Characterization of biochar samples produced by pyrolysis of agricultural and woody biomass

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Due to theirpotential applications in energy storage, catalysis, adsorption,and gas separation and storage,carbon materials areconsidered as ideal candidates for resolving many of thepractical issues encountered (e.g., environmental pollution andglobal warming) (Liu *et al*, 2015).Lignocellulosic biomass obtainable from different agricultural or woody residues and wastes is a naturally abundant resource, almost in every country availablelocally that has great potential as a raw material for synthesizing various carbon-based functional materials.Conversion of biomass by pyrolysis, a thermochemical process performed in an absence of air oxygen, is a typical process for production of biochar (biocoal) - a carbon-rich biomaterial. Properties of biochar allow its application as an energy carrier, gasification feedstock, adsorbent, catalyst support or for soil amendment. More importantly, the large-scale application of biochar-based functional materials is considered to be a sustainable process, because anthropogenic CO_2 emissions can be mitigated when waste biomass is converted into biochar (Liu *et al*, 2015).Biochar properties vary, and characterization of biochars is necessary for assessing their potential to be used in different application.

The aim of this study was to produce and characterize biochar samples prepared by pyrolysis from different types of biomass locally available in Serbia, including agricultural and woody biowaste.

Wheat straw was chosen as representative agricultural biomass source for biochar(BC) production. The collected sample was washed with deionized water and dried at room temperature for 48h. Then it was crushed and subjected to ball-milling treatment at 300 rpm for 1h, followed by passing through 500 μm pore diameter sieve. The pyrolysis was performed at 600°C under N_2 flow rate for 3h in a laboratory horizontal fixed bed pipe oven. The product was cooled down to room temperature in the N_2 atmosphere (denoted as WS-BC-600). The biochar samples originated from the woody waste biomass were supplied from the BASNA d.o.o. company (Čačak, Serbia). Two samples were produced from beech by slow pyrolysis at 700°C and 800°C (denoted as B-BC-700 and B-BC-800, respectively), while the third one was pyrolyzed from the mixture of beech and oak at 700°C (denoted as B/O-BC-700). The as-synthesized samples were subsequently sieved with the same diameter grade as the WS-BC-600 sample and subjected to further characterization.

The structure and the morphology of all BC samples were characterized by scanning electron microscope (SEM). The texture of the samples was investigated by means of specific surface area determined by fitting the BET isotherm equation, while mean pore diameter and pore volume were determined by the Barrett-Joyner-Halenda (BJH) method. Pores were classified according to Brunauer-Deming-Deming-Teller method based on hysteresis loops of adsorption-desorption isotherms (Lowell *et al.* 2004). Corresponding data for textural characterization were obtained by dynamic low temperature N_2 adsorption/desorption (LTNA) method, with He as a carrier gas, using a Micromeritics ASAP 2010 instrument. X-ray diffraction (XRD) measurements were performed on a RigakuMiniflex 600 unit (Cu Kα radiation, λ = 0.15406 nm) using a counting step of 0.3˚ and a counting time per step of 3 s. The average diameters of crystallites were derived using the Scherrer equation.

All biochar samples have heterogeneous surface with well-developed pore structure. During the pyrolytic treatment, the elements of mobile matters are released in the form of small molecules (H_2O, CO, CO_2, CH_4) causing the production of pores (Worasuwannarak*et al*, 2007). The morphology of WS-BC-600 sample exhibitsflake like structure with particles of different shape and size, while the samples obtained from woody waste biomass have quite regular channel structurewith irregular particles of rough edges. Regardlessof the used woody biomass type, the pyrolysis temperature of 700°C promotes the formation of specific structures of honeycomb lattice. The fraction of these structures is much higher in the beech originated sample.

Textural properties of synthesized biochars are given in Table 1. The adsorption-desorption isotherm of B-BC-800 sample is characterized by H3 type hysteresis loop reflecting the presence of slit-shaped mesopores, while the H4 type hysteresis loop was identified in other three samples referring to a small fraction of micropores in these samples as well (Lowell *et al*, 2004). All of the isotherms exhibit a near closed loop hysteresis which is an indication that a certain portion of specific "ink bottle" shaped pores is present. The WS-BC-600 sample has a slightly lower specific surface area compared to the woody derived biochars. The pore size distributions of WS-BC-600, B-BC-700 and B/O-BC-700 samples show similar bimodal profiles with the majority of pores located in the low mesorange (3-5 nm). The influence of pyrolysis temperature can be observed in the case of B-BC sample in terms of total pore volume and pore size distribution. Namely, the increase of biochar production temperature resulted in considerably higher total pore volume of this sample, while its overall porosity is designated only by the amount of smallermesopores (narrow monomodal distribution).

Table 1. Textural properties of biochar samples

Textural property / *Biochar sample*	BET (m^2/g)	Average pore diameter (nm)	Total pore volume (cm^3/g)
WS-BC-600	173.49	5.33	0.014
B-BC-700	291.46	3.45	0.014
B-BC-800	259.13	4.46	0.18
B/O-BC-700	230.18	4.56	0.039

The XRD analysis portrays the crystalline structure and chemical composition of the produced biochars. The corresponding patterns of all the examined samples exhibit two weak and broad peaks at 2Θ range values at 20°-30° and 40°-50°, which can attributed to the diffraction of C(002) and C(101), respectively (PCPDFWIN database, CAS number: 75–1621). The shape and intensity of these peaks indicate the presence of amorphous carbon structure with randomly oriented carbon sheets (Dawodu*et al*, 2014; Zeng*et al*, 2014). Since the narrowing of the C(002) depicts the generation of more ordered graphite like carbon structure, it can be emphasized that the utilization of woody waste biomass favors the formation of more crystalline carbon structure of biochar compared to the wheat straw. The higher temperature of pyrolysis is also beneficial in terms of increasing the amount of graphitic carbon. The XRD results also indicate the presence of mineral calcite ($CaCO_3$) in all biochar samples, differing in the amount and size of crystallites with respect to the biomass source and pyrolysis temperature. The WS-BC-600 sample contains the smallest amount of calcite, while its amount and size of crystallites in woody waste originated biochars are primarily designated by the pyrolysis temperature. The sample obtained at 800°C is characterized by lower amount of calcite with smaller crystallites compared to the samples B-BC-700 and B/O-BC-700, whose mineralogical composition is very similar regardless of the used biomass source. Considering the synthesis of heterogeneous biochar based catalyst for biodiesel production, the initial amount of alkaline or alkaline earth metal salts in generated biochar can have an impact on catalytic performances. Thus, the observation that the inorganic composition of the biochar can be partly tailored by the pyrolysis temperature represents an important step in the design of basic catalysts.

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