Evaluating the suitability of co-processing gardening residues and the organic fraction of municipal solid wastes via thermal and catalytic pyrolysis

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Solid biowastes (SBW) are organic residues from gardens and parks, food wastes from kitchens, organic municipal solid wastes and other comparable side streams from food processing plants that, traditionally, have been incinerated or discarded in landfills. However, such disposal methods present severe consequences for the environment related to land occupation, GHG emissions as well as soil and water pollution. Conversely, within the circular bioeconomy framework, these solid wastes are considered a renewable source of carbon, which can be transformed into biofuels, chemicals and energy; therefore, a sustainable and effective alternative route of conversion is required.

Pyrolysis is a thermal decomposition process, by which organic matter is carbonised at moderate temperatures of 400-700ºC under inter atmosphere into a solid char, a liquid fraction and other gases (CO, CO_2, H_2 and light hydrocarbons), whose yields greatly depend on the operating conditions (Cheng, 2020). In particular, fast-pyrolysis (high heating rates and very short residence times) has been the subject of extensive research as a means of processing organic wastes for energy recovery, and in particular for converting lignocellulosic biomass into valuable liquid (bio-oil). This bio-oil can be further used as precursor for biofuels and high-added value chemicals production. Nevertheless, pyrolysis bio-oils are complex mixtures of numerous oxygenated organic compounds with undesired properties (thermal instability, high viscosity, low heating value and low pH) that are far away from those required in combustion engines (Fermoso, 2017). Bio-oil properties can be upgraded by means of oxygen removal before the condensation of the pyrolysis vapours using heterogeneous catalysts integrated into the pyrolysis system, which is commonly known as catalytic fast-pyrolysis. ZSM-5 zeolite has been widely studied in catalytic pyrolysis of lignocellulosic biomass, given that it presents adequate acidic properties and pore structure, which reduces the formation of coke deposits and favours the production of aromatics (Hernando, 2016).

Processing SBW into valuable liquids via pyrolysis needs to face the challenge of understanding how the different components that constitute these heterogenous wastes can affect the produced pyrolysis fuel. Up to now, most studies have been focused on mixtures of plastics with lignocellulose and/or using microreactors that operate at very different conditions from realistic and scalable reactors (Li, 2020). In this context, the aim of this work was to evaluate the suitability of co-processing two biowastes, gardening pruning residues (GP) and food wastes (FW), mainly formed by peel and fruit seeds, by means of their pyrolysis in a fixed-bed reactor. The effect of the proportion of each biowaste in the mixture composition on the products yields and on the bio-oil properties was addressed. In addition, the incorporation of an acidic catalyst (nanocrystalline ZSM-5 zeolite) was investigated to assess how it can influence the yield and quality of the pyrolysis bio-oil from the pyrolysis of biowaste mixtures.

Thermal and catalytic pyrolysis experiments were carried out in a lab-scale downdraft fixed-bed reactor divided in two separated zones, the upper one for thermal devolatilisation of biowastes, and the lower one for the catalytic upgrading of pyrolysis vapors (in case of catalytic tests). The operating temperatures were set at 500ºC in the thermal zone, selected from the thermogravimetric analysis of both bioresidues, and 450ºC in the catalytic zone according to our previous findings (Hernando, 2016). Bio-oil samples were fully characterized through Karl Fischer titration, elemental analysis and GC-MS.

Figure 1(A) depicts how the production of bio-oil* (water-free basis) decreased with the share of FW in the feed mixture, which is caused by the lower volatile matter of the latter residue (70.5 wt%), in comparison with GP (82.5 wt%) and, in consequence, the remaining solid fraction (char) increased proportionally to the amount of FW. Regarding the water and gas fraction yields, they slightly increased with the amount of FW, being remarkable the opposite trends between CO and CO_2, indicating that FW share favored decarboxylation and dehydration deoxygenation routes of pyrolysis vapors. As a result, bio-oil* oxygen content progressively decreased with FW percentage of biowastes mixture, decreasing from 34 to 22.4 wt.% O in case of GP and FW, respectively.

The molecular composition of bio-oil* was determined by GC-MS. The equipment was previously calibrated to quantify, not only mass yields, but also the fraction of bio-oil that was really visible by this technique. It must be pointed that almost no information can be found in literature regarding bio-oil visible fraction, despite the high importance for the overall process assessment. Such visible fraction (about 40 wt.% in pure GP) decreased as the food waste proportion was higher, in accordance with the higher fixed-carbon determined for this waste by proximate analyzes. Figure 1(B) shows the GC-Ms results, grouped in families of compounds. Acids (AC) (mostly acetic acid), ketones and ethers (KET&ETH), sugars (SUG) and oxygenated aromatic compounds (O-AR) tended to decrease with the FW proportion; while furans (FUR) exhibited the opposite trend due to the emergence of isosorbide, which is the major final product from sorbitol dehydration (Delbecq, 2020). It should be noted the interest of this molecule, whose appearance was limited to those bio-oils produced from mixtures containing FW, as potential polymer precursor and with medicine applications. No apparent synergetic effects were found during the thermal experiments as the experimental yields of the mixtures properly matched with those expected according to the additive rule.

Experiments with n-ZSM-5 exhibited a significant increase in the gas (especially CO, CO_2 and light olefins) and water yields, at the expense of a reduction bio-oil* yield owing to the catalytic promotion of deoxygenation (dehydration, decarboxylation and decarbonylation) and cracking reactions. In this case, the bio-oil* oxygen content gradually decreased from 20.6 wt.% with pure GP up to a minimum value of 12.7 % with FW; the visible fraction determined by GC-MS was improved with the presence of the catalyst and its molecular composition changed drastically, observing a sharp decrease in acid compounds, ketones and ethers, furans and sugar compounds, these last even disappearing. On the contrary, aromatic hydrocarbons production was significantly promoted, this result attributed to Diels-Alder condensation reactions of furans (especially with larger shares of FW due to the presence of isosorbide) and light olefins (from catalytic cracking) promoted by the acidic zeolite. Of special interest is the promotion of xylenes (8-6 wt.% in bio-oil*) and other monoaromatics because of their commercial value in fuels formulation, chemicals production (e.g. solvents) and as plastics manufacturing.

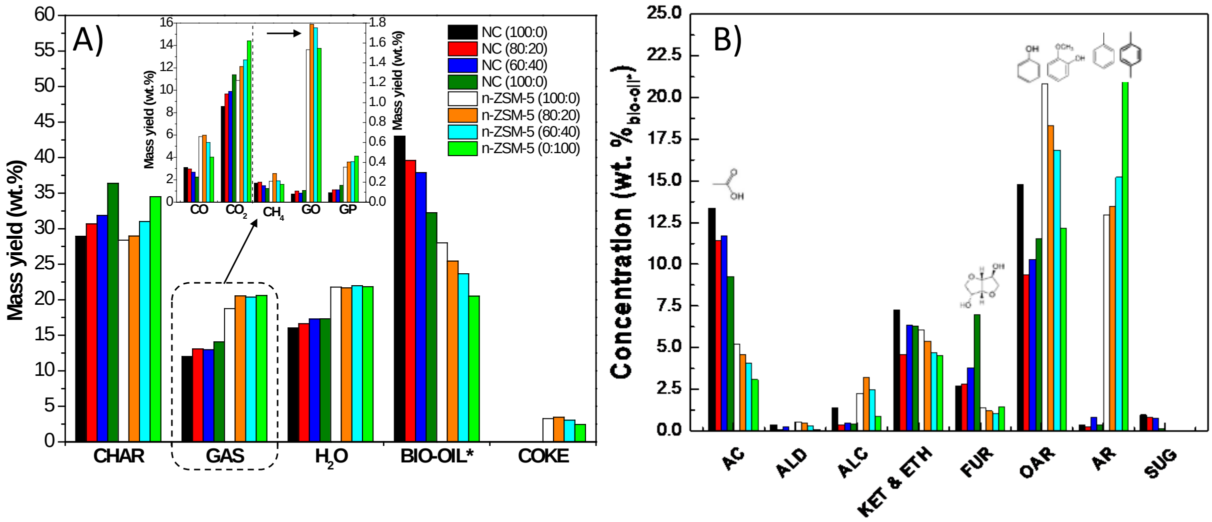

Figure 1. Mass yield of the different products (A), and molecular composition of bio-oil* (B) for the thermal (NC) and catalytic (n-ZSM-5) co-pyrolysis reactions of GP and FW mixtures. Numbers between brackets: weight percentage of GP and FW. Molecules drawn in B show those compounds detected in much higher proportions.

In conclusion, the co-processing of GP and FW biowastes by means of their catalytic pyrolysis at different proportions is a promising valorization route to avoid incineration or landfill disposal. The co-utilisation of FW with GP allows upgrading the pyrolysis bio-oil* by its deoxygenation, this effect being further boosted in presence of n-ZSM-5 zeolite. Moreover, by catalytic pyrolysis with such zeolite the formation of valuable aromatic hydrocarbons (especially xylenes) is highly promoted.

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