The influence of agro-waste type on the characteristics of biochar produced

Nikolaos Mourgkogiannis, Ioannis Nikolopoulos, Eleana Kordouli, Christos Kordulis, Alexis Lycourghiotis, Hrissi K. Karapanagioti
Department of Chemistry, University of Patras, Patras, Western Greece, 26504, Greece
Keywords: Agricultural wastes, biochar, pyrolysis, porous materials agro-waste valorisation.
Presenting author email: nikosmorgan@hotmail.com

Introduction

Biochar is a rich in carbon by product produced from agro-industrial wastes when biomass is heated under various pyrolytic conditions. It can be incorporated into soil as soil amendment due to its high sorptive capacity for nutrients and water. Modern applications of biochars include catalysis, water purification, etc. Pyrolysis is a thermal process through which organic substances decompose under limited oxygen conditions at a range of 300 to 1300ºC. Studies have showed that biochar produced at high temperatures present higher surface area, and porosity compared to those produced at lower temperatures (1). Even though, a great number of researches have reported the production of biochar by several type of biomass (1, 2, 3); the production of biochar from raw spent coffee grains (SCG), sediment from Greek coffee (SGC), rice husks (RH), grapes seeds after wine production (GSW), and grape seeds after distillation for tsipouro production (GST) has not been examined extensively. In the present work, the aforementioned waste biomass materials have been used for biochars production aiming to their valorisation. The obtained biochars have been characterized using various physicochemical techniques in order to determine their properties related with catalytic and sorptive functionalities.

Experimental

Raw materials were placed in a Memmet oven at 50 ± 5ºC for several hours to remove the moisture. Dried samples were placed in a custom-made ceramic saggar box and pyrolyzed at 850ºC for 1 h in large electric furnace with heating range 30-1100ºC (Type Nabertherm, Controller B 180, Germany).

Surface area and porosity: The determination of the SSA, the external surface area, the pore volume, the micropore volume and the average pore size were performed using gas (N_2) adsorption−desorption in a Micromeritics TriStar 3000 Analyser system.

Suspension pH: Suspension pH of raw materials and biochars were measured according to Manariotis et al. (1). Approximately, 20 mL of electrolyte solution 0.1 M $NaNO_3$and an amount of 0.32 g of each sample were placed in glass bottles of 40 mL and the pH of suspension was measured after 24 h with a portable multi-parameter pH-meter (Consort C862) equipped with a glass electrode.

FTIR Analysis: The raw materials and produced biochars were studied in a PerkinElmer FTIR spectrometer. The corresponding spectra were recorded in the range of 4000-400 cm^{-1} and analysed by IRSearchMaster 6.0 software.

XRD analysis: X-ray diffraction patterns of the materials studied were recorded in the range of 10-80º using a Bucker D8 Advance Diffractometer equipped with nickel-filtered Cu K_α (1.5418Å) radiation source.

Thermo-Gravimetric Analysis (TGA): Thermal behavior of the samples was recorded in a Diamond TGA/DTA apparatus (Perkin Elmer Instruments) in a temperature range 25 - 1000°C under N_2 (200 $mLmin^{-1}$).

SEM-EDS: The morphology of the samples and their composition were examined using scanning electron microscopy (SEMJEOL JSM6300) equipped with an Energy Dispersive Spectrometry accessory.

Ash content: A standard method was used for ash content determination.

Results and Discussion

Biochar Surface Area and Porosity: All raw materials used had SSAs lower than 0.53 m^2g^{-1} and almost no pores. Table 1, presents the SSA, the micropore area, the external area, the pore volume, the micropore volume, and the average pore size of biochars

Table 1. Material properties after charring at 850ºC.

Sample	BET Surface Area (m^2g^{-1})	Micropore Area (m^2g^{-1})	External Area (m^2g^{-1})	Pore Volume (cm^3g^{-1})	Micropore volume(cm^3g^{-1})	Pore size (Å)
SCG	751	514	238	0.39	0.24	31
SGC	870	587	283	0.44	0.27	31
RH	367	230	137	0.23	0.11	43
GSW	529	416	113	0.27	0.19	38
GST	464	360	104	0.24	0.17	38

The results disclose that biochars have high SSA and that micropore area is higher than external surface area. The t-plot for the SGC shows that the pyrolysis of raw SGC leads to the highest SSA (870 m^2g^{-1}) and micropore area (587m^2g^{-1}) compared to the other samples. On the other hand, the lowest SSA and the highest pore size (43

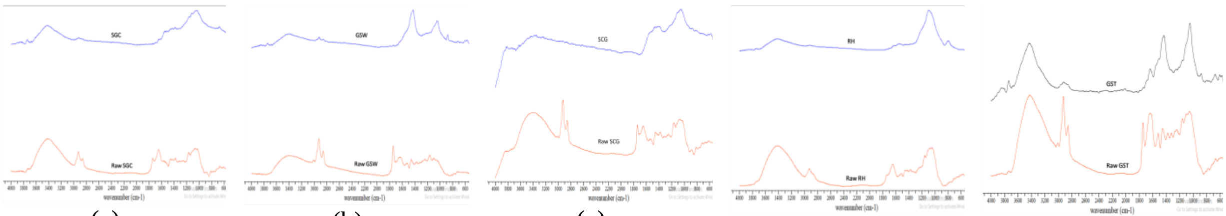
Å) were observed for RH. Generally, biochars obtained are highly microporous materials, exhibiting low percentage of macropores.

Acid-Base Behavior of Biochars: Besides GST raw material which was neutral (suspension pH: 7) the other raw materials were slightly acidic (suspensionpH: 5.5 to 6.4).In contrast, the biochars obtained appear to be alkaline in nature, exhibiting suspensions pH in the range 9.4 to 10.7.GST biochar showed the highest suspension pH (10.7). The alkaline nature of biochars, could be attributed to the existence of alkaline oxides in their mass.

Functional groups determination: Figure 1 shows the FTIR spectra for the raw materials and the corresponding biochars. Raw materials spectra present various peaks showing that the samples contained different functional groups. High temperature pyrolysis results to the disappearance of several peaks and the weakening of the rest.

Biochars crystallinity: XRD patterns of the biochars (not presented here) studied revealed that all these materials are almost amorphous, exhibiting two weak and broad diffraction peaks at 2θ: 25 & 43^o.

Thermal stability: TGA analysis of biochars showed that increasing the temperature RH biochar loses the lowest mass in all temperature range (main mass loss at temp.< 150^{o}C). The rest of biochars lost mass at two distinct temperature ranges. At low temperature (<150^{o}C) the mass lose could be attributed to the adsorbed water removal. The high temperature (>850^{o}C) loss could be related with further pyrolysis of the materials.



(a) (b) (c) (d) (e)

Figure 1. FTIR spectra of (a) raw SGC and SGC, (b) raw GSW and GSW, (c) raw SCG and SCG, (d) raw RH and RH, (e) raw GST and GST

Conclusions

All biochars obtained by pyrolysis at 850^{o}C of the agro-waste raw materials examined are highly porous exhibiting mainly micropores. Their porous texture is combined with high SSA following the order: SGC>SGC>GSW>GST>RH. Although, the untreated agro-wastes are either slightly acidic or neutral in nature, their produced biochars are alkaline. FTIR spectra showed that pyrolysis leads to the removal of several functional groups. All biochars obtained exhibit low crystallinity and are quite stable for temperatures lower than the pyrolysis one. This study reveals that different agro-waste materials can be transformed to biochars with interesting properties making them very promising as sorbents and catalyst materials (e.g. supports) satisfying the principals of circular economy.

ACKNOWLEDGMENT

We acknowledge support of this work by the project “Research Infrastructure on Food Bioprocessing Development and Innovation Exploitation – Food Innovation RI” (MIS 5027222), which is implemented under the Action “Reinforcement of the Research and Innovation Infrastructure”, funded by the Operational Programme "Competitiveness, Entrepreneurship and Innovation" (NSRF 2014-2020) and co-financed by Greece and the European Union (European Regional Development Fund).

European Union European Regional Development Fund | HELLENIC REPUBLIC MINISTRY OF DEVELOPMENT & INVESTMENTS SPECIAL SECRETERIAT OF STRUCTURAL PROGRAMMES MANAGING AUTHORITY OF EPAnEK | EPAnEK 2014–2020 OPERATIONAL PROGRAMME COMPETITIVENESS ENTREPRENEURSHIP INNOVATION | ΕΣΠΑ 2014-2020 ανάπτυξη - εργασία - αλληλεγγύη Partnership Agreement 2014 - 2020

Co-financed by Greece and the European Union

REFERENCES

1. I.D. Manariotis, K.N. Fotopoulou, H.K Karapanagioti. I&EC Research **54**, 9577-9584 (2015).
2. A.B. Fuertes, M. Camps Arbestain, M. Sevilla, J.A. Maciá-Agulló, S. Fiol, R. López, R.J. Smernik, W.P. Aitkenhead, F. Arce, and F. Macias.Australian Journal of Soil Research **48**, 618-626 (2010).
3. H. Moayedi, B. Aghel, M.M. Abdullahi, H. Nguyen, A.S.A. Rashid.Journal of Cleaner Production 237, 1-10 (2019).