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Characterization of biochar and syngas obtained from pellets of grape vine and sun flower husk using a pyrolysis system

A.Sorgonà ^a, L.Longo ^{b,*}, A.R.Proto ^a, P.Cavalletti^b, M.Cecchini ^b, L.Salvati ^c, F.Gallucci ^c, A.Colantoni ^b

^aDepartment of Agriculture, Mediterranean University of Reggio Calabria, Feo di Vito 89122, Reggio Calabria, Italy

^bTuscia University, Department of Agricultural and Forestry sciENcEs (DAFNE), Viterbo, Italy

^cConsiglio per la ricerca in agricoltura e l'analisi dell'economia agraria (CREA) Unità di ricerca per l'ingegneria Agraria, Roma, Italy

Abstract

Biochar produced from pellet obtained from grapevine (GV) and sunflower husk (SFH) at different temperature (400 and 500°C) were studied by pyrolysis batch reactor. Chemical and physical evolution of biomass under pyrolysis conditions was determined and products characterization was evaluated, including main organic components in gaseous stream. The Biochar is a "porous carbonaceous solid" produced by thermochemical conversion of organic materials in an oxygen depleted atmosphere, which has physiochemical properties suitable for the safe and long-term storage of carbon in the environment and, potentially, soil improvement. Results have shown a decrease in yield as an increase in temperature. The objective of this work is to improve the acknowledgment for the alternative use of the biochar gained from agro-forestry biomass residuals grapevine and sunflower husks by means of modern chemical and physical characterization tools.

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1. Introduction

Renewable wastes such as biomass-related agricultural (Proto, Zimbalatti, Abenavoli, Bernardi & Benalia, 2014) agri-food residues (Gelsomino, Abenavoli, Princi, Attinà, Cacco & Sorgonà, 2010; Sorgonà, Abenavoli, Cacco & Gelsomino, 2011), and forestry residues (Friso, Grigolato & Cavalli, 2011) are being increasingly recognized as valuable feedstock for bioenergy production.

* Corresponding author. Tel.: +39 0761 357357.

E-mail address: leonardolongo@unitus.it

In Austria, crop residues are used both to increase organic carbon content in top-soil and for production of biofuels. Pyrolysis, which is one of the widely used thermo-chemical conversion technologies, refers to the thermal decomposition of organic components in biomass in an inert gas atmosphere, at medium temperature, for the production of biochar and condensable and non-condensable components (including water, highly oxygenated bio-oil, and synthesized gas). Biochar is a porous carbonaceous solid product of pyrolysis or incomplete combustion of organic materials, similar to charcoal but also utilized for agricultural and biological activities and/or environmental applications (Moneti, Delfanti, Marucci, Bedini, Gambella, Proto & Gallucci, 2015). Pyrolysis depolymerizes dry feedstock under an oxygen free environment. When the pyrolysis temperature is moderately high (450 – 550 °C), the volatiles arisen from pyrolysis process can be condensed to become a liquid product, called pyrolysis oil. The potential benefits for the environment are the reduction and sequestration of CO₂ emission, and for the farmers an additional income through the energy production like coal or for production of adsorbents (Dersch & Böhm, 2001). Pyrolysis temperature greatly affected the biochar characteristics in relation to its elemental composition and surface chemistry: biochars produced at low temperature have lower values of pH and may be suitable to improve the fertility of high pH soils in arid regions or amendments for acid soils (Boscaro, Pezzuolo, Grigolato, Cavalli, Marinello & Sartori, 2015). During the pyrolysis the raw material are degraded at temperature between 350 – 1000 °C (Colantoni, Allegrini, Boubaker, Longo, Di Giacinto & Biondi, 2013; Monarca, Cecchini, Colantoni & Marucci 2011). The temperature at which the biochar is produced had a significant effect on its physico-chemical properties. The loss of mass of the starting product depends on the variation of the temperature and duration of the combustion process. Generally, the char yield decreases at high temperatures. Starting from this background, a proposal of experimentation was submitted to the BRISK project technical committee and therefore approved. This enabled the chance to establish a collaboration between the University of Tuscia, Bioenergy 2020+ (Graz) and Graz University of Technology. The aim of this work is to improve the acknowledgment of the biochar gained from agro-forestry biomass residual for alternative use, through chemical-physical characterizations. The effect of the pyrolysis parameters on the properties of products was thoroughly investigated.

2. Materials and methods

2.1 Feedstock preparation

Two biomass materials including sunflower husk (*Helianthus annuus* L.) pellets (SFH) and grape vine (*Vitis vinifera* L.) pellets (GV) were used as a feedstock for biochar production. The pellets, 4 mm in diameter, were obtained from local residual biomass (Austria). The materials underwent subjected to an ultimate chemical analysis before and after the pyrolysis experiments (Fig. 1) in order to obtain detailed information about composition of biochar produced and the release of inorganic species from the fuel to the gas phase.



Fig. 1. Sample holder with Biomass inserted in the reactor (left); Lab reactor setup (right).

2.2 Product characterization

Characterization of biomass and biochar in terms of the C, H, and N contents was done in according to the standard EN 15104 by combustion and subsequent gas-phase chromatographically separation and measurement in an elemental analyzer. Cl content was performed according to EN 15289, applying a digestion step based on bomb combustion in oxygen and absorption in NaOH (0.05 M), followed by a measurement by ion chromatography. For the determination of the contents of major and minor ash forming elements (excluding Cl), a multi-step pressurized digestion with HNO₃ (65%)/HF (40%)/H₃BO₃ followed by measurement by inductively coupled plasma–optical emission spectroscopy (ICP–OES) or inductively coupled plasma–mass emission spectroscopy (ICP–MS) (depending upon detection limits) was applied. For TIC analyses, an aliquot is treated with acid and the generated CO₂ was measured by infrared (IR). The Cl content of ashes was measured by ion chromatography after elution for 24 h with deionized water.

2.3 Batch pyrolysis tests

Pyrolysis runs were performed at a temperature of 400 and 500°C for each sample (Table 1). The core of the reactor used in the experimental tests and kindly supplied by Bioenergy 2020+ and Graz (Austria) University of Technology in the framework of the BRISK EU project, is a cylindrical retort (height, 35 cm; inner diameter, 12 cm), which is heated electrically and controlled by two separated proportional integral derivative (PID) controllers. The fuel is put in a cylindrical sample holder of 100 mm height and 95 mm inner diameter. The reactor used has been especially developed for the investigation of fuel decomposition under fixed bed conditions. It consists of a cylindrical retort (height 350 mm, inner diameter 120 mm) which is heated electrically by two separated PID controllers (Fig. 2). The fuel (100 to 400 g depending on the fuel density) is put in a cylindrical holder measuring 100 mm in height and 95 mm in inner diameter. Both parts are made of fibre-reinforced SiC ceramics. Air, as well as different gas mixtures, can be applied as reaction media. With this setup it is possible to continuously measure the mass reduction of the sample during the pyrolysis/combustion process. The sample is introduced into the pre-heated reactor and therefore, rapid heating, comparable with the one in real thermal conversion processes, can be achieved. The sample holder is equipped with five thermocouples to monitor the fuel bed temperatures during the test run (Fig. 2).

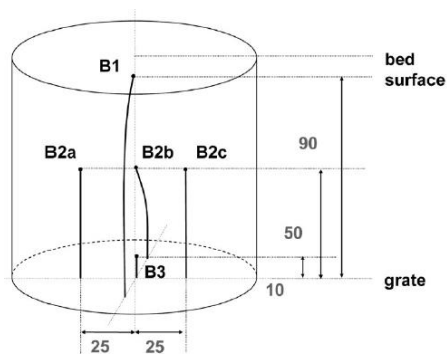


Fig. 2. Position of thermocouples in biomass bed.

The material of the reactor wall and the sample holder is silicon carbide. The sample holder and the sample are placed on the plate of a scale. The scale is mechanically separated from the retort by a liquid sealing and is used to determine the weight loss of the sample over the test run period. To enable an inert gas atmosphere and avoid the presence of oxygen inside the reactor a flow of nitrogen is applied. Flue gas samples are extracted from the gas volume above the fuel bed, partly treated, respectively conditioned (dilution and temperature stabilization), and introduced into the gas analysis systems used in this study: (i) Fourier transform infrared spectroscopy (FTIR) (Ansyco), to measure CO₂, H₂O, CO, CH₄, NO, NH₃, HCN, NO₂, N₂O, light hydrocarbons and light condensable

species; (ii) Emerson NGA 2000; with paramagnetic based measure of O₂; no dispersive infrared analysis (NDIR) of CO₂ and CO; and heat conductivity sensor for H₂. The basic idea was to develop, design, and construct a lab-scale batch reactor, which is capable for the simulation of the fuel decomposition behavior in real-scale fixed-bed thermal biomass conversion systems. Therefore, the following constraints were given: (i) reasonable sample intake to consider secondary reactions in the fuel bed appropriately, (ii) high heating rates of the fuel comparable to real scale grate furnaces, (iii) inert reactor material to avoid reactions of the gases with the reactor, (iv) high flexibility regarding analytical equipment connected with the reactor, and (v) online recording of relevant operation data and emissions as well as the mass loss. The testing protocol was defined as follows: (i) Before the test run, the fuel is pre-dried to 10 wt% wet basis (wb), moisture content and a sub-sample of the fuel is forwarded to wet chemical analyses. (ii) The fuel is filled into the sample holder and lightly compressed to gain a packed bed with a realistic density. (iii) Then, the reactor is preheated, applying 200 and 600/650 °C as pre-settings for the upper and lower heating element. These settings are kept constant during the whole test run. (iv). Thereupon the sample holder with the fuel is introduced into the reactor, and the inert gas flow through the grate and the fuel bed is activated. All experiments documented in this paper have been performed with N₂ as the inert agent at a gas flow of around 3 LN/min. (v) All parameters mentioned above are continuously recorded in a 2 s interval over the whole test run, which usually lasts between 30 and 60 min depending upon the fuel mass applied. (vi). At the end of the test run, first the residues (biochar) are visually evaluated and then removed and forwarded to chemical analyses. The schematic resume of the experimental setup is given in Fig. 3.

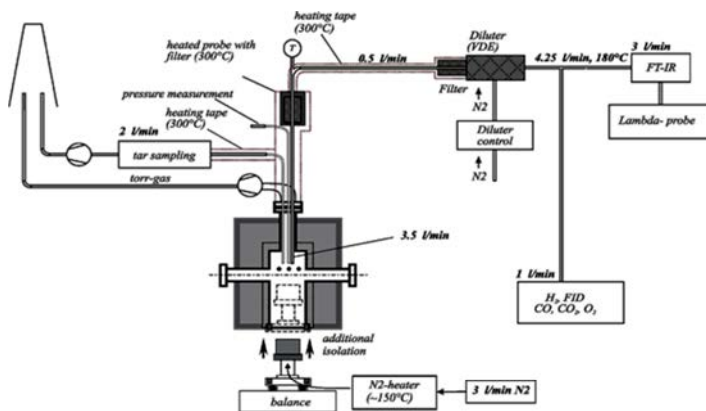


Fig. 3. Scheme of the lab-scale reactor setup used for pyrolysis test runs.

Table 1. Sample codes to each tests.

Test No.	Sample name short	Sample name long	Temperature of pyrolysis (°C)
1			400
2	SFH	Sun flower husk pellet	500
3			400
4	GV	Grape vine pellet	500

3. Results and discussions

3.1 Biochar analysis

The reactor temperature had a significant effect on biochar's physico-chemical properties (Table 2). The yield of biochar decreased as pyrolysis temperature increased because the amount of volatile matter rises; a low value of yield (lower or slightly above 40%) occurred at 400°C and 500°C, agreeing with the observation of Brewer et al. 2009. The data showed that in biochar pyrolyzed at 400°C, carbon content was about 70%, hydrogen content just

over 4%, oxygen content ranging from 24% to 25%, nitrogen about 1% and the sulfur content could be considered negligible, similar to the results obtained from Kwapinski, Byrne, Kryachko, Wolfram, Adley & Leahy (2010). Increasing biochar production temperature corresponded to an increase over 3% in carbon and a decrease of about 2,5% in oxygen and 1% in hydrogen; more significant data were observed in other studies at higher temperature. A further comparison with original feedstock biochar exhibit enhanced carbon concentrations in comparison with original biomass samples. The ash content moderately increases with increasing temperature and it was a little higher in SFH than GV feedstock. The content of minors chemical elements was evaluated for each feedstock sample, sunflower husk pellet (SFH) and grape vine pellet (GV) as well as for the corresponding biochars obtained (Table 3). An increase of concentration of all the elements occurred after pyrolysis (Lehmann, 2007). It can be observed that the pyrolysis process strongly influences also the concentrations of potentially fertilizer elements too (e.g. phosphorus, potassium, etc.) and a substantial increase of them could be observed; in SFH potassium concentration increased from 8.070 to 20.200 mg/kg and in GV from 3.440 to 8.590 mg/kg. The phosphorus content also rose up from 663 to 1.610 mg/kg by SFH and from 1.080 to 2.590 mg/kg. In case of GV. These results suggest that biochar could be applied individually as a conventional fertilizer application or blended with compost in order to improve the growth of plants and increase the yield of crops. The raw material and the related pyrolyzed product are shown in Fig. 4.



Fig. 4. Pictures of feedstock investigated in the batch reactor: GV sample before (a) and after (b) and SFH before (c) and after (d) the test runs.

3.2 Thermogravimetric analyses

In Fig. 5 (a, b) it can be observed that the mass loss of GV and SFH increased with the increase of pyrolysis temperature. At the beginning mainly drying took place, indicated by a moderate mass loss, low fuel bed temperatures (Fig. 6), and the release of water. After about 200 s, fuel decomposition started, indicated by an increase of CO₂ concentrations in the flue gas. The release of volatiles and parallel charcoal gasification took place until around 3.300 s of the test run duration. Diagrams show that GV and SFH had the same mass reduction trend both at 400°C and 500°C because the biomass material was typically composed of cellulose, hemicellulose and lignin. Literature reports that hemicellulose began to thermally decompose at 250°C and the process goes on until 380°C,

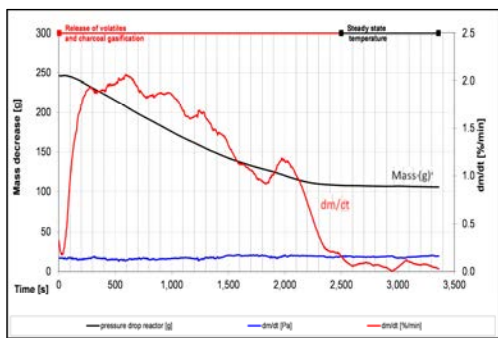
cellulose degradation occurs between 300°C and 400°C and lignin degradation take place at 200°C – 500°C. Anyway, the mass followed a steady trend decrease until about 2.000 s on each test runs. At this time of the test also the stabilization of the thermocouples temperature occurred (Fig. 5-6). The duration of the two main reaction phases, the release of volatiles and char coal pyrolysis, and the charcoal combustion generally increase with an increasing fuel sample mass.

Table 2. Physicochemical properties of biochar.

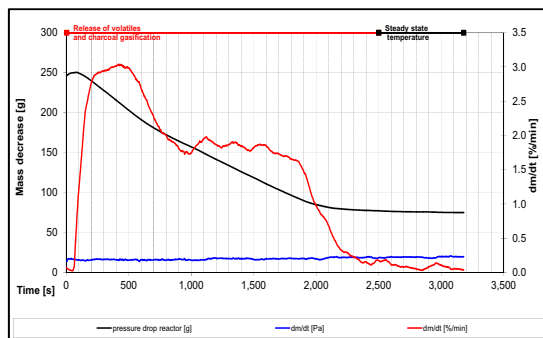
Feedstock	Temperature (°C)	Duration (s)	Yield (%)	Ash content	C (%)	H (%)	O (%)	N (%)	S (%)
GV	400	3.600	40,36	7,05	69,68	4,34	25,22	0,76	0,04
SFH	400	3.600	36,17	7,53	70,26	4,47	23,98	1,29	0,19
GV	500	3.600	30,12	8,24	73,77	3,45	21,99	0,79	0,04
SFH	500	3.600	33,19	9,49	72,10	3,69	22,82	1,39	0,20

Table 3. Chemical composition of biomass and corresponding biochar samples investigated (mg/kg dry basis); TIC - total inorganic carbon.

Parameter	unit	SFH		GV	
		pellet	biochar	pellet	biochar
Cl	mg/kg d.b.	577	699	96,90	81,40
Ca	mg/kg d.b.	3.960	9.800	6.200	15.200
Si	mg/kg d.b.	321	801	1.740	4.180
K	mg/kg d.b.	8.070	20.200	3.440	8.590
Mg	mg/kg d.b.	2.160	5.500	1.020	2.470
P	mg/kg d.b.	1.080	2.590	663	1.610
Na	mg/kg d.b.	11	25	63	157
Zn	mg/kg d.b.	18	44	26	67
Pb	mg/kg d.b.	< 4,85	< 5,50	< 4,82	< 5,67
Al	mg/kg d.b.	62	130	360	685
Fe	mg/kg d.b.	312	260	346	761
Mn	mg/kg d.b.	14	23	61	153
Cu	mg/kg d.b.	11,10	25,70	19,50	48,80
Cd	mg/kg d.b.	< 0,291	< 0,33	< 0,289	< 0,34
TIC	mg/kg d.b.	36.000	42.600	58.400	60.400



(a)



(b)

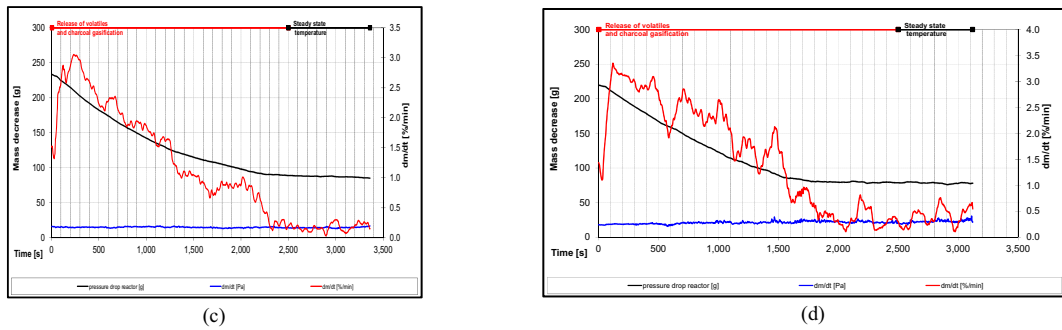


Fig. 5. Thermogravimetric analyses under different temperatures: (a) GV – 400°C, (b) GV – 500°C, (c) SFH – 400°C, (d) SFH – 500°C.

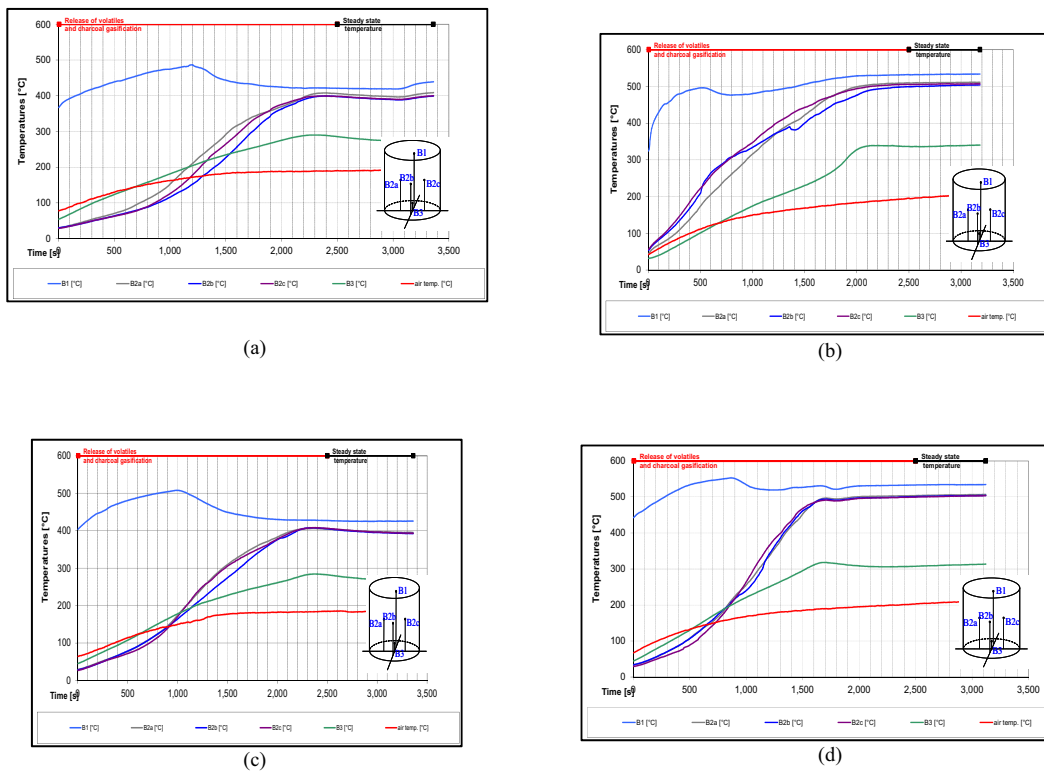


Fig. 6. Fuel bed and flue gas temperatures trend during (a) GV – 400°C, (b) GV – 500°C, (c) SFH – 400°C and (d) SFH – 500°C running tests.

4. Conclusions

Our study was able to demonstrate the capacity to produce biochar using the residual biomass derived from agricultural residues. Results of this experiment have shown that the biochar obtained is characterized by good chemical and physical characteristics for an agronomic use or an energetic use; with regard to this last aspect it is important to underline that the lower heating value and carbon content are similar to lignite's values meaning that biochar can be used, as a coal, in thermo-chemical processes to energy production. Regarding on use as fertilizer it is important to highlight that this biochar has good impact on soil characteristics with an increase of soil's water retention capacity and a reduction of soil acidity in consequence of the alkaline pH value. In addition the agronomic use tests of biochar have shown absence of negative impact on crops growth. With other specific analysis it will be

possible to have the determination of additional characteristics necessary for the insert of biochar in the list of soil amendament for an agricultural use.

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