INFLUENCE OF CITRIC ACID LEACHING ON THE YIELD AND CHEMICAL COMPOSITION OF PYROLYSIS PRODUCTS FROM SUGARCANE RESIDUES

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The integration of fast pyrolysis (FP) and biomass pretreatment processes (e.g. demineralization, torrefaction, drying, etc.) is an effective way of controlling the composition of pyrolysis vapors to obtain bio-oils of higher quality. Accordingly, this study focusses on analysing the effects of leaching sugarcane trash (SCT) and sugarcane bagasse (SCB) with citric acid (CA) on the yields and chemical composition of FP products. The effectivity of CA as a leaching solution was compared to other solutions, commonly used with the same purpose (i.e. water or solutions of HCl, H_2SO_4). The efficiency of the leaching pretreatment was analyzed on the basis of the alkali and alkaline earth metals contents in the biomass. These inorganics affect the quality of the produced bio-oil, by catalysing depolymerisation and other degradation processes taking place during bio-oil storage. Approximately 100 g of biomass were demineralized at fixed conditions (25 °C and 1 h of leaching time). Pyrolysis trials were carried out in a lab scale fluidized bed reactor at 500 °C in inert gas atmosphere (N_2) with 1.5 kg pure silica sand as the bed material. The products obtained from FP were divided into liquids (i.e., organics and water), the char and the non-condensable gases. Results from the pyrolysis of SCT leached with CA or the reference acids (i.e., solutions of HCl, H_2SO_4) reveal higher yields (44-50 wt.%) of the organic fractions compared to those from untreated and water–leached (33 wt.%) feedstock, but lower yields of water and char (about 11 and 15 wt.%, respectively). Meanwhile, the yields of non-condensable gases (NCGs) stay below 25 wt.%. This fraction is composed mainly of carbon dioxide, carbon monoxide and small amounts of methane, hydrogen and C_2–C_3 hydrocarbons. The H_2 concentrations in NCGs are below 2 g kg^{-1} for all pyrolysed samples.

The characterization of the liquid fractions from CA–leached SCT and SCB revealed comparable or even better quality bio-oils than those obtained from leaching with water or solutions of HCl, H_2SO_4. The most important observations related to the effect of leaching with CA on the chemical composition of the liquid fraction are a significant increase of the sugars, as well as a decrease of carboxylic acids, ketones, furans and phenols with respect to the untreated biomasses. These results are close to those obtained with well-known leaching agents like H_2SO_4 and HCl, despite their strong acidic nature. Levoglucosan (1,6-anhydro-β-D-glucopyranose) is the major constituent of the liquid fraction obtained from untreated and leached SCT and SCB. It increased from 24.46% (untreated SCT) to the range of 59-70% of the normalized Total Ion Chromatogram (TIC) area (GC-MS analysis of the resulting bio-oil) when biomasses are treated with acids, including CA despite its weak acidic nature. Meanwhile, it reduces lignin derivatives in pyrolytic products and increases hydrocarbon yields that could decrease the oxygen content of the final product. Other major components of the pyrolysate are the acetic acid and 2-hydroxyacetaldehyde. The liquid fractions from the pyrolysis of CA–leached SCT and SCB have lower water mass fractions (0.175 and 0.193 kg kg^{-1}, respectively) and higher HHVs (13.68 and 13.80 MJ kg^{-1}) than reference leaching solutions (i.e. water or solutions of HCl, H_2SO_4). In addition, the total acid number (TAN) of bio-oils obtained with CA-leaching, showed the lowest acidity among all leached SCB samples. The yields and the quality of the liquid fractions obtained from the FP allow to conclude that CA is a technically viable option as an effective leaching agent to demineralize biomasses, such as SCT and SCB; aiming high yield of organic fraction (in particular, levoglucosan).