments, nitrogen was fed to the equipment at a flow rate of 50 mL/min and the temperature was varied from 50°C to 900°C.

Table I

Proximate and ultimate analysis, chromium oxide content and HHV of the leather trimmings.

Proximate analysis (total basis - % w/w)	Ultimate analysis (total basis - % w/w)*	Chromium oxide (total basis - % w/w)	HHV (MJ/kg)
Moisture – 14.8	C – 43.2	2.1	18.5
Volatiles – 68.5	N – 11.4		
Ash – 7.4	H – 5.6		
Fixed carbon – 9.3	O – 17.6		

* As described in reference.⁵

The influence of the heating rate was studied using HR of 5, 10, 20 and 30°C/min, and a sample mass of 3 mg. The Proteus software was used to acquire, store and analyze the data.

Experimental Set-Up

Pyrolysis of the tannery waste was carried out in a refractory steel, vertical semi-batch reactor, 78 cm in height and 9.7 cm in internal diameter (Figure 1). It was heated by means of a split furnace lined with Kanthal electrical wire resistances, allowing a maximum power of 5000 W. A Shimaden MR 13 control unit monitored the temperature. Two K-type thermocouples were linked to the control unit: the first, 1.5 m in length and 3 mm in diameter, measured the temperature in the reactor (T_p inside the sample); the second, the set-point control, was installed in the oven (temperature TC) to protect against overheating. The experimental set up included a trapping system for condensing the volatiles produced during pyrolysis (the trapping glass bottles were immersed in a bath of ice and water). The gas phase then passed through a silica gel fixed bed in order to remove humidity. During each experiment several samples of the gas phase were collected for further analysis by gas chromatography. A Horiba portable gas analyzer PG-250 was also connected to the system.

During each run a wire mesh basket was loaded with 30 g of ground leather waste, which was then placed in the heating zone of the reactor. Nitrogen was fed into the top of the reactor, at a flow rate of 2.27×10^{-5} kg/s, for a period of 15 min, in order to purge the system (the concentration of O_2 in the system was monitored by the gas analyzer). The heating system was then switched on and a heating rate and a maximum operating temperature were set in the control unit. Continuous monitoring of the temperatures was carried out. The experiment was run for at least half an hour after the maximum temperature was attained, depending on the operating conditions. At the end of the experiment, the heating system was switched off, leaving the carrier gas on for approximately two more hours. When the apparatus was cold, the

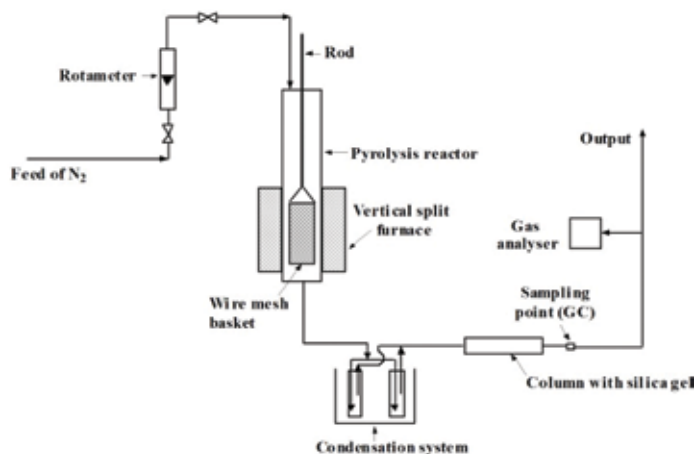


Figure 1. Schematic diagram of the experimental set-up.

char and the condensed phase were weighed. The mass of gas produced was determined by material balance.

The condensed phase, which consisted of an aqueous and an oil phase, was weighed and placed inside an oven at a temperature of 105°C in order to evaporate the water. The drying continued until constant weight was reached. As mentioned by Gonzalez *et al.*⁷ when using this procedure other hydrophilic compounds, miscible with water, could also be removed.

Experiments were performed at maximum furnace temperatures set in the controller (TC_{set}) of 600, 700, 800 and 900°C (for $HR_{set} = 30^\circ\text{C}/\text{min}$), corresponding to final temperatures within the sample (T_f) of 490, 610, 700 and 800°C, respectively. Runs were also carried out at $HR = 10^\circ\text{C}/\text{min}$, for temperatures TC_{set} of 600 and 900°C (corresponding to T_f final values of 490 and 800°C, respectively). From the graphs of temperature TC versus time it was observed that, for the heating rate of 30°C/min set in the controller, the actual HR varied depending on the final temperature reached. Figure 2 shows the temperature profiles TC and T_f for $TC_{set} = 900^\circ\text{C}$. Table II summarizes the temperatures T_f and the actual heating rates reached during the various runs. For the experiments at a heating rate of 10°C/min, the actual HR matched the one set in the controller.

All of the pyrolysis experiments were repeated at least twice in order to test the reproducibility of the results.

Solid, Liquid and Gas Phase Characterization

The char was characterized in terms of its proximate analysis (moisture, volatiles, ash and fixed carbon), HHV and chromium oxide content, following the methods mentioned in the Materials section.

Table II

Heating rates and temperatures reached in the thermocouples placed in the furnace (TC) and inside the sample (T_f).

TC (°C)	Set HR (°C/min)	Actual HR (°C/min)	T_f (°C)
600	30	19	490
700	30	22	610
800	30	24	700
900	30	27	800
600	10	10	490
900	10	10	800

Samples of the oil phase (after the water was removed) were analyzed using the Nicolet 6700 Fourier Transform Infrared Spectrometer with a Smart Orbit diamond crystal attenuated total reflectance accessory, and EZ Omnic software (Thermo Nicolet Corporation, United States of America). The samples were scanned 32 times per analysis at 4 cm^{-1} resolution within the 400–4000 cm^{-1} infrared region.

The gas samples evolved from the experimental system were analyzed in a Dani 1000 DPC gas chromatograph. This apparatus is equipped with an OPT333 injector suitable for packed columns and a thermal conductivity detector (TCD OPT266). A 60/80 Carbonex 1000 column was used with argon as the carrier gas. The compounds analyzed were CO_2 , CO , H_2 , CH_4 , O_2 and N_2 .

Results and Discussion

Thermogravimetric Analysis of Leather Trimmings

The thermal decomposition of the leather trimmings was studied under pyrolysis conditions. Figure 3 represents the mass loss of the sample as a function of the temperature, for $HR = 30^\circ\text{C}/\text{min}$. It is observed that at high temperatures (over about 500°C) the decomposition proceeds very slowly and at 900°C, the mass of the leather continues to decrease. A similar trend was observed by Simioni *et al.*,¹⁶ when they performed thermogravimetric analysis of chrome leather waste shavings.

The differential weight loss (DTG) curves of the leather trimmings at heating rates of 5, 10, 20 and 30°C/min are shown in Figure 4. The first stage of pyrolysis runs from 50 to 100°C, for HR of 5 and 10°C/min, and from 50 to 175°C for the higher heating rates (20 and 30°C/min). This step could be linked to the release of moisture and other volatile compounds. The second stage appears for a range of temperatures between 170 and

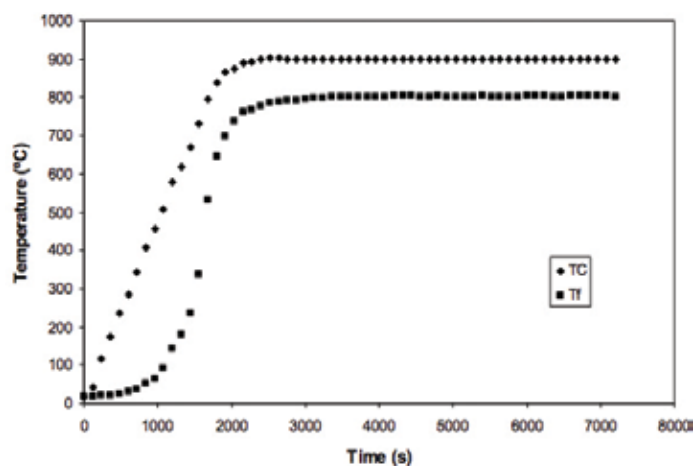


Figure 2. Temperature profiles for the thermocouple inside the furnace (TC) and the corresponding temperatures in the sample (T_f), for a set $HR = 30^\circ\text{C}/\text{min}$ and $TC_{set} = 900^\circ\text{C}$.

530°C, for HR = 5 and 10°C/min, and for 175 to 550°C, when using heating rates of 20 and 30°C/min. This second phase could be due to the decomposition of leather. Table III summarizes the maximum peak temperatures obtained and the respective DTG values, for the different heating rates and the two stages of thermal degradation.

The DTG curve presented by Simioni *et al.*¹⁶ for chrome leather waste shavings, obtained from an experiment carried out for the range of temperatures between 25 and 800°C, HR = 20°C/min, and for an N₂ flow rate of 50 mL/min, showed a maximum peak temperature of 87°C for the first stage of decomposition, and a T_{max} = 329°C corresponding to the second stage. These results are in agreement with the ones provided by the present investigation, also carried out for a residue of leather tanned with chromium.

Figure 4 and Table III show the influence of the heating rate on the DTG curves of the residues under study. As the heating rate is increased, the DTG curves are shifted towards higher temperatures, and the respective DTG values also increase. This phenomenon was explained by Quan *et al.*¹⁹ as follows: with an increase in the heating rate, a larger instantaneous thermal energy is provided to the system and a longer time may be required for the purge gas to reach equilibrium with the sample temperature because of heat transfer limitations. At the same time, higher heating rate has a shorter reaction time, and therefore the temperature needed for the sample to decompose is also higher. This phenomenon was also observed by other researchers.²⁰

Product Yields

One of the purposes of this study was to investigate the influence of heating rate and operating temperature on the product yields obtained from pyrolysis.

Figure 5 shows the variation of the yields of char, condensed phase, and gas as a function of the final temperatures attained inside the reactor. The yields were calculated as the ratio between the weight of each phase and the initial weight of the leather residue (on a total basis). The values reported in this figure were obtained as the average of at least two experimental runs. For each temperature, the difference in yields for replicate runs is less than 3.2%.

For temperatures changing from 490 to 800°C, the yield of the char decreased from 30.1 to 21.4% and the gas yield increased from 52.0 to 66.4%. The liquid yields remained constant, and equal to about 18% for 500 and 610°C, and then decreased to around 12% for 800°C. This decrease, for higher temperatures, could be due to gas phase secondary cracking reactions that promote the formation of lower molecular weight components. This type of behavior was also reported by other researchers.^{5,6,7,9,10}

As previously mentioned and shown in Table II, for a set HR = 30°C/min in the controller, the actual heating rate varied

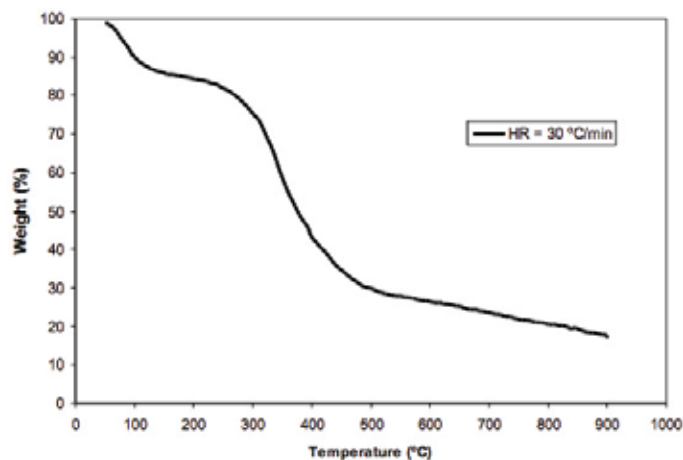


Figure 3. Thermogravimetric analysis curve for leather trimmings at a HR = 30°C/min.

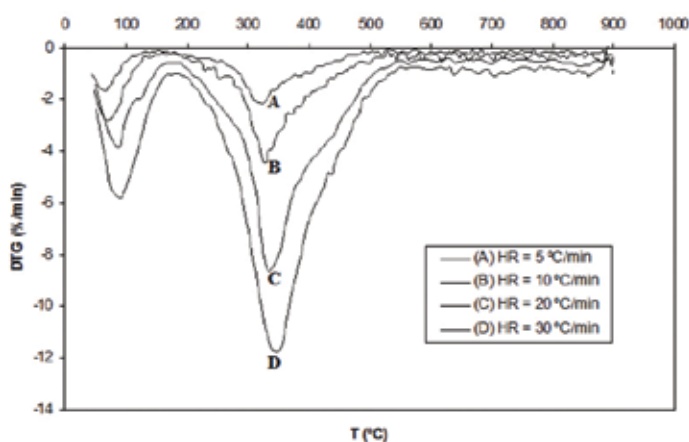


Figure 4. DTG curves for the decomposition of leather residues at four different heating rates (5 to 30°C/min).

Table III
Maximum peak temperatures and respective DTG values obtained from the thermogravimetric analysis, for the two stages of thermal degradation and for the various heating rates used.

		HR = 5°C/ min	HR = 10°C/ min	HR = 20°C/ min	HR = 30°C/ min
1 st stage	T _{peak} (°C)	65.6	66.2	87.9	91.6
	DTG (%/min)	-1.749	-2.875	-3.810	-5.777
2 nd stage	T _{peak} (°C)	319.4	329.3	336.0	348.3
	DTG (%/min)	-2.154	-4.433	-8.664	-11.760

according to the maximum temperature attained (from 17 to 29°C/min). However, studies by González *et al.*,⁷ Kaytel *et al.*,¹¹ Ayllon *et al.*¹² and Moralı and Şensöz¹³ show that for this range of heating rates, HR has little influence on the yield of the char, condensates, and gas produced from pyrolysis (see Introduction).

Table IV shows the influence of the heating rate on the yields of the solid, the liquid and the gas phases obtained for temperatures

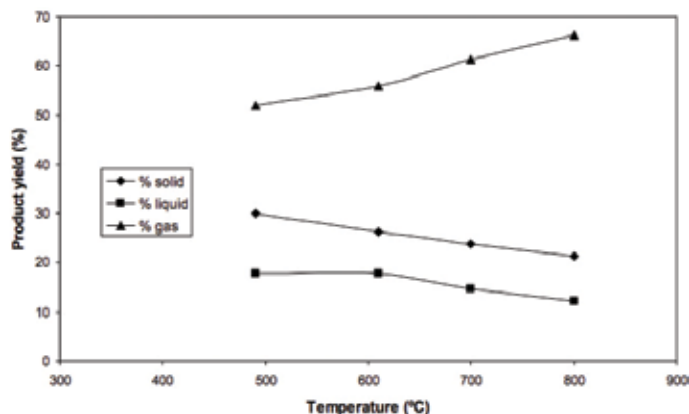


Figure 5. Variation of the yields of the pyrolysis products as a function of the temperature inside the reactor (T_r).

Table IV

Influence of the heating rate on the product yields obtained at two temperatures and two heating rates.

T_r (°C)	HR (°C/min)	% solid	% liquid	% gas
490	10	29.0	16.3	54.7
490	19	30.1	17.9	52.0
800	10	22.1	9.9	68.0
800	27	21.4	12.2	66.4

of 490°C and 800°C, and at two heating rates (the values are the average of two runs). The maximum difference between the yields obtained at the two different HR (for a constant temperature) is 2.7%. Considering that for each temperature, the variation in yields for replicate runs is less than 3.2%, it can also be concluded that for the range of conditions of the present experiments, heating rate has very little effect on product yield.

Characterization of the Chars

Table V presents the proximate analysis, chromium oxide content, and HHV of the chars obtained after pyrolysis for the different operating temperatures (T_r). An analysis of this table indicates that as the operating temperature increases, the percentage of volatiles present in the char decreases, ash content increases and, in general, fixed carbon decreases. The amount of chromium oxide tends to increase for higher temperatures. The higher heating value of all chars is approximately 18 MJ/kg.

Studies by Simioni *et al.*¹⁶ show that chars present higher chromium levels than their precursors (chromium leather waste shavings). Chars produced from chromium tanned leather by Yilmaz *et al.*⁹ at temperatures of 450 and 600°C (HR = 5°C/min) had ash contents of 19.5% and 22.6%, respectively. Results from the proximate analysis of chars by Gonzalez *et al.*⁷ showed an increase in the ash content and the fixed carbon, and a decrease in the volatile contents, as operating temperature of the reactor was raised.

The chars can be burned as fuel, safely disposed in landfills since the heavy metals are fixed inside the carbonaceous residues, or used to produce activated carbon.²¹

Liquid Phase Analysis

As described in the experimental section, the condensed phase was analyzed in terms of its water content, by drying it at 105°C. The results obtained show that the water content in the liquid phase was not influenced by the final operating temperature and had an average value of 78%. Results by Yilmaz *et al.*⁹ for the condensed phase obtained from pyrolysis of chromium-tanned

Table V

Proximate analysis, chromium oxide content, and HHV of the chars for different temperatures (T_r) at a set HR = 30°C/min.

Maximum temperature	Moisture (total basis -% w/w)	Volatiles (total basis -% w/w)	Ash (total basis -% w/w)	Fixed carbon (total basis -% w/w)	Chromium oxide (total basis -% w/w)	HHV (MJ/kg)
490	3.4	28.3	26.2	42.1	5.9	18.06
610	4.1	19.0	30.4	46.5	7.2	17.65
700	3.4	15.3	50.9	30.4	6.8	17.92
800	3.0	14.5	60.7	21.8	7.8	17.65

leather, at operating temperatures of 450 and 600°C, obtained a water content of 65.9% and 67.5% respectively.

The samples of the bio-oil (obtained by water evaporation of the condensed phase) were subjected to FTIR analysis, as this technique allows functional group analysis. Figure 6 shows the FTIR reflectance spectra of the bio-oils for the experiments performed at final temperatures inside the reactor of 490, 610, 700 and 800°C. In general the spectra are very similar for all the runs. However, a slight difference can be observed in the 3200 - 3500 cm^{-1} range. In this region, which indicates the presence of O-H stretching vibrations that are characteristic of phenols and alcohols, the intensity of the band seems to decrease as the operating temperature of the run increases from 490 to 800°C. Analyzing the remaining data, and taking as an example the curve at $T_f = 800^\circ\text{C}$, the peaks at 2922 and 2852 cm^{-1} (band between 2800 and 3000 cm^{-1}) refer to C-H stretching vibrations and could indicate the presence of alkanes. The peaks at 1716

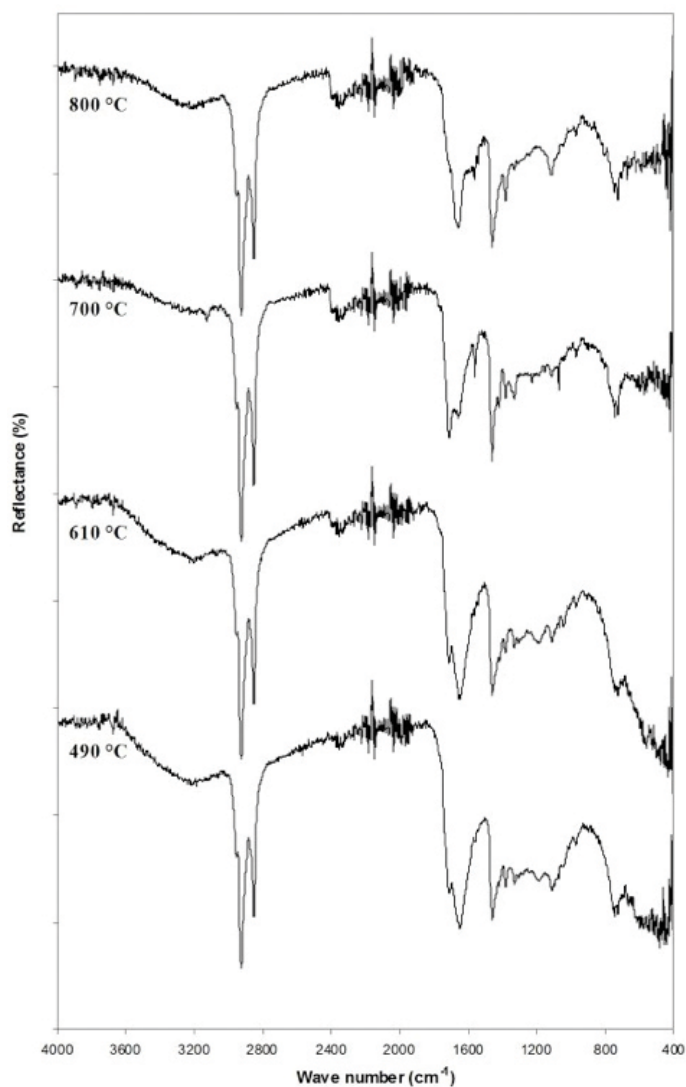


Figure 6. FTIR analysis of the pyrolysis oil obtained at temperatures T_f from 490 to 800°C. Gas Composition

and at 1660 cm^{-1} (included in the range of 1650-1750 cm^{-1}), could be connected to C=O stretching vibrations, indicating the presence of aldehydes, ketones and carboxylic acids. The peak at 1461 cm^{-1} (within the 1460-1455 cm^{-1} range) could be linked to the C=C stretching vibrations and indicate the presence of aromatic compounds in the oil. Similar results were obtained by Simioni et al.,¹⁶ Morali and Şensöz¹³ and Yorgun and Yildiz.²²

Gas Composition

The compounds in the gas product stream analyzed by gas chromatography were: CO_2 , CO, H_2 and CH_4 . Figures 7 and 8 show the variation of the concentration of these components as a function of time, for temperatures inside the reactor of 490°C and 800°C respectively. In these graphs the temperature evolution inside the reactor is also represented.

Figure 6 shows that the predominant gas produced at 490°C is CO_2 , which reaches a maximum concentration of 3.6% at temperatures inside the reactor of approximately 455°C. CO reaches a maximum concentration of 1.9% at temperatures below 400°C. Hydrogen appeared at higher temperatures, reaching a peak composition of 1.8% at 475°C. Finally, methane is the least produced gas, with a maximum production of 0.9% at around 450°C.

Figure 7 presents an example of the concentration profiles obtained at 800°C, the highest temperature studied in this work. Hydrogen is the most abundant gas, reaching a peak concentration of 11.5% at a temperature of 702°C, followed by CO with a maximum production of 7.8% at approximately the same temperature. The variation in concentration for the CO_2 presents a peak at 7.1%, at a temperature of 585°C. Finally, CH_4 is the gas present in the least quantity, with a maximum concentration of 4.8% at $T = 660^\circ\text{C}$.

The total molar amount of each component released during a pyrolysis run was obtained by calculating the area under the curve of the graph of molar flow rate of each gas versus time, and

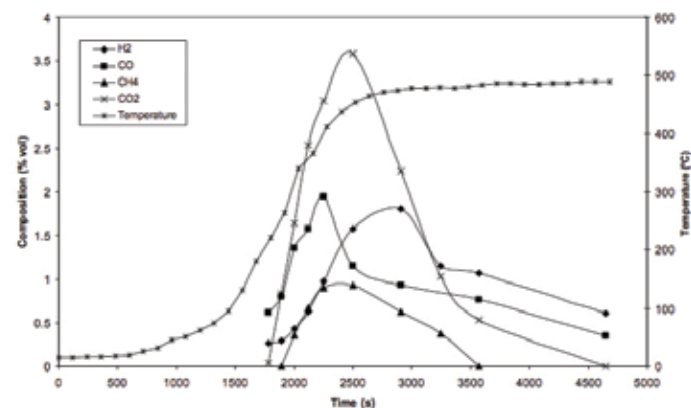


Figure 7. Variation of the concentration of the gases produced and temperature evolution, during slow pyrolysis, up to a maximum bed temperature of 490°C and at a set heating rate of 30°C/min.

assuming that the nitrogen flow rate was constant (at 2.27×10^{-5} kg/s). Figure 9 represents the total amount of each gas produced against the temperature inside the reactor, and the variation of the higher heating value of the mixture.

The higher heating value of the gas produced, HHV_g , was calculated according to the equation:²³

$$HHV_g = [30.52x(\%H_2) + 30.18x(\%CO) + 95x(\%CH_4)] \times 4.1868 \quad (\text{kJ/Nm}^3)$$

with the concentration of gases expressed in volume percent. For temperatures inside the reactor from 490°C to 800°C, HHV_g varied from 303.5 to 1079 kJ/(Nm³), indicating that higher temperatures favor the production of a richer combustible gas.

Analysis of gas production indicates that CO₂ is the most abundant gas at 490°C, and shows that its amount increases

slightly with temperature: it varies from 1.36 to 2.83 mol gas/kg leather when temperature changes from 490 to 800°C. Hydrogen is the most abundant gas at temperatures of 610, 700 and 800°C, reaching a maximum of 9.4 mol gas/kg leather at 800°C. CO is present in relatively low amounts, 0.76 and 1.0 mol gas/kg leather at 490 and 610°C, but increases for higher temperatures, reaching 5.3 mol gas/kg leather at 800°C. Methane is the least produced gas, with amounts varying from 0.30 to 2.0 mol gas/kg leather at temperatures of 490 and 800°C respectively.

The formation of the gaseous species is a result of the decomposition of char and tar cracking at high temperatures, and reactions among components formed during pyrolysis. According to González *et al.*,⁷ hydrogen is produced by the cracking of volatiles, methane is produced by cracking and depolymerization reactions, carbon monoxide and carbon dioxide by decarboxylation and depolymerization reactions, and by secondary oxidation reactions of carbon. These reactions are favored by increasing the temperature, leading to better gas production.

The presence of H₂, CO₂, CO and CH₄ in the produced gas was also reported by other authors in pyrolysis studies of other biomasses including González *et al.*⁷ for cherry stones, Ayllón *et al.*¹² for meat and bone meal, Becidan *et al.*⁸ for brewer spent grains, fiberboard and coffee bean waste, and Gil *et al.*²⁴ for vegetable tanning of bovine leather. Marcilla *et al.*¹⁰ presented the detection of carbon oxides, alkanes, alkenes, alkynes and aromatics in the composition of their gas phase from pyrolysis of chromium tanned leather. However, they did not mention the presence of H₂ in their analysis.

Conclusions

In the present work, new experimental data on the slow pyrolysis of leather trimmings in a vertical semi-batch reactor with an ID of 9.7 cm are presented. The effect of temperature and heating rate (HR) on the composition and distribution of the different phases obtained after pyrolysis was studied. Leather trimmings were also tested using thermogravimetric analysis. For temperatures in the range of 490 to 800°C, the yield of the char decreased from 30.1 to 21.4% and the gas yield increased from 52.0 to 66.4%. The yields of the liquid remained constant for 500 and 610°C (about 18%), and then decreased for 700 and 800°C (14.8 and 12.2% respectively). For the conditions under study, HR has little influence on the yield of the char, condensates and gas produced from pyrolysis. From the proximate analysis of the chars, the percentage of volatiles present decreases as the operating temperature increases, ash content increases and, in general, fixed carbon decreases. The amount of chromium oxide tends to increase for higher operating temperatures. The higher heating value of all chars is approximately 18 MJ/kg. FTIR analysis of the bio-oil indicates the presence of phenols and

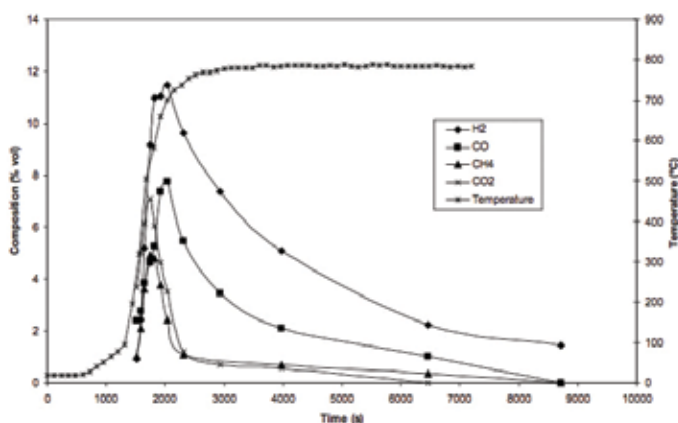


Figure 8. Variation of the concentration of the gases produced and temperature evolution during slow pyrolysis, up to a maximum bed temperature of 800°C and at a set heating rate of 30°C/min.

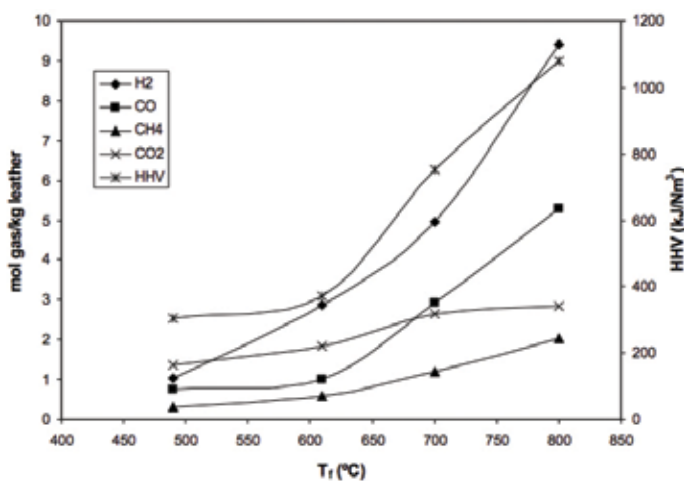


Figure 9. Total amount of each gas produced (H₂, CO₂, CO and CH₄) against the final temperature inside the reactor and the variation of the higher heating value of the gas mixture produced.

alcohols, alkanes, aldehydes, ketones and carboxylic acids and aromatic compounds. Analysis of the gas phase in terms of CO₂, CO, H₂ and CH₄, indicates that CO₂ is the gas most produced at 490°C, while hydrogen is the most abundant at temperatures of 610, 700 and 800°C. Methane is the least produced gas at any temperature (490, 610, 700 and 800°C). TG analysis for different heating rates shows that within the temperature interval tested (50 to 900°C), the DTG curves were shifted towards higher temperatures as the heating rate was increased.

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