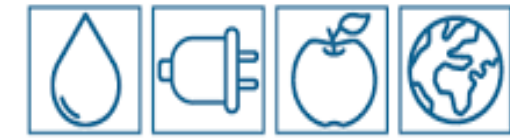


# Valorisation of leather wastes from footwear industry via pyrolysis: product yields and characterisation



**ICoWEFS**  
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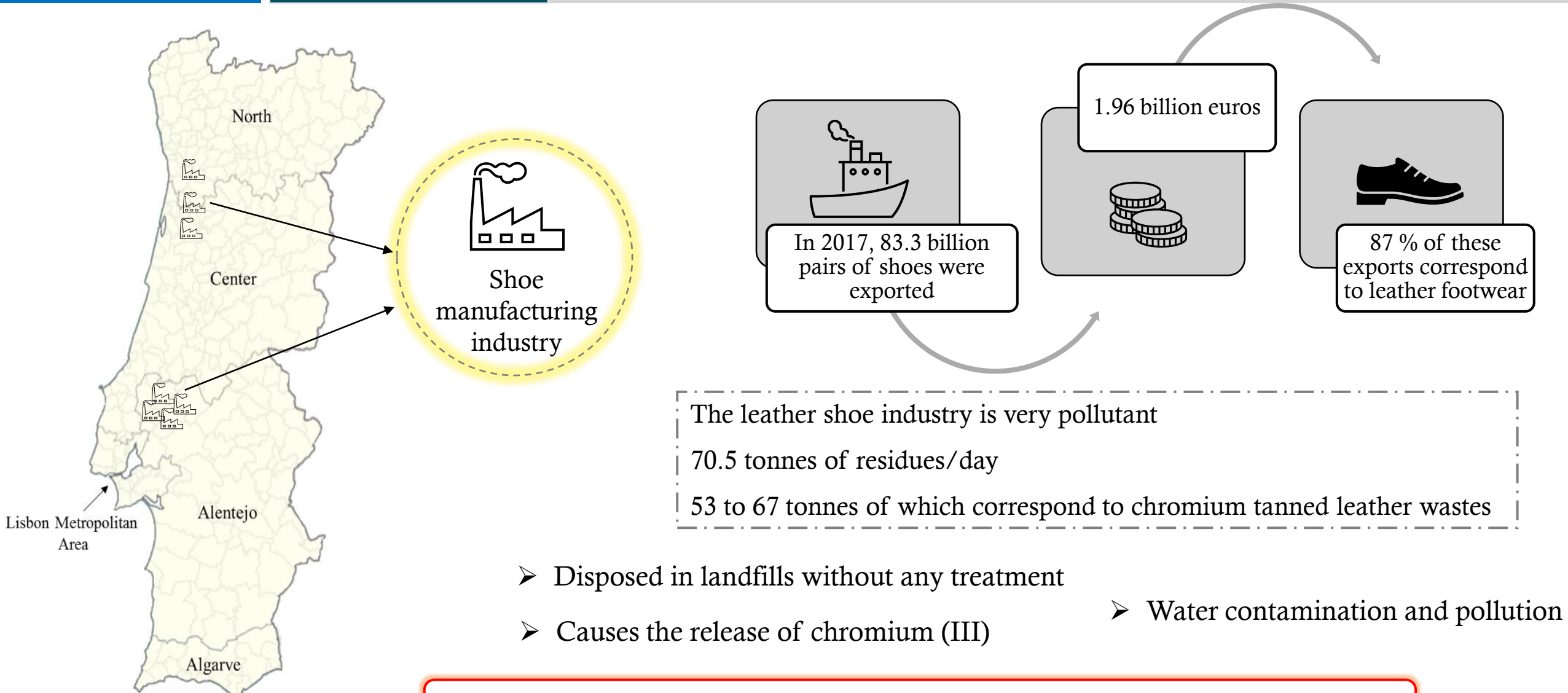
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The leather shoe industry is very pollutant

70.5 tonnes of residues/day

53 to 67 tonnes of which correspond to chromium tanned leather wastes

- Disposed in landfills without any treatment
- Causes the release of chromium (III)
- Water contamination and pollution

It is very important to find efficient techniques to manage this toxic waste.

## PYROLYSIS

Raw material

Conversion technology

Products

Thermally decomposed in an inert atmosphere at temperatures ranging from 400 to 1000 °C.

Gases

CO CO<sub>2</sub>  
CH<sub>4</sub> H<sub>2</sub>

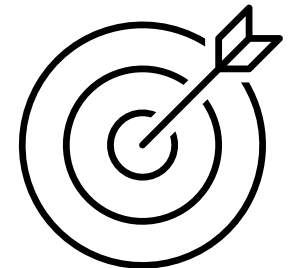


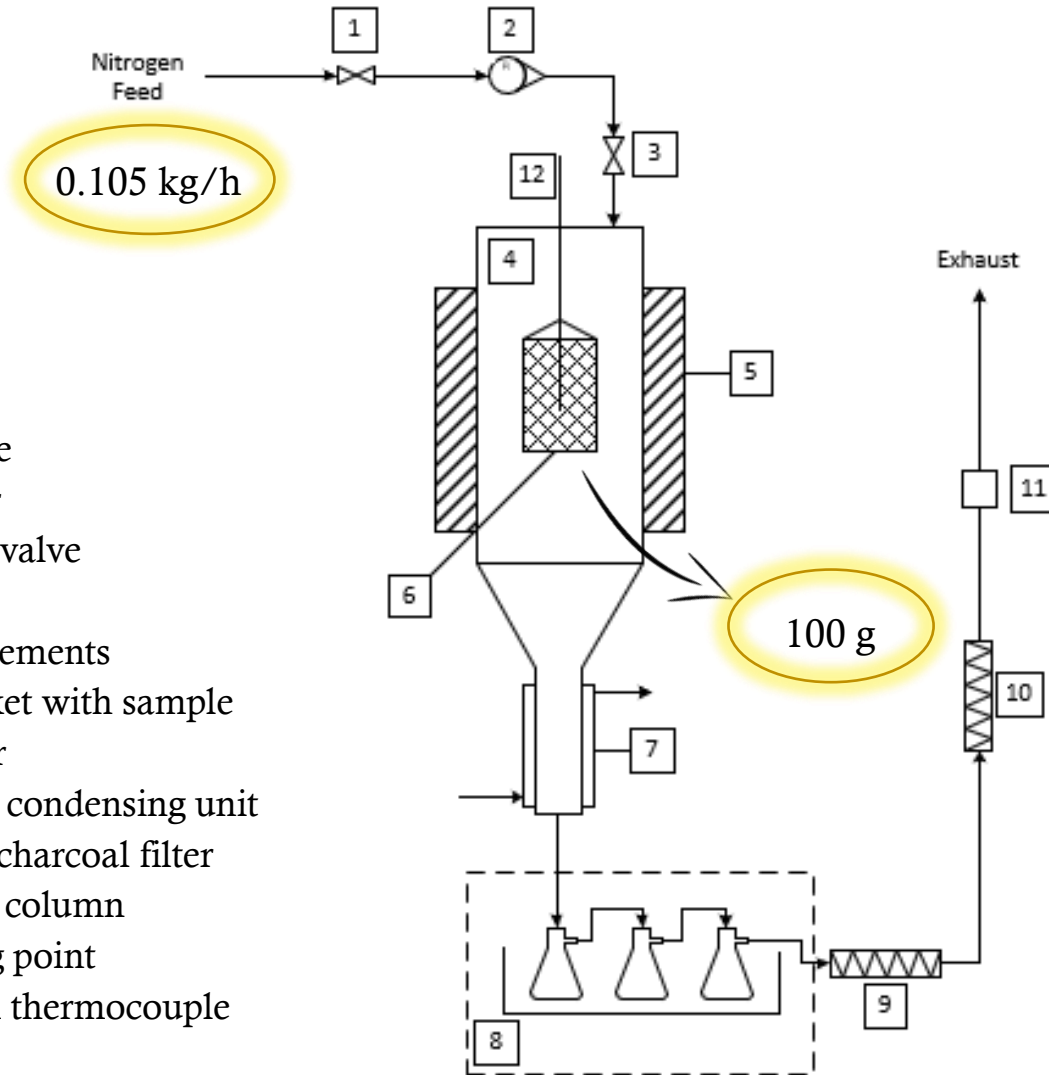
LEATHER TRIMMINGS



All of these are value-added products that can be used as energy sources by other industries, thus contributing to a circular economy.

- The influence of temperature on the pyrolysis of leather trimmings from the footwear industry.
- Characterization of leather waste used in the pyrolysis process;
- The physical-chemical characterizations of biochar, bio-oil and non-condensable gases.





Legend:

- 1 – Main valve
- 2 – Rotameter
- 3 – Regulator valve
- 4 – Reactor
- 5 – Heating elements
- 6 – Mesh basket with sample
- 7 – Condenser
- 8 – Ice cooled condensing unit
- 9 – Activated charcoal filter
- 10 – Silica gel column
- 11 – Sampling point
- 12 – Rod with thermocouple

Experimental Installation

➤ Leather residues:

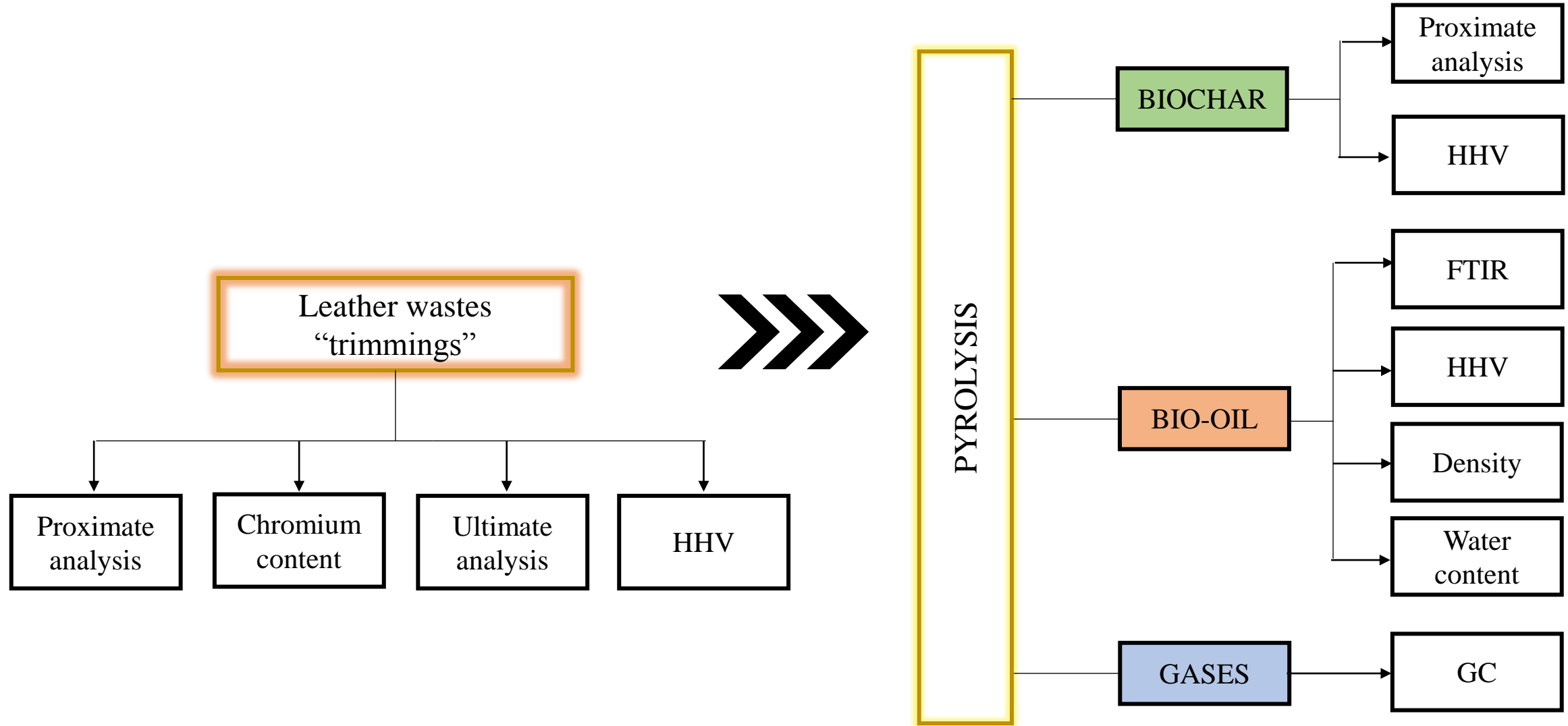
Particle size between 5.3 – 6 mm.

$T_{set}$  in the range of 565 to 1030 °C

$T_i$  in the range of 444 to 875 °C;

➤ Preliminary experiments were done to verify the effect of particle size on biochar yield.

➤ Using leather squares with 10 mm side length, for  $T_i$  = of 444 and 630 °C.

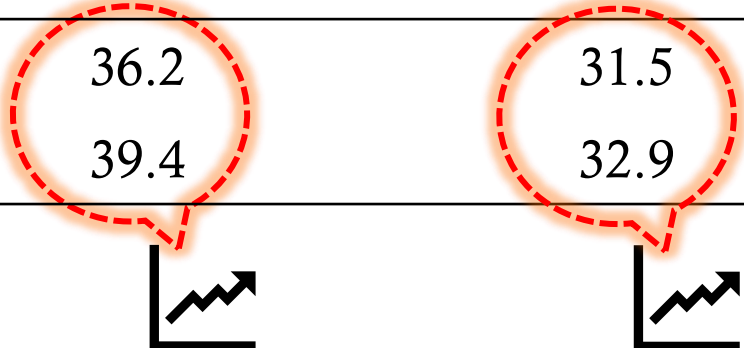


Proximate and ultimate analysis, chromium oxide content and HHV of the residues

	This work	Fang et al. [8]	González-Lucas et al. [10]
Moisture (wt%)	12.3	9.2	36.9
<b>Proximate analysis (db - wt%)</b>			
Ash	6.4	10.32	7.16
Volatiles	73.1	74.60	-
Fixed carbon	20.5	15.08	-
<b>Ultimate analysis (db - wt%)</b>			
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

## EFFECT OF PARTICLE SIZE ON BIOCHAR

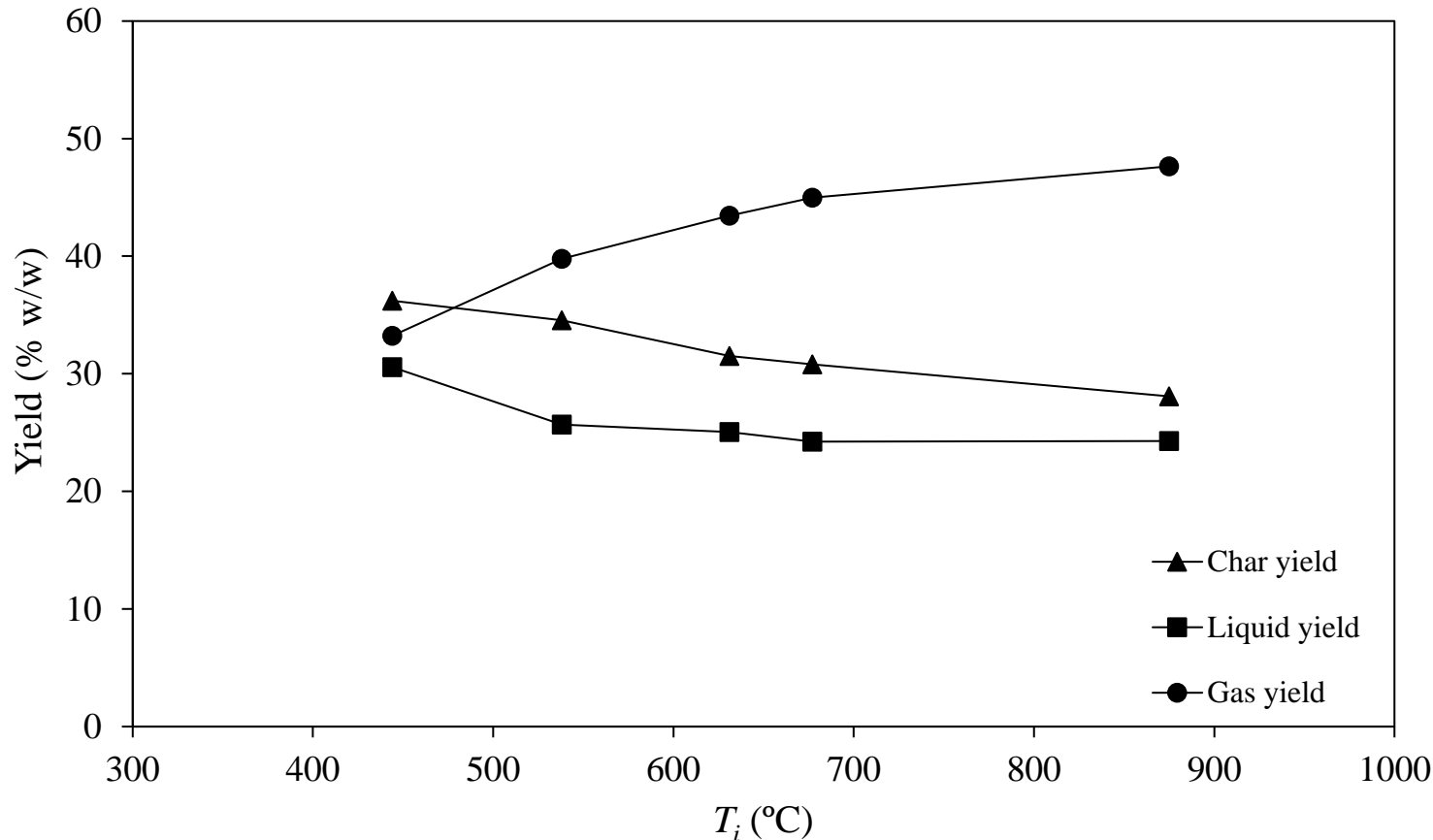
Biochar Yield (%)		
	Temperature (°C)	
	444	630
5.3 – 6 mm	36.2	31.5
10 mm	39.4	32.9



Larger particles offer more resistance to the escape of condensable gases, leading to secondary cracking which results in an increase in solid yield.

## EFFECT OF PYROLYSIS TEMPERATURE

Particle size between 5.3 - 6 mm  
 $T_i$  of 444 to 875 °C



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

With increasing temperature:

Biochar yield decreased from 36.2 to 28.1 %;

The gas yields increased from 33.2 to 47.6 %;

The highest liquid yield, 30.6 %, was obtained at a temperature of 444 °C and then decreased to 24.3 % at 875 °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.

**BIOCHAR**

Proximate analysis (db) and HHV of biochars.

T <sub>set</sub> (°C)	T <sub>i</sub> (°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

The chars from leather wastes can be used in the metallurgical industry, as a fuel, in the production of activated carbon and as an adsorbent.

**BIO-OIL**

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

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

**BIO-OIL**

Density and heating values of the liquid phases.

T <sub>set</sub> (°C)	T <sub>i</sub> (°C)	Density (kg/m <sup>3</sup> )	HHV (MJ/kg)
565	444	1110	12.7
765	630	1120	13.2
1030	875	1120	15.1

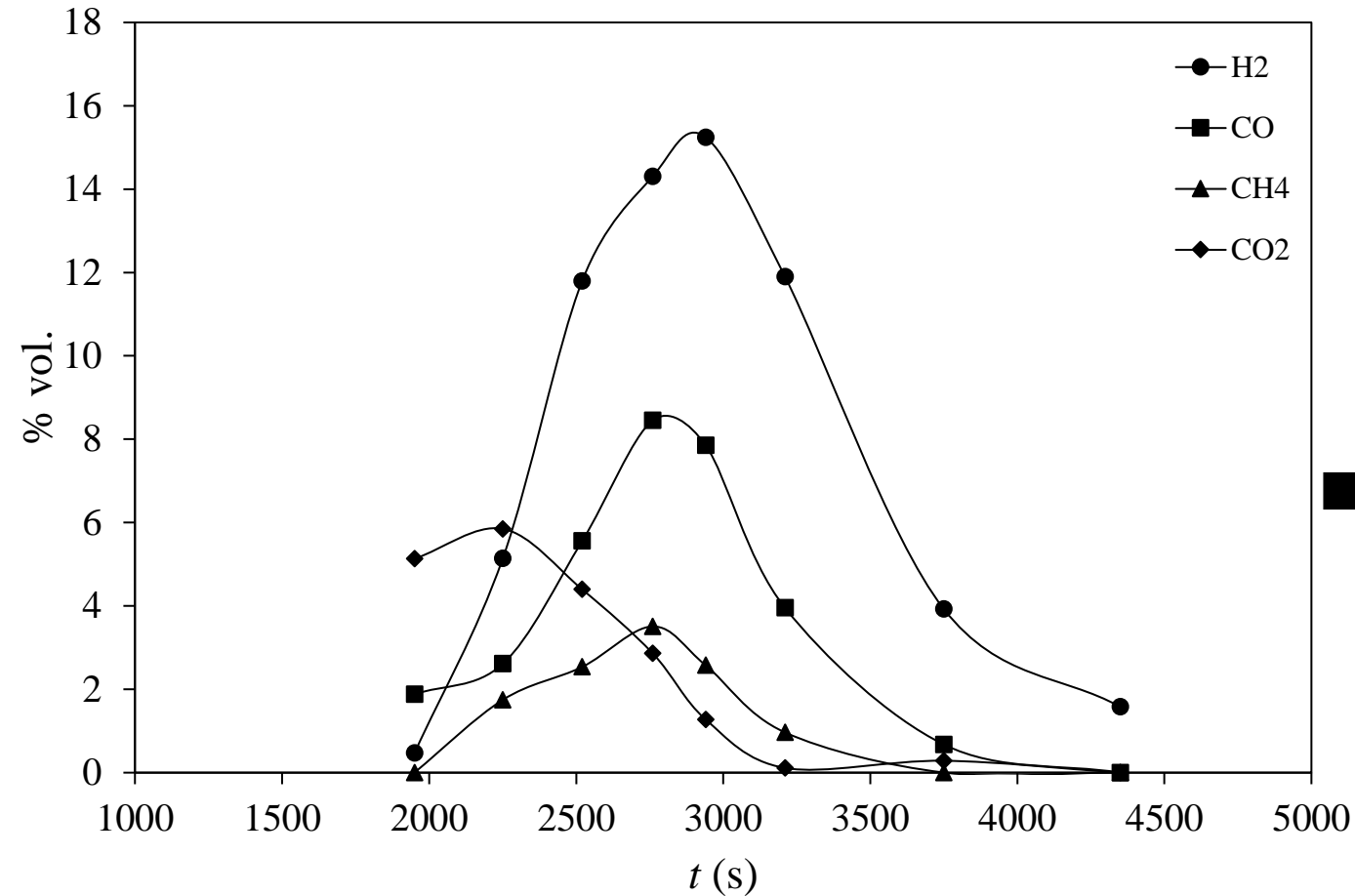
- With increasing temperature, the HHV increased slightly.
- The density of the liquid phase showed similar values.

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.

## GAS CHROMATOGRAPHY ANALYSIS



Volumetric fraction of gases (%)				
T (°C)	maximum volumetric fraction (%)			
	H <sub>2</sub>	CO	CO <sub>2</sub>	CH <sub>4</sub>
538	5.5	2.2	6.8	1.0
<b>875</b>	<b>15.2</b>	<b>8.5</b>	<b>5.8</b>	<b>2.9</b>

Variation of the concentrations of CO<sub>2</sub>, CO, CH<sub>4</sub> and H<sub>2</sub> with time, for  $T_i = 875$  °C

**GAS CHROMATOGRAPHY ANALYSIS**

Total amount of H<sub>2</sub>, CO, CH<sub>4</sub> and CO<sub>2</sub> produced during the experiments at  $T_i = 538$  and  $875$  °C and HHV of the gas mixture.

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

- The higher temperature provided greater gas production (mol/kg of leather) and consequently impacted the higher heating value, being almost three times greater.

➤ Leather waste showed to have great potential for thermal conversion, as well as good properties to produce biochar and bio-oil.

- The yields of bio-oil and biochar were higher at 444°C;
- In qualitative terms, the temperature (875°C), provided better results for biochar with respect to fixed carbon and HHV;
- For this same temperature, the bio-oil and gases, presented better results regarding HHV.

- The bio-oil is constituted by a complex mixture consisting of a wide variety of organic compounds, can be used as a source a source of chemical products.
- Another possibility its use as a fuel, after treatment, because of the higher heating value.