Journal of Analytical and Applied Pyrolysis 122 (2016) 160–168

Contents lists available at ScienceDirect

Journal of Analytical and Applied Pyrolysis

journal homepage: www.elsevier.com/locate/jaap

Comparison of chemical and physical indices of thermal stability of biochars from different biomass by analytical pyrolysis and thermogravimetry

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ARTICLE INFO

Article history:
Received 5 July 2016
Received in revised form
27 September 2016
Accepted 3 October 2016
Available online 6 October 2016

Keywords:
Biochar
TGA
Py-GC–MS
Lignocelluosic biomass
Algae
Manure

ABSTRACT

A set of 22 biochars from different feedstock and pyrolysis conditions were produced using the same fixed bed pyrolysis reactor. Original substrates included softwood, hardwood and herbaceous biomass (pine, bark, cornstalk, miscanthus, poplar, switchgrass), microalgae (*Desmodesmus communis,* spirulina), wastes and residues (chicken manure, mushroom litter, olive pomace). Biochars were characterized by ultimate and proximate analysis and by analytical pyrolysis (Py-GC–MS). Parameters characteristics of the thermally labile fraction were obtained from thermogravimetric analysis (volatile matter, Tmax) and Py-GC–MS (molecular ratios). Volatile matter of biochars from a cornstalk thermosequence was strongly correlated with H/C ratios, while Tmax could be measured only for poorly carbonized biomass. Pyrolysis yields from Py-GC–MS were correlated with volatile matter. The molecular ratio toluene/naphthalene was governed by the extent of carbonisation and the presence of proteins in the original substrate. The 1-methylnaphthalene/naphthalene ratio was a general index of the thermal stability of biochar less influenced by the composition of the original feedstock. The indole/1-methylnaphthalene ratio was correlated with N/C ratio, while methylthiophene and benzothiophene were detected in the pyrolysate of sulphur-rich biochars from manure and litter. A coherent set of indices were obtained from TGA and Py-GC–MS for biochars with H/C > 0.3. In addition, Py-GC–MS provided information on the origin of biochar.

1. Introduction

Biochar is the porous material directly produced by pyrolysis of biomass or as a secondary by-product that must be economically valorized to increase the attractiveness of thermochemical processes in energetic conversion of biomass. The interest in biochar is for economic and environmental sustainable applications as soil amendment and fertilizer [1,2], sink of carbon [3,4] or filter/adsorbent material [5–7].

The use of biochar requires a deep chemical-physical characterization in order to evaluate its environmental behavior and stability [8].

Many authors have investigated the characteristics of biochars produced at different temperatures and from several types of biomass [9–13]. For a given biomass component the thermal conditions of pyrolysis are important to determine the type and the amount of products [14]. The crystalline structure of biochar is developed during pyrolysis from small quantities of aromatic units randomly arranged in an amorphous matrix to a highly ordered graphitic structure which is resistant to degradation [15].

The thermally labile fraction given by the incomplete carbonization of the biomass is related to the matter that could be removed through a complete pyrolytic process. This volatile matter constitutes the less stable fraction of biochar made up of heteroatoms and functional groups that can contribute to the reactivity of biochar [16].

Thermogravimetric analysis (TGA) provides quantitative information on volatile matter (VM), which is a useful index to evaluating biochar stability [17,18]. However, a qualitative-support analysis is required to know the chemical composition of VM to better understand the role of labile fraction on biochar properties [17].

Analytical pyrolysis (Py-GC–MS) is a reliable method to gather information on the molecular structure of complex organic mate-

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http://dx.doi.org/10.1016/j.jaap.2016.10.003
0165-2370/

rials which was applied to the characterization of natural black carbon and charcoal [17,19–25]. By analysing the composition of pyrolysates evolved from a variety of charred biomass samples, Kaal et al. evidenced benzene, toluene, benzonitrile, benzofuran and naphthalene as general markers of the carbonisation intensity [20–23]. On a semi-quantitative base, their ratios (e.g. toluene/benzene, naphthalene/toluene, benzofuran/naphthalene) were proposed as molecular indicator (or proxies) of the charring degree. The compound ratios were intended to compare products with/without methyl groups, oxygen, polyaromatic rings on the ground that alkylated, oxygenated and monoaromatic structures become less important over dealkylated polyaromatic regions as carbonisation proceeds [19,23].

The validity of these compound ratios as molecular proxies of thermal stability was supported by studies performed on biochar samples obtained from the same feedstock and pyrolysis apparatus under different pyrolysis conditions (thermosequence) showing good correlations with the atomic hydrogen to carbon ratio (H/C) [22,23,25]. However, when these ratios were applied to biochar samples from different substrates and pyrolysis reactors their relationship with the carbonization degree resulted weaker [19]. The role played by the feedstock to these molecular proxies remains fairly unexplored. The reliability of the compound ratio approach when comparing biochars produced from different substrates under the same pyrolysis conditions needs to be evaluated. Moreover, the results arising from TGA and Py-GC–MS were seldom compared in the literature [17]. In particular, the concept that Py-GC–MS is capable to provide molecular information on VM was not tested on a large set of biochar samples.

The aim of this study was to investigate cornstalk biochars obtained at different pyrolysis conditions and biochars obtained from different feedstock pyrolysed under the same conditions in order to investigate both the effect of synthesis conditions and feedstock source on the parameters of thermal stability derived from TGA and Py-GC–MS analysis.

2. Experimental

2.1. Biomass feedstock

In this study 11 different feedstock divided in 4 groups were investigated (the short name utilized in this study is reported in brackets): i) woody biomass: Pine sawdust (Pine), Poplar chips (Poplar) and hardwood bark (Bark); ii) herbaceous biomass: Corn stalks (Corn), *Panicum virgatum* (Switchgrass) and *Mischantus* (Mischantus); iii) 2 Algal biomass: *Desmodesmus communis* (*D. communis*) and *Arthrospira platensis* (Spirulina); iv) agro industrial residual biomass represented by mushroom litter (Litter), olive pomace (Olive) and chicken manure (Manure). All feedstock are provided by Interdepartmental Center for Research in Environmental Science of University of Bologna.

2.2. Biomass pyrolysis

Biomass was processed in a laboratory-scale quartz tube fixed bed reactor following a published procedure [25]. Approximately, 3.0 ± 0.1 g of biomass was pyrolysed under N_2 flow of 1500 $cm^3\ min^{-1}$, at a specified temperature and time, here indicated as °C*min (for instance, biochar 500*20 corresponds to biochar obtained from pyrolysis at 500 °C for 20 min).

In addition, cornstalk biochars at different temperature (T°C) and time (min) conditions (400*1; 450*5; 450*20; 500*1; 500*20; 550*5; 550*20; 650*5; 650*10; 650*20; 700*1) were obtained.

2.3. Ultimate and proximate analysis

The determination of C, H, N and S was performed using the elemental analyzer Flash 2000 series (Thermo Scientific). A quantity of 4–5 mg of biomass or biochar was introduced into a tin crucible mixed with 10 mg of vanadium pentoxide (Thermo Scientific) that is necessary for the best identification of sulphur. The oxygen content was calculated by mass difference: $O = 100\text{-}\Sigma_{CHNS+ash}$.

Proximate analysis of biomass and biochar was carried out according to ASTM D7582 method with slight modification. The method determines relative moisture (M), volatiles (VM), fixed carbon (FC) content during different condition steps of analysis. Ash content was calculated by difference of all these fractions. Before analysis, samples were crushed in an agate mortar to a fine powder.

For each analysis about 3–5 mg of sample was introduced in aluminum oxide crucible (volume of 70 μL) and covered with the specific lid. Then the crucible is inserted in the thermogravimetric analyzer (Mettler Toledo TGA/SDTA 851e).

2.4. Py-GC–MS

Py-GC–MS analyses were performed using an electrically heated platinum filament CDS 5250 pyroprobe interfaced to a Varian 3400 GC equipped with a GC column (HP-5-MS; Agilent Technologies 30 m × 0.25 mm, 0.25 μm,) and a mass spectrometer Saturn 2000 ion trap, Varian Instruments. Sample were pyrolysed at 900 °C (set temperature) for 100 s with helium as carrier gas. Further Py-GC–MS conditions used were reported elsewhere [25]. Internal standard (1 μL of 1000 mgL^{-1} *iso*-eugenol solution in acetonitrile) was added to the sample for quantitative analysis. However, yields calculated by internal calibration with isoeugenol presented a high variability due to the variability of the internal standard peak area (RSD 56%). This variability was be ascribed to greater absorption of internal standard into the highly charred biochars. Therefore, the quantity of evolved pyrolysis products (Py-yield) was calculated by dividing the GC peak area by sample amount (area/μg).

A set of 32 pyrolysis products were quantified indicative of *polysaccharides* (hydroxyacetone,2,5-dimethyl-furan, furaldehyde, furfuryl alcohol, 2-cyclopentanedione, 3-hydroxy-2-methyl-cyclopentenone, 5-hydroxymethyl-2-furaldehyde, levoglucosan); *lignin* (guaiacol, 4-ethyl phenol, cathecol, 4-vinyl phenol,4-methyl guaiacol, 4-vinyl guaiacol, syringol, 4-methyl syringol, *trans*-isoeugenol, 4-vinyl syringol, 4-propenyl syringol); *lignin/protein* (phenol, 4-methyl phenol*); protein* (indole, 2-methylthiophene, benzothiophene); *charred biomass* (benzene, pyrrole, toluene, ethyl benzene, m/p-xylene, benzonitrile, benzofuran, methyl benzofurans (three isomers), naphthalene, 1-methylnaphthalene, dibenzofuran.

3. Results and discussion

3.1. Biomass TGA

The results of proximate and ultimate analysis of original biomass samples are presented in Table 1. The observed range of values are indicative of the different nature of the selected substrates that included hard/softwood and herbaceous lignocellulosic biomass, protein-rich microalgae, mushroom litter, olive pomace and chicken manure.

The H/C ratios ranged from 1.5 to 1.8, while O/C values from 0.42 of spirulina to 1.1 of litter. The most important feature from elemental analysis was the relative high content of N and S in algal biomass (*D. communis*, spirulina), mushroom litter and chicken manure which was associated to the presence of proteinaceous materials.