FATE OF LEAD AND OTHER HEAVY METALS DURING PYROLISIS OF LIGNOCELLULOSIC BIOMASS

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In latest years, lignocellulosic biomass is being considered widely as an alternative energy source to fossil fuels, both for its direct utilization and, mostly, for its upgrading to more valuable biofuels through several chemical and thermos-chemical processes, among which there is the pyrolysis process. To supply the rising demand for lignocellulosic biomass while avoiding iLUC (indirect land use change) related concerns, there is the need for growing biomass also on marginal lands and contaminated soils; this practice, however, could lead to the contamination of the biomass itself by different pollutants, such as heavy metals (HMs). The presence of heavy metals in the biomass structure could hinder both its processing through pyrolysis and the subsequent use of the potentially contaminated pyrolysis products.

The aim of this work is to evaluate the fate of HMs during contaminated lignocellulosic biomass pyrolysis both in terms of HMs distribution between pyrolysis products and HMs chemical transformations; moreover, it has to be considered that the presence of HMs can also modify the yields and properties of pyrolysis products. The experimental campaign tested a variety of combinations of pyrolysis temperatures (i.e. 450, 600 and 800 °C) and biomass pretreatments (i.e. untreated or doped with HMs salts) for a total of 9 pyrolysis tests. The employed biomass is a poplar (*Populus nigra*) that grew on contaminated land and retained naturally only a small amount of lead (20 ppm). To better trace the HMs during pyrolysis, the poplar biomass was doped via wet impregnation with two different lead salts, lead acetate and lead nitrate, to achieve a much higher concentration of lead (nominal concentration = 1000 ppm). Moreover, by using two different salts, information can be gained on the effect of the starting chemical form of HMs on their fate during pyrolysis. All the pyrolysis tests are conducted in a jacketed slow pyrolysis reactor [1] which allows for finely controlling the final temperature and heating rate, while also minimizing the elutriation of solid biomass/char particles toward the condensation section at the exit of the reactor. All the pyrolysis solid and liquid products, as well as the untreated and doped biomass, are characterized extensively in their physical-chemical properties such as elemental composition, moisture and ash content, pore content and pore size distribution. Among the various analytical techniques, the ICP-MS (Induced Coupled Plasma Mass spectroscopy) represents a key tool for the purpose of this work, since it detects HMs in the biomass and pyrolysis products at ppm levels, granting the possibility to track lead displacement during pyrolysis. Another analytical technique that, despite being applicable only to solid samples (biomass and char), can give useful information is the BCR sequential extraction. This technique consists of a sequence of extractions carried out with different solvents characterized by a growing degree of aggressivity: each solution removes some specific metal compounds so that useful hints on the speciation of HMs (and in particular of lead) can be gained from the ICP-MS analysis of the leachates and of the final solid residue.
In summary, the present work aims to shed light on the basics of heavy metals beahviours and transfer mechanisms during the pyrolysis of HMs contaminated lignocellulosic biomass. Moreover, the possible effects of HMs on pyrolysis products yield and properties are also considered.

[1] Ragucci, R., Giudicianni, P., & Cavaliere, A. (2013). Cellulose slow pyrolysis products in a pressurized steam flow reactor. *Fuel*, *107*, 122-130.