Biofuels production potential from industrial biocollagenic wastes of vegetable tanning using pyrolysis technologies fitting to circular economy and sustainability criteria

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Introduction

The energy transition towards a more sustainable model is based on the circular economy, energy efficiency, the integration of renewable energies, the use of synthetic fuels and the electrification of mobility. Nowadays many companies are exploring alternatives to fossil fuels in favor of so-called biofuels, fuels that maintain the qualities of traditional fuels, but are created from renewable raw materials and represent a very significant reduction in net CO_2 emissions. In the transportation sector, renewable fuels are gradually being incorporated; the fuels used in the gasoline and diesel engines of cars and trucks already incorporate a percentage of these sustainable fuels (11%). The use of biofuels is also extending to maritime and air transport, where little by little they are beginning to be used to replace diesel and kerosene. Depending on their origin, it can talk of first-generation biofuels (from food crops such as sugar cane, grains, beets or wheat) and second-generation biofuels that are produced from organic waste (surpluses and waste from livestock farms or agricultural products, forest biomass, used cooking oil, etc.) (Sathish Kumar *et al.*, 2024; Mohr and S. Raman, 2013). These biofuels promote the circular economy and the sustainability.

Pyrolysis technology is based on the heating, without oxygen and at high temperature, of organic matter (or waste) obtaining different products (gas, bio-oil and bio-char) that can be used, among others, as biofuel or as raw material for the development of chemical products and/or adsorbents. Gas, bio-oil and bio-char yields are influenced by the experimental conditions of the pyrolysis process and by the raw material properties.

This research study provides insights into the importance of converting a vegetable tanned leather waste and pre-tanned skin through conventional and flash pyrolysis (CP and FP, respectively) into biofuels, biomaterials and bioenergy for environmentally friendly applications, which is intrinsically linked to circular economy concepts.

Methodology

The vegetable-tanned leather waste used in this work, called BCT (Biomaterial-Collagen-Tanning), is a mixture of shavings, trimmings and buffing dust that are found in the same proportion (84%, 15% and 1% respectively) as those coming from the leather industry. Pre-tanned skin (dehydrated and degreased skin) was also studied. This sample was called BCD (Biomaterial-Collagen-Dehydrated). The comparative study of both samples through conventional and flash pyrolysis processes will allow establishing differences in the yields and quality of the biofuels obtained. The bio-wastes, in the form of strips or large pieces, were reduced by grinding to a fine particle size suitable for physicochemical characterization and pyrolysis. These biomass wastes were characterized (proximate and ultimate analysis, inorganic composition, calorific value, thermogravimetric analysis, etc.) to know their physical-chemical properties and to know if they are suitable for pyrolysis. The thermogravimetric analysis showed the thermal behavior of the leather and skin waste; with this information, the experimental pyrolysis variables in the oven were set (750 °C for conventional pyrolysis and 750 and 850 °C for flash pyrolysis). After conventional and flash pyrolysis of these biomass wastes, three products (bio-char, bio-oil and gas) were obtained which were suitably characterized to determine their possible application as biofuels or other uses.

Results

Proximate analysis of these bio-wastes showed low ash content (<5% and <1.5% in BCT and BCD) and substantial volatile matter content (≈69% in BCT). The ultimate analysis of BCT and BCD showed a high carbon content (≈50%) and a substantial nitrogen content (7.2% and ≈18% for BCT and BCD, respectively). The chemical characterization of the bio-wastes indicated that they are suitable for conversion in pyrolysis processes. The yield of pyrolysis products varies greatly depending on the experimental conditions. **Fig. 1** shows the performance results of bio-char, bio-oil and gas obtained after subjecting BCT to conventional and flash pyrolysis at 750 ºC (BCTCP750 and BCTFP750). The high gas yield is justified since, at high pyrolysis temperatures, there is a higher yield of gas due to the secondary cracking of volatiles (Guedes *et al.*, 2018). FP always generated the highest gas yield, higher the higher the temperature.

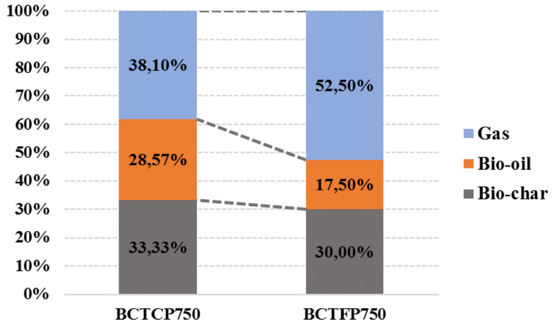

Fig. 1. Products yields in CP and FP of BCT at 750 °C

The chemical composition of the biochars (≈78% carbon content, ≈ 5% nitrogen content) indicated that they could be used as precursors of adsorbents or as additives for soil fertilization. They could also be used as fuels due to their calorific value (higher than 28 MJ/kg). The composition of pyrolysis gases showed great differences between those obtained by CP and those obtained by FP; the predominant gases were CO_2, CO, CH_4, and H_2, but in very different percentages depending on the type of pyrolysis, **Fig. 2.** The FP favored the increase of CO, CH_4 and H_2 and the decrease of CO_2, which makes it have a much higher calorific value. Conventional bio-oils presented a high oxygen content; however, flash bio-oils, with higher carbon content and much lower oxygen content, approach the characteristics of fossil fuels. Bio-oils showed an aromatic organic character. In flash bio-oils there is a clear predominance of PAHs, practically absent in conventional bio-oils. Given the nature of the bio-oils, it can be estimated that they will have great potential in the synthesis of organic compounds.

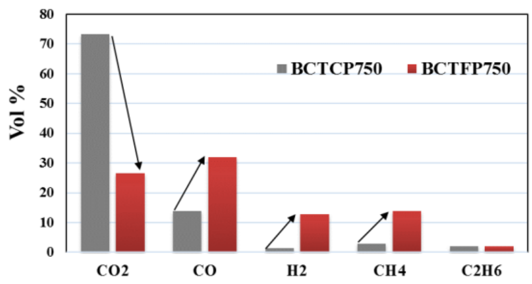

Fig. 2. *Gas composition obtained by CP and FP of BCT at 750°C*

Conclusions

The physical-chemical characterization of vegetable tanned leather waste and pre-tanned skin indicated that they are suitable materials for pyrolysis with the final objective of obtaining biofuels or biomaterials. The bio-chars properties make it suitable as a precursor to activated carbons, to fertilize soil or as fuel. Flash pyrolysis gases, with a higher fuel gas content and higher calorific value, can be used as bio-fuels. Bio-oils, given their organic nature, can be used for the production of chemical products. This study is presented as an alternative to burning or landfilling of vegetable tanned leather waste to obtain products with high added value and, all of this, framed in a more environmentally friendly scenario and following circular economy criteria

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