RECYCLING OF TANNERY WASTES BY PYROLYSIS IN A VERTICAL LAB SCALE REACTOR

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Abstract

The thermal degradation of a chromium-tanned waste (bobine split leather) under inert atmosphere has been carried out in a vertical reactor. Process conditions have been selected to optimize the liquid fraction obtained (bio-oil). Flash pyrolysis at three different temperatures (450, 500 and 550ºC) and slow pyrolysis up to 725ºC have been performed. Experiments with collagen were also carried out. Although tannery waste is a biomass that can be valorized through thermal degradation processes, the results reveal the complexity of the gas and liquid fractions generated, which include a significant proportion of oxygenated, nitrogenated and sulphured gases. A clear relationship was observed between the weight loss of the sample during its thermal degradation and the evolution of pyrolytic gases detected. From the three fractions obtained, char fraction has the highest calorific value, followed by the gas evolved. The heating value of the liquid fraction is about 20% of that of the original leather. Further treatments of the bio-oil obtained would be needed to improve its fuel potential.

Keywords: *Flash and slow pyrolysis, chromium-tanned wastes, GC-MS, Thermogravimetric analysis, vertical reactor*

1. Introduction

Wide literature about leather waste treatment and recycling can be found: mechanical recycling, protein recuperation and chromium reutilization [1,2], or energetic use (combustion). However, specific information related to the pyrolysis of tannery wastes is scarce [3,4].

Pyrolysis presents an interesting alternative to the conventional combustion process. Gas and liquid fractions are also susceptible to generate useful chemicals. Moreover as a fuel, used alone or mixed with other fuels, the char obtained can also be used as a cheap adsorbent.

In this paper, pyrolysis of chromium-tanned wastes is proposed to convert these wastes into a gas or liquid fuel, trying to optimize the production of liquid fraction.

2. Materials and Methods

The experiments were carried out on a chromium-tanned waste (bobine split leather) supplied by Palomares Piel, S.L. and collagen powder from the Achilles tendon of a bovine species supplied by SIGMA-ALDRICH without any tanning treatment. Table 1 shows the ultimate analysis of these materials.

Table 1. Ultimate Analysis.

	N	C	H	S
Leather	12.94	41.49	6.85	0.83
Collagen	12.82	48.14	7.25	0

The leather was subjected to thermal degradation with TG analysis in nitrogen atmosphere using a heating rate of 10ºC/min until 800ºC.

The experiments were carried out in a fluidized bed reactor (71cm x 5.8cm) under different conditions:

- flash pyrolysis at 450ºC, 500ºC and 550ºC (leather)
- slow pyrolysis (10 ºC/min) up to 725ºC (leather)
- flash pyrolysis 500ºC sand bed (leather and collagen)

Gas fractions were collected in tedlar bags. In the case of slow pyrolysis, specific gas samples were collected at intervals of 50ºC approximately. Condensed volatiles were collected in glass traps. Gas and liquid compounds were identified by GC-MS.

3. Results and Discussion

The fraction distribution obtained in the experiments carried out is shown in Table 2.

Table 2. Product distribution

	Gas (%)*	Liquid (%)	Solid (%)
F 450ºC	20.47	41.01	38.52
F 500ºC	25.08	44.52	30.40
F 550ºC	26.62	42.34	31.04
S 725ºC	41.83	29.61	28.56
FB leather	12.05	53.49	34.03
FB collagen	9.81	55.36	34.83

F Flash; S Slow; FB Flash sand bed 500ºC
(*) Calculated by difference

For the leather, there are not significant differences between gas products generated from flash and slow pyrolysis, although the yields obtained in each case depend on the heating rate and the process temperature. The major components found are hydrocarbons (methane, ethane, ethylene, propane, propylene, isobutene), although a high number of oxygenated components are also identified. It has to be noticed the significant proportion of nitrogenated and sulphured gases, such as HCN, acetonitrile and CH_3SH as well as other minor sulphured and chlorated components such as COS, H_2S and $ClCH_3$.

In the slow pyrolysis, it is observed that the evolution of volatiles is comparable with the weight loss obtained in thermogravimetric analysis.

Figure 1 shows the DTG curve obtained in the TG and the evolution of gases (CO, CO_2 and other gases such as light hydrocarbons) in the slow pyrolysis reactor. As can be seen, the weight loss at around 250-360ºC is mainly due to the CO_2 formation together with a small contribution of CO. In the range 360-450ºC, the evolution of other gases different from carbon oxides plays an important role in the weight loss of the sample. CO_2 generation is also detected in this range. Above that temperature, the solid seems not to suffer further reactions, however gases are detected in the reactor experiments (CO mainly and hydrocarbons). These results show that in a slow pyrolysis gases formed above 540ºC are due to secondary reactions of heavy volatiles that remain in the hot zone of the reactor but they do not come from the decomposition of the solid.

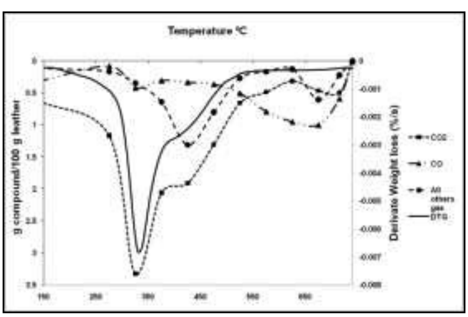

Fig. 1. DGT and % gas compounds of slow pyrolysis

In liquid fraction, the spectrum of compounds found is mainly formed by aromatics and heteroatoms containing compounds. Figure 2 shows the yields of the groups obtained on the flash pyrolysis (500ºC) of chromium leather: ketones, phenol derivatives, nitro-aromatics, esters, paraffins and olefins, aromatics, sulphurs and alcohols. Derivatives of naphthalene (aromatics) and pyridine (nitro-aromatics) seem to be more characteristics of slow than flash pyrolysis.

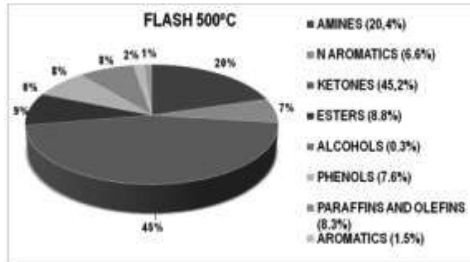

Fig. 2. Percentages of groups of liquid compound obtained in flash pyrolysis at 500 º C

The presence of sand in the reactor has reduced its free volume, thus reducing the residence time of the volatiles in the reactor. As a consequence, the gas yields in the experiments have diminished. By comparing results from pyrolysis of collagen and leather, higher yields of ketones and paraffins and olefins has been found in collagen.

4. Conclusions

Tannery waste is a biomass that can be valorized through pyrolysis process. The maximum evolution of pyrolytic condensable volatiles is produced in the range 400 - 500ºC. The major products obtained in gas fraction are hydrocarbons although nitrogenated, oxygenated and sulphured compounds need to be taken into account. Ketones and amines are the major functional groups detected in the liquid fraction, although a wide distribution of heterocompounds are also found in minor proportions.

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