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Experimental investigation of moisture influence on biochar and biochar-soil blends thermophysical properties

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Abstract. Biochar is a carbonaceous and porous material obtained through pyrolysis or gasification. It can be extremely valuable as soil amendment since it increases the organic matter content and fertility, the microbial activity, the water retention, and the crop yields. Moreover, biochar soil application has the potential for long-term carbon sequestration which makes its application to soil interesting even outside agricultural crops. In recent years, the study of the variation of the thermophysical properties of the soil induced by mixing with biochar has attracted interest.

In this work, the effect of the water content on thermal conductivity of biochar was investigated by means of the guarded hot plate apparatus λ-Meter EP500e. The same procedure was applied to various mixtures of biochar and soil. Furthermore, the specific heat was measured in order to obtain the thermal diffusivity in the various conditions through a calorimeter. Solar reflectance was also measured following the ASTM C1549 using a solar spectrum reflectometer SSR-ER. The obtained thermophysical properties can be used for the evaluation of the temperature trend of soil at different depths during the seasonal variations.

Keywords: *Thermophysical properties, biochar, conductivity, reflectance, specific heat*

1. Introduction

In line with the objectives of the 2030 agenda, with the Sustainable Development Goal 7 "Affordable and clean energy", the scientific community and institutions are focusing their efforts on reducing energy consumption, making energy production systems and energy usage more efficient and identifying new technologies, materials and/or combinations of these to achieve the common goals set by the 2030 Agenda of the United Nations [1].

One of the main targets is to "increase the share of renewable energy in the global energy mix, by 2030". In addition, the European Union has set as an important objective the zeroing of CO_2 emissions by 2050 [2]. In this context of energy sustainability and energy efficiency there must be space for technologies and materials that allow for a significant reduction in global GHG emissions and among them the atmospheric carbon capture and storage technologies find a prominent position. In particular, bioenergy with carbon capture and storage (BECCS) is one of the most promising strategies and it is based on the production of biochar through pyrolysis and gasification. Biochar is a vegetable carbon composed of up to 80% of biogenic carbon: it is a highly porous charcoal like an activated carbon with high recalcitrance that allows it to remain stable for decades when it is buried into the soil.

When biochar fulfils specific requirement it can be used as soil improver [3]. Its soil application can increase crop productivity, organic matter, water retention and microbial activity, thus it decreases the need for fertilizers and erosion [4,5,6]. The scientific community recognizes this material as a long-term storage medium for atmospheric CO_2 [7, 8, 9], in fact, 100 kg of biochar prevent the emission of about 150 kg of equivalent CO_2 [10]. In the last two decades several scientific studies have proven the benefit of the direct application of biochar in soil, but nowadays the attention of the scientific community has been shifting to more complex applications such as water filtering, microbial remediation of contaminated soil, sludge treatments, electronic and electric application and building technology like new materials and bricks [11, 12, 13, 14].The scientific community has moved a long way to understand the interactions between biochar and its retention capacity [15], and several studies have already confirmed the high capacity to retain large quantities of water, aiming to obtain more fertile soils and water saving [16]. Unlike agricultural applications, there are still few works that investigate the exploitation of the water holding capacity to improve existing technological processes in the energy sector. Most of them report the characterization of thermal properties of biochar as a function of the water content [17, 18, 19], but these studies focus on the characteristics of the biochar or soil-biochar matrices to characterize the material.

This work instead focuses on the thermal characterization of biochar, soil and soil-biochar mixtures related to the use of biochar as a geothermal backfill material, in particular on specific heat, thermal conductivity and solar reflectance of the previously mentioned solid matrices. Measurements were performed on three samples: a matrix composed of soil only (SOIL) and matrix composed of 80% soil and 20% biochar (SOIL-CHAR) and a matrix composed of char only (CHAR). The objective of these measurements was to compare a standard soil and the thesis (addition of biochar) to quantify the improvement obtained with the application of biochar and the positive or negative contribution in moist soil conditions. Biochar, in fact, with its water retention capacity improves the thermal conductivity conditions of the soil [18] in which it is applied as it causes the soil to remain moist for a longer time.

In addition, solar reflectance was investigated to study the effect on albedo that would occur when biochar or soil-biochar mixture is applied on the surface of a geothermal field rather than deep into the soil. The aim of this measure is to investigate the best way to apply these mixtures, also taking into consideration any effects of variation of solar reflection of earth surface.

2. Materials and methods

A laboratory analysis campaign for the evaluation of the thermophysical was carried out.

The properties of the biochar are not well-known, aside from a few properties such as the hydrophilicity of the biochar if obtained under specific conditions [3, 17, 18]. Since biochar has a pronounced ability to make the soil saturated with water, an increase of soil heat transfer performance is expected. Moreover, biochar can be obtained from different raw materials and with different methodologies, and this could heavily impact the resulting thermophysical properties, thus a final product can be better than others (as perlite or bentonite) [6, 20]. During the measurement campaign three different samples were taken into consideration under different humidity content. SOIL and SOIL-CHAR matrices were tested at three different degrees of humidity: 0% (DRY), 20% w/w wet basis (20) and 30% w/w (30) wet basis. In addition to these, SOIL-CHAR and CHAR were also tested at higher moisture content. SOIL-CHAR_36 and CHAR_67 samples were made by adding water to the matrices until they can retain water to study the thermal characteristics in saturation conditions. Table 1 summarizes and explains the composition of all the samples.

Table 1. Samples name, composition and humidity content.

Sample	Solid matrix composition	*Moisture content* kg_{water}/kg_{tot}
SOIL_DRY	Soil 100%	0%
SOIL_20	Soil 100%	20%
SOIL_30	Soil 100%	30%

SOIL-CHAR_DRY	Soil 90% + biochar 10%	0%
SOIL-CHAR_20	Soil 90% + biochar 10%	20%
SOIL-CHAR_30	Soil 90% + biochar 10%	30%
SOIL-CHAR_36	Soil 90% + biochar 10%	36%
CHAR_DRY	Biochar 100%	0%
CHAR_50	Biochar 100%	50%
CHAR_67	Biochar 100%	67%

2.1 Biochar

The biochar used during the experimental campaign is a commercial biochar purchased from the Italian company Bio-Esperia Srl and produced through an updraft gasifier with a nominal power of 170 kW.

The biochar production capacity of the gasifier is 900 m^3 per year, obtained from quality biomass deriving from secondary cuts of the forest in non-humanized areas. The producer declares that from 1000 kg of dry biomass, it is possible to produce 250-300 kg of biochar. This biochar is certified as a soil improver, according to Italian legislation, and can therefore be applied to the soil. Table 2 summarizes the characteristics of the BioDea White Onyx biochar used in this research.

Table 2 BioDea White Onyx biochar characteristics declared by the company [21].

Parameter	Value
Total Nitrogen (N)	< 0.5%
Carbon from carbonates (C)	< 0.1 %
Maximum water retention	115 %
Total Carbon of biological origin - dry basis	70 %
Salinity	110 mS/m
pH	9.85
Ash content	4.6 % dry basis
H/C - mole fraction	0.2
Fraction of grain size < 0.5 mm	1 %
Fraction of grain size < 2.0 mm	1 %
Fraction of grain size < 5.0 mm	60 %

The BioDea biochar was then minced using a mixer to make the material uniform: all the grains reached a size of less than 1 mm.

2.2 Thermal conductivity measurements

2.2.1 Sample preparation

The thermal conductivity measurement was performed by means of a guarded hot plate apparatus, λ-Meter EP500e.

The instrument consists of a fixed plate on which the specimen is placed and a motorized plate which is positioned on the upper face of the specimen to be analysed. The use of 0.5×0.5 m specimens is recommended to obtain more precise data. The minimum thickness is 0.02 m and the maximum 0.2 m. In addition to the set-point temperature at which the measurement is performed and the temperature difference between the two plates, it is possible to choose the pressure with which to compress the specimen, in a range between 250 Pa and 2500 Pa.

The tests during the experimental campaign were performed at a set point temperature of $T_{set} = 20°C$ and a temperature difference between the two plates equal to $\Delta T = 15$ K. The plate maintains the horizontal centre line of the sample at the setpoint temperature and the two horizontal surfaces (upper and lower) to the difference ΔT. The pressure was set to 2500 Pa. The instrument ended the measurement when it converged to a unique conductivity value λ *[W/ (m K)]* with variations lower than 1% around the identified value. In addition to the λ value, the instrument returned the error on the measurement performed *S [W/m K]* and the thickness of the sample analysed as $L \pm 0.01$ *[mm]*. As the

SOIL and CHAR samples are composed of solid but not compact matrices, it was necessary to place them in a box. An OSB wooden box open on the upper side was used, having dimensions of 0.5×0.5×0.07 m and walls with a thickness of 0.012 m, waterproofed with epoxy resin. A 0.005 m thick neoprene tape was placed along the entire upper perimeter to facilitate compression in the hot plate.

For each test, the procedure was the following: the desired sample was prepared according to Table 1, it was placed in the box and levelled, it was uniformly compressed using a weight of 50 kg and finally the whole box was coated with a layer of transparent film to preserve the instrument from water. Finally, the box was placed in the hot plate.

The samples were made of the same soil which had previously been dried and homogenized in terms of grain size. 50 kg of soil were divided into two equal parts, one destined for SOIL samples and one destined for SOIL-CHAR samples. This second was finally mixed with a quantity of biochar equal to 10% of the sample final weight, Eq. 1. In this way SOIL-CHAR_DRY samples were obtained.

$$M_{biochar} = \frac{M_{soil} \times 10}{100-10}\ [kg] \tag{1}$$

Once the tests with the DRY samples were completed, water was added to create the wet samples at 20% w/w wet basis, following Eq. 2, where M_{sample_dry} represents the considered sample (SOIL_DRY, SOIL-CHAR_DRY and CHAR_DRY). Similarly, water was added for testing the other wet basis samples.

$$M_{water} = \frac{M_{sample\_dry} \times 20}{100-20}\ [kg] \tag{2}$$

2.2.2 Experimental measurements campaign

For each sample two measurements were performed (rotating 90° the samples).

In addition to the measurements on the SOIL, SOIL-CHAR and CHAR samples, two measurements of the thermal conductivity of the wooden base of the waterproofed box were also carried out. This data is necessary to find the thermal conductivity of the sample contained in the box.

All the variables used in every test for the calculation of the thermal conductivity are summarized in Table 3. Figure 1 shows the layers of the sample.

Table 3. Variables for thermal conductivity calculation.

Variable	Symbol	Error	*Notes*
Thickness of the wood base	L_{wood}	$1 \times 10^{-5}\ m$	Data from hot plate
Sample thickness (box base + unknown sample)	L_{sample}	$1 \times 10^{-5}\ m$	Data from hot plate
Thickness of the unknown sample	L_x[a]	ε_{L_x}[a]	Data from calculation
Wood base thermal conductivity	λ_{wood}	ε_{wood}	Data from hot plate
Sample thermal conductivity (box base + unknown sample)	λ_{sample}	ε_{sample}	Data from hot plate
Unknown sample thermal conductivity	λ_x[a]	ε_{l_x}[a]	Data from calculation
Wood base thermal resistance	R_{wood}[b]	ε_{wood}	Data from calculation
Sample thermal resistance (box base + unknown sample)	R_{sample}[b]	ε_{sample}	Data from calculation
Unknown sample thermal resistance	R_x[a]	ε_{R_x}[a]	Data from calculation

[a] Values of the unknown sample, "x" generically represents the SOIL, SOIL-CHAR and CHAR samples.

[b] The thermal resistance is considered "specific thermal resistance", in fact the surface area is not considered since it is the same for all the samples

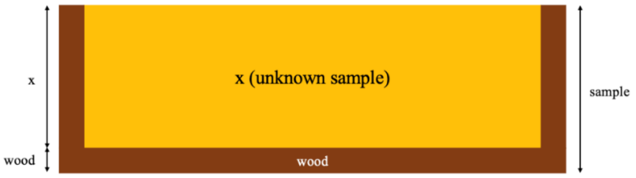

Figure 1: Simplified scheme of the sample layers and related nomenclature.

The equations used for the calculation of λ_{SOIL}, $\lambda_{SOIL\text{-}CHAR}$ and λ_{CHAR} are described in Eq 3., 4. and 5.

$$R_{wood} = \frac{L_{wood}}{\lambda_{wood}} \left[\frac{m^2K}{W}\right] \quad (3)$$

$$R_{sample} = \frac{L_{sample}}{\lambda_{\text{sample}}} \left[\frac{m^2K}{W}\right] \quad (4)$$

$$\lambda_x = \frac{(L_{sample} - L_{wood})}{(R_{sample} - R_{wood})} \left[\frac{W}{m\,K}\right] \quad (5)$$

Where $\boldsymbol{\lambda_x}$ represents the thermal conductivity of the unknown sample. The thermal conductivity value $\boldsymbol{\lambda_x}$ for each sample was calculated as the average value of the two tests performed.

$$\lambda_x = \frac{\lambda_{x_1} + \lambda_{x_2}}{2} \quad (6)$$

The measurement errors were calculated according to the propagation of uncertainties proposed by Kline McClintock [22], Eq 7.

$$\varepsilon_f = \left[\left(\frac{\partial f}{\partial x_1} * \varepsilon_{x_1}\right)^2 + \left(\frac{\partial f}{\partial x_2} * \varepsilon_{x_2}\right)^2 + \cdots + \left(\frac{\partial f}{\partial x_n} * \varepsilon_{x_n}\right)^2\right]^{1/2} \quad (7)$$

where $f = f(x_1, x_2, \ldots, f_n)$ is a generic equation with generic variables $x_1, x_2, \ldots, x_n$.

2.3 Specific heat measurements.

2.3.1 Sample preparation

Only two samples were characterized: biochar and soil.

Once the specific heat of both elements has been obtained, it is possible to proceed with the combination in different percentages to calculate the composition of different matrices.

2.3.2 Experimental measurements campaign

The experimental apparatus was composed of a 2-liter glass beaker which was placed in a specially created extruded polystyrene box with a minimum thickness of 0.10 m.

The beaker was filled with water at room temperature which was constantly mixed by a stirrer placed on the lid of the box. A thermocouple measured the water temperature T_{H_2O} (Figure 2).

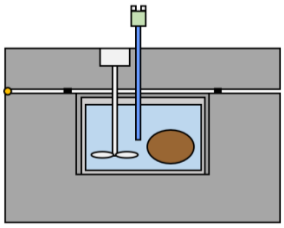

Figure 2: Simplified scheme of the apparatus for specific heat measurement

The analysed sample, closed in an airtight bag, was immersed for three hours in a water bath maintained at the temperature of $T_{\text{bath}} = 30°C$ through a Julabo ME thermostatic bath. In this way the sample was completely brought to 30°C. The sample was then extracted from the thermostatic bath, immersed in the beaker water and the stirrer was activated. The temperatures T_{H_2O} and T_{air} were logged using a Pico-Technology TC08 data logger. The test was interrupted when the water temperature stabilized at an intermediate value between the ambient temperature T_{H_2O} and T_{bath}.

Two blank tests of the insulating box, without samples, were carried out to evaluate the dispersion through the walls. The computation of the heating value of the unknown sample starts from the Eq. 8.

$$\begin{aligned} m_{H_2O} \times Cp_{H_2O} \times (T_{H_2O\_end} - T_{H_2O\_start}) \\ = m_{sample} \times Cp_{sample} \times (T_{sample\_start} - T_{sample\_end}) \end{aligned} \tag{8}$$

Where $\text{Cp}_{\text{sample}}$ is the specific heat (the unknown value of the equation). $T_{sample\_start} = 30\ °C$ due to thermal conditioning in the thermostatic bath and $\text{T}_{\text{sample\_end}} = \text{T}_{\text{H}_2\text{O\_end}}$ as the equilibrium has been reached.

2.4 Measurements of solar reflectance

The solar reflectance of the samples was measured through a solar spectrum reflectometer, (Model SSR-ER version 6) following the ASTM C1549.

For each sample five measurements of solar reflectance were made in five different areas of the surface of the 0.5×0.5 m samples. The final value was calculated as the average value.

3. Results and discussion

Thermal conductivities measured for every sample are summarized in Table 4.

Table 4. Samples thickness and thermal conductivity

	Sample thickness[mm]	Thickness uncertainty [mm]	Thermal conductivity λ_x [W/(mK)]	Thermal conductivity uncertainty ε_{λ_x} [W/(mK)]
WOOD	11.37	0.01	102.54×10^{-3}	1×10^{-3}
SOIL_DRY	40.00	0.01	228.50×10^{-3}	0.05×10^{-3}
SOIL_20	84.16	0.01	380.66×10^{-3}	0.22×10^{-3}
SOIL_30	84.36	0.01	1200.00×10^{-3}	1.11×10^{-3}
SOIL-CHAR_DRY	83.89	0.01	221.86×10^{-3}	0.06×10^{-3}
SOIL-CHAR_20	84.98	0.01	376.24×10^{-3}	0.12×10^{-3}
SOIL-CHAR_30	86.83	0.01	1132.24×10^{-3}	0.90×10^{-3}
SOIL-CHAR_36	32.28	0.01	1867.93×10^{-3}	0.1×10^{-3}
CHAR_DRY	19.40	0.01	70.00×10^{-3}	0.02×10^{-3}
CHAR_50	22.2	0.01	500.00×10^{-3}	0.02×10^{-3}
CHAR_67	21.7	0.01	2480.20×10^{-3}	0.03×10^{-3}

Literature values for biochar thermal conductivity are between 0.10 to 0.13 W m^{-1} K^{-1}, depending on the temperature of the process which is responsible for the microstructure, mineralogy, and physicochemical properties [20]. Biochar thermal conductivity is lower compared to soil thermal conductivity. The addition of biochar to soil does not significantly affect its thermal conductivity in dry conditions, while the effect of humidity is dominant. This effect is confirmed also by SOIL-CHAR_36 sample whose thermal conductivity value is the highest for the soil – char matrices. The CHAR_50 and CHAR_67 enable the attribution of a significant role to water in the thermal conductivity value of this material. In fact, an increase in humidity of only 17% produces a significant increase in the $\boldsymbol{\lambda}_x$ value.

Table 5. Solar reflectance and specific heat

	Solar reflectance [-]	Specific Heat [J/(kg K)]
SOIL_DRY	0.283	930
SOIL_20	0.201	-
SOIL_30	0.240	-
SOIL-CHAR_DRY	0.134	-
SOIL-CHAR_20	0.136	-
SOIL-CHAR_30	0.139	-
CHAR_DRY	0.109	1310
CHAR_20	0.098	
CHAR_30	0.095	

The specific heat of the mixture can be calculated as weighed average of the specific heat of the components of the matrices, for this reason the measurements were performed only on soil and biochar and not on their mixtures. The specific heat of pure soil was in line with literature values that range from 1.17 to 2.25 kJ kg^{-1} $°C^{-1}$ for clay and from 0.83 to 1.67 kJ kg^{-1} $°C^{-1}$ for sand (moisture content 20/25%) and density of 1300 kg m^{-3} [23]. Specific heat of biochar was similar to soil (slightly higher). Therefore, the addition of biochar could alter the specific heat of the mixture primarily because of its higher water retention capacity. This, in turn, increases the maximum soil moisture and extends its duration, while the contribution of the specific heat of the carbonized material can be considered negligible. Concerning solar reflectance, it was lower for biochar than soil and adding biochar to soil is reduces its solar reflectance. From Table 5 it can be seen that the humidity seems to reduce the solar reflectance of the matrix, however the relationship humidity-solar reflectance is not straightforward.

4. Conclusion

Biochar and soil thermal properties measured in this work are in line with scientific literature for the agronomic field.

Soil thermal conductivity can be properly measured by means of a hot plate instrument. This method, compared to the most common one consisting in the dual needles probes, allows a fast measurement of different soil matrices with different compositions (lamoy soil, clay soil, sandy soil) and also of different biochar/soil mixtures with different humidity even with little amount of available material. It would be also possible to simulate different soil depths by compressing the soil with the proper pressure. All this data can be extremely useful for studying possible new soil applications such as low enthalpy geothermal heating and cooling systems that combine energy efficiency and carbon sequestration and storage. The addition of biochar to soil does not significantly modify its thermal conductivity in dry condition, but through biochar water retention capability a higher conductivity can be reached at high moisture content. Biochar reduces solar reflectance of soil.

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