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Editorial

Biomass Chars: Elaboration, Characterization and Applications

Mejdi Jeguirim * and Lionel Limousy

Institut de Sciences des Matériaux de Mulhouse, 15 rue Jean Starcky, 68057 Mulhouse CEDEX, France; lionel.limousy@uha.fr

* Correspondence: mejdi.jeguirim@uha.fr

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1. Introduction

This book contains the successful invited submissions [1–15] to a Special Issue of *Energies* on the subject area of "Biomass Chars: Elaboration, Characterization, and Applications". The invited editors have decided to focus the Special Issue on the specific topic of biomass transformation and use. In fact, biomass can be converted to energy, biofuels, and bioproducts, via thermochemical conversion processes such as combustion, pyrolysis, and gasification. Combustion technology is most widely applied on an industrial scale. However, biomass gasification and pyrolysis processes are still in the research and development stage. The major products from these processes are syngas, bio-oil, and char (called also biochar for agronomic applications). Among these products, biomass chars have been receiving increasing attention for different applications such as gasification, co-combustion, catalyst or adsorbent precursors, soil amendment, carbon fuel cells, and supercapacitors.

This Special Issue provides an overview for biomass chars production methods (pyrolysis, hydrothermal carbonization, etc.), the characterization techniques (scanning electronic microscopy, X-ray fluorescence, nitrogen adsorption, Raman spectroscopy, nuclear magnetic resonance spectroscopy, X-ray photoelectron spectroscopy, temperature programmed desorption, mass spectrometry, etc.), their properties and their suitable recovery processes.

Topics of interest for the call included, but were not limited to the production of biochar for:

- Biofuel production
- Soil amendment
- Carbon sequestration
- Heterogeneous catalysis
- Syngas production
- Pollutant adsorption

Responses to our call had the following statistics:

- Submissions (25);
- Publications (15);
- Rejections (10);
- Article types: research article (15).

The authors' geographical distribution (published papers) is:

- China (4)
- USA (2)
- Canada (2)

- France (2)
- Italy (1)
- Spain (1)
- Korea (1)
- Lithuania (1)
- Tunisia (1)

Published submissions are related to biochar elaboration, characterization and application. The different papers show the diversity of research conducted recently on biochars. Agriculture, biofuel, adsorbent, catalyst, these versatile materials can be used for various applications. Recent developments have shown that the return to soil is a promising issue since the carbon balance is negative due to the carbon sequestration. Other benefits are described below, new developments are still under progress, encouraging the organization of a second edition of this special issue.

2. Short Review of the Contributions in This Issue

Concerns about climate change and food productivity have spurred interest in biochar, a form of charred organic material typically used in agriculture to improve soil productivity and as a means of carbon sequestration. Zambon et al. [1] have shown an innovative approach in agriculture by the use of agro-forestry waste for the production of soil fertilizers for agricultural purposes and as a source of energy. A common agricultural practice is to burn crop residues in the field to produce ashes that can be used as soil fertilizers. This approach is able to supply plants with certain nutrients, such as Ca, K, Mg, Na, B, S, and Mo. However, the low concentration of N and P in the ashes, together with the occasional presence of heavy metals (Ni, Pb, Cd, Se, Al, etc.), has a negative effect on soil and, therefore, crop productivity. Their work describes the opportunity to create an innovative supply chain from agricultural waste biomass. Olive (*Olea europaea*) and hazelnut (*Corylus avellana*) pruning residues represent a major component of biomass waste in the area of Viterbo (Italy). In this study, the authors have evaluated the production of biochar from these residues. Furthermore, a physicochemical characterization of the produced biochar was performed to assess the quality of the two biochars according to the standards of the European Biochar Certificate (EBC). The results of this study indicate possible cost-effective production of high-quality biochar from olive and hazelnut biomass residues.

Characteristics of biochar vary with pyrolysis temperature. Chloropicrin (CP) is an effective fumigant for controlling soil-borne pests. Liu et al. [2] have investigated the characteristics of biochars prepared at 300°C, 500°C, and 700 °C by *Michelia alba* (*Magnolia denudata*) wood and evaluated their capacity to adsorb CP. The study also determined the potential influence of biochar, which was added to sterilized and unsterilized soils at rates of 0%, 1%, 5%, and 100%, on CP degradation. The specific surface area, pore volume, and micropores increased considerably with an increase in the pyrolytic temperature. The adsorption rate of biochar for CP increased with increasing pyrolytic temperature. The maximum adsorption amounts of CP were similar for the three biochars. Next, this study examined the degradation ability of the biochar for CP. The degradation rate constant (k) of CP increased when biochar was added to the soil, and k increased with increased amendment rate and pyrolysis temperature. The results indicate that biochar can accelerate CP degradation in soil. The findings of this study will be instructive in using biochar as a new fertilizer in fumigating soil with CP.

Biochar is increasingly applied in agriculture; however, due to its adsorption and degradation properties, biochar may also affect the efficacy of fumigant in amended soil. In their research, Fang et al. [3] have intended to study the effects of two types of biochars (BC-1 and BC-2) on the efficacy and emission of methyl isothiocyanate (MITC) in biochar amendment soil. Both types of biochars can significantly reduce MITC emission losses, but, at the same time, decrease the concentration of MITC in the soil. The efficacy of MITC for controlling soil-borne pests (*Meloidogyne* spp., *Fusarium spp. Phytophthora* spp., *Abutilon theophrasti*, and *Digitaria sanguinalis*) was reduced when the biochar

(BC-1 and BC-2) was applied at a rate higher than 1% and 0.5% (on a weight basis) (on a weight basis), respectively. However, increased doses of dazomet (DZ) were able to offset decreases in the efficacy of MITC in soils amended with biochars. Biochars with strong adsorption capacity (such as BC-1) substantially reduced the MITC degradation rate by 6.2 times, and increased the MITC degradation rate by 4.1 times following amendment with biochar with high degradability (e.g., BC-2), compared to soil without biochar amendment. This was attributed to the adsorption and degradation of biochar that reduces MITC emission losses and pest control.

Long and Boyette [4] have chosen Yellow poplar (*Liriodendron tulipifera*) as the woody biomass for the production of charcoal for use in a liquid fuel slurry. Charcoal produced from this biomass resulted in a highly porous structure similar to the parent material. Micronized particles were produced from this charcoal using a multi-step milling process and verified using a scanning electron microscope and laser diffraction system. Charcoal particles greater than 50 μm exhibited long needle shapes much like the parent biomass while particles less than 50 μm were produced with aspect ratios closer to unity. Laser diffraction measurements indicated D10, D50, and D90 values of 4.446, 15.83, and 39.69 μm, respectively. Moisture content, ash content, absolute density, and energy content values were also measured for the charcoal particles produced. Calculated volumetric energy density values for the charcoal particles exceeded the no. 2 diesel fuel that would be displaced in a liquid fuel slurry.

Biomass pyrolysis and the valorization of co-products (biochar, bio-oil, syngas) could be a sustainable management solution for agricultural and forest residues. Depending on its properties, biochar amended to soil could improve fertility. Moreover, biochar is expected to mitigate climate change by reducing soil greenhouse gas emissions, if its C/N ratio is lower than 30, and sequestrating carbon if its O/C and H/C ratios are lower than 0.2 and 0.7, respectively. However, the yield and properties of biochar are influenced by biomass feedstock and pyrolysis operating parameters. The objective of the research study carried by Brassard et al. [5] was to validate an approach based on the response surface methodology, to identify the optimal pyrolysis operating parameters (temperature, solid residence time, and carrier gas flowrate), in order to produce engineered biochars for carbon sequestration. The pyrolysis of forest residues, switchgrass, and the solid fraction of pig manure, was carried out in a vertical auger reactor following a Box–Behnken design, in order to develop response surface models. The optimal pyrolysis operating parameters were estimated to obtain biochar with the lowest H/C and O/C ratios. Validation pyrolysis experiments confirmed that the selected approach can be used to accurately predict the optimal operating parameters for producing biochar with the desired properties to sequester carbon.

In the work of Fuente-Hernández et al. [6], the liquid phase hydrogenation of furfural has been studied using a biochar-supported platinum catalyst in a batch reactor. Reactions were performed between 170 °C and 320 °C, using 3 wt % and 5 wt % of Pt supported on a maple-based biochar under hydrogen pressure varying from 500 psi to 1500 psi for reaction times between 1 h and 6 h in various solvents. Under all reactive conditions, furfural conversion was significant, whilst under specific conditions furfuryl alcohol (FA) was obtained in most cases as the main product, showing a selectivity around 80%. Other products as methylfuran (MF), furan, and trace of tetrahydrofuran (THF) were detected. Results showed that the most efficient reaction conditions involved a 3% Pt load on biochar and operations for 2 h at 210 °C and 1500 psi using toluene as solvent. When used repetitively, the catalyst showed deactivation, although only a slight variation in selectivity toward FA at the optimal experimental conditions was observed.

Investigation into clean energies has been focused on finding an alternative to fossil fuels in order to reduce global warming while at the same time satisfying the world's energy needs. Biomass gasification is seen as a promising thermochemical conversion technology, as it allows useful gaseous products to be obtained from low-energy-density solid fuels. Air–steam mixtures are the most commonly used gasification agents. The gasification performances of several biomass samples and their mixtures were compared by González-Vázquez et al. [7] in the present work. One softwood (pine) and one hardwood (chestnut), their torrefied counterparts, and other Spanish-based biomass wastes such as almond shells, olive stones, grape and olive pomaces, or cocoa shells were tested, and their behaviors at several different stoichiometric ratios (SR) and steam/air ratios (S/A) were compared. The optimum SR was found to be in the 0.2–0.3 range for S/A = 75/25. At these conditions a syngas stream with 35% of H_2 + CO and a gas yield of 2 L gas/g fuel were obtained, which represents a cold-gas efficiency of almost 50%. The torrefaction process does not significantly affect the quality of the product syngas. Some of the obtained chars were analyzed to assess their use as precursors for catalysts, combustion fuel, or for agricultural purposes such as soil amendment.

Waste residues produced by agricultural and forestry industries can generate energy and are regarded as a promising source of sustainable fuels. Pyrolysis, where waste biomass is heated under low-oxygen conditions, has recently attracted attention as a means to add value to these residues. The material is carbonized and yields a solid product known as biochar. In the study presented by Yang et al. [8], eight types of biomass were evaluated for their suitability as raw material to produce biochar. Material was pyrolyzed at either 350 °C or 500 °C and changes in ash content, volatile solids, fixed carbon, higher heating value (HHV), and yield were assessed. For pyrolysis at 350 °C, significant correlations ($p < 0.01$) between the biochars' ash and fixed carbon content and their HHVs were observed. Masson pine wood and Chinese fir wood biochars pyrolyzed at 350 °C and the bamboo sawdust biochar pyrolyzed at 500 °C were suitable for direct use in fuel applications, as reflected by their higher HHVs, higher energy density, greater fixed carbon, and lower ash contents. Rice straw was a poor substrate as the resultant biochar contained less than 60% fixed carbon and a relatively low HHV. Of the suitable residues, carbonization via pyrolysis is a promising technology to add value to pecan shells and Miscanthus.

Material dielectric properties are important for understanding their response to microwaves. Carbonaceous materials are considered good microwave absorbers and can be mixed with dry biomasses, which are otherwise low-loss materials, to improve the heating efficiency of biomass feedstocks. In the work of Ellison et al. [9], dielectric properties of pulverized biomass and biochar mixtures were presented from 0.5 GHz to 20 GHz at room temperature. An open-ended coaxial-line dielectric probe and vector network analyzer were used to measure dielectric constant and dielectric loss factor. Results have shown a quadratic increase of dielectric constant and dielectric loss with increasing biochar content. In measurements on biochar, a strong dielectric relaxation was observed at 8 GHz as indicated by a peak in dielectric loss factor at that frequency. Biochar was found to be a good microwave absorber and mixtures of biomass and biochar can be utilized to increase microwave heating rates for high temperature microwave processing of biomass feedstocks. These data can be utilized for design, scale-up, and simulation of microwave heating processes of biomass, biochar, and their mixtures.

Wood pellets are a form of solid biomass energy and a renewable energy source. In 2015, the new and renewable energy (NRE) portion of wood pellets was 4.6% of the total primary energy in Korea. Wood pellets account for 6.2% of renewable energy consumption in Korea, the equivalent of 824,000 TOE (ton of oil equivalent, 10 million kcal). The burning phases of a wood pellet can be classified into three modes: (1) gasification; (2) flame burning; and (3) charcoal burning. At each wood pellet burning mode, the volume and weight of the burning wood pellet can drastically change, these parameters are important to understand the wood pellet burning mechanism. Kang et al. [10] have developed a new method for measuring the volume of a burning wood pellet that involves no contact. To measure the volume of a wood pellet, they have taken pictures of the wood pellet in each burning mode. The volume of a burning wood pellet was calculated by image processing. The difference between the calculation method using image processing and the direct measurement of a burning wood pellet in gasification mode was less than 8.8%. In gasification mode, mass reduction of the wood pellet is 37% and volume reduction of the wood pellet is 7%. Whereas in charcoal burning mode, mass reduction of the wood pellet was 10% and volume reduction of the wood pellet was 41%. By measuring volume using image processing, continuous and non-interruptive volume measurements for various solid fuels were possible and could provide more detailed information for CFD (computational fluid dynamics) analysis.

Annually, the olive oil industry generates a significant amount of by-products, such as olive pomace, olive husks, tree prunings, leaves, pits, and branches. Therefore, the recovery of these residues has become a major challenge in Mediterranean countries. The utilization of olive industry residues has received much attention in recent years, especially for energy purposes. Accordingly, the primary experimental study carried out by Tamošiūnas et al. [11] aimed at investigating the potential of olive biomass waste for energy recovery in terms of synthesis gas (or syngas) production using the thermal arc plasma gasification method. The olive charcoal made from the exhausted olive solid waste (olive pomace) was chosen as a reference material for primary experiments with known composition from the performed proximate and ultimate analysis. The experiments were carried out at various operational parameters: raw biomass and water vapor flow rates and the plasma generator power. The producer gas principally involved CO, H_2, and CO_2 with the highest concentrations of 41.17, 13.06, and 13.48%, respectively. The produced synthesis gas has a lower heating value of 6.09 MJ/nm^3 at the H_2O/C ratio of 3.15 and the plasma torch had a power of 52.2 kW.

Solid char is a product of biomass pyrolysis. It contains a high proportion of carbon, and lower contents of H, O, and minerals. This char can have different valorization pathways such as combustion for heat and power, gasification for syngas production, activation for adsorption applications, or use as a soil amendment. The optimal recovery pathway of the char depends highly on its physical and chemical characteristics. In the study presented by Guizani et al. [12], different chars were prepared from beech wood particles under various pyrolysis operating conditions in an entrained flow reactor (500–1400 °C). Their structural, morphological, surface chemistry properties, as well as their chemical compositions, were determined using different analytical techniques, including elementary analysis, scanning electronic microscopy (SEM) coupled with an energy dispersive X-ray spectrometer (EDX), Fourier transform infrared spectroscopy (FTIR), and Raman spectroscopy. The biomass char reactivity was evaluated in air using thermogravimetric analysis (TGA). The yield, chemical composition, surface chemistry, structure, morphology, and reactivity of the chars were highly affected by the pyrolysis temperature. In addition, some of these properties related to the char structure and chemical composition were found to be correlated to the char reactivity.

Zhao et al. [13] have studied the structure and physicochemical properties of biochar derived from apple tree branches (ATBs), whose valorization is crucial for the sustainable development of the apple industry. ATBs were collected from apple orchards located on the Weibei upland of the Loess Plateau and pyrolyzed at 300, 400, 500, and 600 °C (BC300, BC400, BC500, and BC600), respectively. Different analytical techniques were used for the characterization of the different biochars. In particular, proximate and element analyses were performed. Furthermore, the morphological, and textural properties were investigated using scanning electron microscopy (SEM), Fourier-transform infrared (FTIR) spectroscopy, Boehm titration, and nitrogen manometry. In addition, the thermal stability of biochars was also studied by thermogravimetric analysis. The results indicated that the increasing temperature increased the content of fixed carbon (C), the C content and inorganic minerals (K, P, Fe, Zn, Ca, Mg), while the yield, the content of volatile matter (VM), O and H, cation exchange capacity, and the ratios of O/C and H/C decreased. Comparison between the different samples has shown that highest pH and ash content were observed in BC500. The number of acidic functional groups decreased as a function of pyrolysis temperature, especially for the carboxylic functional groups. In contrast, a reverse trend was found for the basic functional groups. At a higher temperature, the Brunauer–Emmett–Teller (BET) surface area and pore volume are higher mostly due to the increase of the micropore surface area and micropore volume. In addition, the thermal stability of biochars also increased with the increasing temperature. Hence, pyrolysis temperature had a strong effect on biochar properties, and therefore biochars could be produced by changing the pyrolysis temperature in order to better meet their applications.

Wanassi et al. [14] have investigated the use of phenolic resin and waste cotton fiber as green precursors for the successful synthesis using a soft template approach of a composite carbon with carbon nanofibers embedded in a porous carbon network with ordered pore structure. The optimal composite carbon (PhR/NC-1), exhibited a specific surface area of 394 $m^2 \cdot g^{-1}$ with the existence of both microporosity and mesoporosity. PhR/NC-1 carbon was evaluated as an adsorbent of Alizarin Red S (ARS) dye in batch solution. Various operating conditions were examined and the maximum adsorption capacity of 104 $mg \cdot g^{-1}$ was achieved under the following conditions, i.e., T = 25 °C, pH = 3, contact time = 1440 min. The adsorption and desorption heat was assessed by flow micro-calorimetry (FMC), and the presence of both exothermic and endothermic peaks with different intensities were shown, indicating a partially reversible nature of ARS adsorption. A pseudo-second-order model proved to be the most suitable kinetic model to describe the ARS adsorption according to the linear regression factor. In addition, the best isotherm equilibrium has been achieved with a Freundlich model. The results have shown that the eco-friendly composite carbon derived from green phenolic resin mixed with waste cotton fibers improved the removal of ARS dye from textile effluents.

The treatment of NO_x from automotive gas exhaust has been widely studied, however the presence of low concentrations of NO_x in confined areas is still under investigation. As an example, the concentration of NO_2 can approximate 0.15 ppmv inside vehicles when people are driving on highways. This interior pollution becomes an environmental problem and a health problem. In the work carried out by Ghouma et al. [14], the abatement of NO_2 immission was studied at room temperature. Three activated carbons (ACs) prepared by physical (CO_2 or H_2O) or chemical activation (H_3PO_4) were tested as adsorbents. The novelty of this work consisted in studying the adsorption of NO2 at low concentrations that approach real life emission concentrations and was experimentally realizable. The ACs presented different structural and textural properties, as well as functional surface groups, which induced different affinities with NO_2. The AC prepared using water vapor activation presented the best adsorption capacity, which may originate from a more basic surface. The presence of a mesoporosity may also influence the diffusion of NO_2 inside the carbon matrix. The high reduction activity of the AC prepared from H_3PO_4 activation was explained by the important concentration of acidic groups on its surface.

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