MINERALS-CARBON INTERACTION DURING BIOMASS PYROLYSIS: IMPLICATIONS TO BIOCHAR CARBON SEQUESTRATION AND BIOENERGY

Ling Zhao, School of Environmental Science and Engineering, Shanghai Jiao Tong University, China
wszhaoling@sjtu.edu.cn
Ondřej Mašek, School of Geosciences, University of Edinburgh, Kings Buildings, Edinburgh, UK

Key Words: Inherent minerals, Doped minerals, Thermochemical decomposition, Surface oxygen-containing functional groups, Small molecule compounds.

Biomass carbon could be sequestrated in form of biochar, an aromatized carbon structure produced by pyrolysis. Minerals are reactive constituents, which could transform species and interact with organic fractions during pyrolysis, significantly affecting the products, biochar and bio-oil. This study reviewed researches by authors recent years related to removing inherent minerals from biomass and doping alkaline and alkaline earth metal (K, Na, Ca and Mg), as well as phosphorus (P) into biomass to understand their influences on carbon (C) retention and C stability in biochar during pyrolysis; How this minerals-doping induces the alteration of primary products in bio-oil? Some conclusions have been drawn by other researchers. It is of great importance that this should be analyzed synthetically with C sequestration in biochar. Some of our key conclusions are as follows:

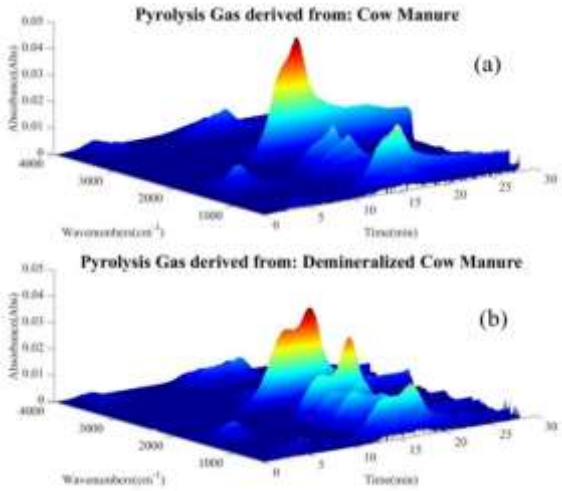

Figure 1 – TG-FTIR curves of the pyrolysis gas for the original (a) and demineralized (b) cow manure

The presence of all types of minerals could catalyze the thermal decomposition of C lowering its initial decomposition temperature due to they could decrease the activation energy and promote the cleavage of hydrogen bond, glycosidic linkage [1, 2]. Removal of inherent minerals reduced emissions of low molecular weight organic compounds (CO_2, CH_4, C_3H_6O, etc.), and promoted more C retention (3.5-30.1%) in biochar. The ordered structure and stability of biochar-C were increased.

Significant influences of inherent minerals on the pyrolytic bio-gas appeared from the beginning of pyrolysis to the end, resulting in more release of C as aromatized molecules (Figure 1a). More O-containing substances (wavenumber around 1000 cm^{-1}) released as large molecular substances for the demineralized cow manure (Figure 1b), which was consistent with the result that less O-containing functional groups retained on the demineralized biochar surface.

It was attractive to study the influences of each mineral on the pyrolysis process concerning C behavior. When we tried to dope common minerals into the biomass, it was found surprisingly that these added substances induced a significant increase of C retention. Doping $MgCl_2$ and $CaCl_2$ at dose of 20% (w/w) increased the C retention in biochar after pyrolysis by 31.5% and 29.1%, respectively. Mašek et al. also proved K doping increases biochar C sequestration potential by 45% [3]. Mg and Ca could form surface compounds (MgO, $MgO_3(CO_3)_2$, $CaCO_3$) as physical barriers and adsorbent to resist volatilization of small molecule compounds. Similarly, adding phosphate with main component $Ca(H_2PO_4)_2$ would react with biomass-C to form C–O–PO_3 or C–P, leading to greater C retention.

This study elaborated the different interactions of inherent and doped minerals with C in pyrolysis and suggested a potential strategy of regulating biochar-C sequestration by minerals-doping to build a physical barrier and chemical adsorbing layer.

[1] Nan H-Y, Yang F, Zhao L, Mašek O, Cao X-D, Xiao Z-Y. Interaction of inherent minerals with carbon during biomass pyrolysis weakens biochar carbon sequestration potential. ACS Sustain Chem. Eng. 2019;7:1591–1599.

[2] Safar M, Lin BJ, Chen WH, Langauer D, Chang JS, Raclavska H, et al. Catalytic effects of potassium on biomass pyrolysis, combustion and torrefaction. Appl Energy 2019;235:346–355.

Mašek O, Buss W, Brownsort P, Rovere M, Tagliaferro A, Zhao L. Potassium doping increases biochar carbon sequestration potential by 45%, facilitating decoupling of carbon sequestration from soil improvement. Scientific Reports 2019;9:5514