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## Article

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## Biochar from pyrolysis of biological sludge from wastewater treatment

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### Abstract

It was studied the production of biochar by pyrolysis of biological sludge from wastewater treatment in the pulp and paper industry. The pyrolysis process was conducted in bench-scale fixed-bed reactor using distinct operating conditions of heating rate (2, 10, 20 and 30 °C/min) and peak temperature (300, 375, 450, 525, and 600 °C). The biochar yield is in the range 0.40 to 0.73 kg/kg dry sludge, and decreases with increasing peak temperature and heating rate. The organic matter content of the biochar is in the range 55.9 to 75.3%wt. (dry basis). Both the temperature increase and the heating rate increase promote the decrease of biochar volatile matter content within values between 14.4 and 48.4%wt. (dry basis). The biochar ash content increases with peak temperature and heating rate, and it has values in the range 24.7 to 44.1%wt. (dry basis). The corresponding fixed carbon content is between 26.2 and 42.4%wt. (dry basis), and increases with an increase in the peak temperature. The carbon concentration in the biochar is in the range 42.8 to 47.0%wt. (dry basis). The biochar pH is in the range 6.9 to 11.2, and the electrical conductivity (EC) is in the range 2.2 to 5.0 mS/cm.

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**Keywords:** Biological sludge; Pyrolysis; Heating rate; Peak temperature; Biochar

### 1. Introduction

Solutions for management of biological sludge from treatment of liquid effluents in the pulp and paper industry have been applied [1], such as the use as fertilizer in agricultural soils or their composting in combination with residual forest biomass or their combustion. However, it is recognized the need of alternative treatment options to support proper management of this waste [2], e.g., in result of more restrictive environmental regulations.

The energy recovery from biological sludge has been gaining importance as management alternative, integrated in thermochemical conversion processes, namely combustion, with recovery of thermal energy. However, among

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the reasons that have been contributing to the low penetration of this technology as a management solution for the biological sludge are those related with the high moisture and inorganic (ash) content, and in particular the negative effects (e.g., corrosion) promoted by the inorganic constituents in the energy conversion equipment [3,4].

The conversion of the biological sludge by pyrolysis process can prevent technical problems as those observed during combustion and gasification processes and related to the inorganics, and allows to obtain a solid organic product, the char (biochar), more stabilized and rich in carbon and inorganics. In fact, the biochar produced by pyrolysis of biomass has emerged as a product with potential for use in several environmental applications [5–8]. The biochar has relevant properties as soil amendment and also as carbon storage in the soil [9], improving the chemical and biological properties of the soil, e.g., increases soil water retention, behaves like pH buffer, allows the recycling of some plant nutrients, and constitutes an important reservoir of carbon in the soil. Another advantage that seems to arise from the conversion of biomass to biochar is that the bioavailability and ecotoxicity related to the heavy metals present in the biomass are reduced in the biochar, because the metals become in more stable forms after the pyrolysis process, resulting in a lower leaching of heavy metals in the biochar [10], and therefore less impact in the soil when compared to the original material.

However, for forest biomass the pyrolysis process and technology have undergone significant developments [5,11,12], but the information on pyrolysis of biological sludge for biochar production is limited. In fact, the few existing studies are mostly related to sludge from treatment of domestic wastewater [13–18], and are scarce for sludge from the biological treatment of liquid effluents from the pulp and paper industry [10,19]. In addition, the analysis of the information produced on sludge pyrolysis does not allow a systematic and unequivocal conclusion about the relationship between the characteristics of the biomass feedstock material, the operating parameters of the pyrolysis process and the properties of the biochar produced, in order to support the development of this technology. Taking into account the variability in sludge characteristics, it is needed detailed knowledge of the behavior in each particular circumstance. It is recognized that the characteristics of the original biomass, and the operating conditions of the pyrolysis process, e.g., the heating rate and the peak temperature, influence the properties of the biochar produced, among them the physical–chemical properties such as density, surface area, porosity, chemical composition, pH, electrical conductivity [5,6,8,20,21], important in the context of further uses of biochar.

In this work it was studied the pyrolysis of biological sludge from wastewater treatment at the pulp and paper industry, to produce biochar and some of its characteristics were evaluated. The goal is to turn the biological sludge in a new product, contributing to the goals of circular economy.

## 2. Materials and methods

The experimental setup used in this work for the pyrolysis experiments is composed of a fixed-bed tubular quartz reactor with 20 mm internal diameter, 23 mm outer diameter and 350 mm length, and a tubular furnace with 25 mm internal diameter and 300 mm length. The tubular furnace is operated by means of a control and data acquisition electronic system that allows the definition of heating rate and peak temperature of the tubular quartz reactor. A thermocouple type K is located at the central region of the quartz tubular reactor in order to allow the monitoring of the temperature and the retrofitting of the unit for control of heating rate and peak temperature. During the pyrolysis experiments the temperature is continuously recorded by the electronic control and data acquisition system. The reactor is operated in batch mode, and for each pyrolysis experiment a mass of sample (biological sludge) of around 20 g was located in the central region of the tubular quartz reactor. The thermocouple is located in the middle of the batch of biological sludge sample. The operation procedure consists in weighting the mass of sample (biological sludge), inserting the batch of sample in the quartz tube, and insert the quartz tube in the furnace. A gas flow composed of  $N_2$  with a flow rate of around 250 mL<sub>NPT</sub>/min was used in the quartz reactor as purge gas in order to prevent the entering of  $O_2$  and to remove the pyrolysis gas released during the process. Thereafter, the electronic control system was switched on for operation of the electric furnace and heating the quartz reactor at the desired pre-programmed heating rate and peak temperature, and soak time. The set of experimental conditions used in this work included heating rates of 2 °C/min, 10 °C/min, 20 °C/min and 30 °C/min. For each heating rate, peak temperatures of 300 °C, 375 °C, 450 °C, 525 °C and 600 °C were used. The soak time used for all experiments was 30 min. Immediately after the soaking time, the quartz tube reactor was removed from the furnace and left at room conditions for quenching, always with a purge of  $N_2$  passing through the pyrolysis reactor.

Samples of biochar produced under distinct operating conditions of peak temperature and heating rate were characterized for several physical–chemical parameters with relevance in the context of environmental applications

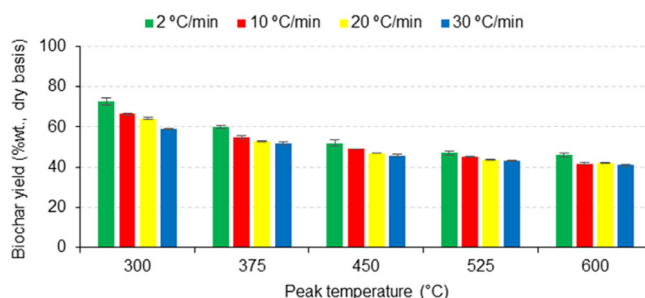
of biochar, e.g., as soil amendment. Among these characteristics are the particle size, proximate analysis (volatile matter, fixed carbon and ashes) and ultimate analysis (CHNS), volumic mass, pH and electrical conductivity following standard procedures for biomass.

The raw biological sludge used was received with an average moisture content (determined at 105 °C) of 89.2%wt. (wet basis), an ash content (determined at 550 °C) of 18.1%wt. (dry basis), volatile matter content of 69.3%wt. (dry basis) and fixed carbon content of 12.6%wt. (dry basis). The biological sludge was pre-dried at atmospheric conditions, and for the pyrolysis experiments the samples were used with an average moisture content of 8.3%wt. (wet basis).

### 3. Results and discussion

The results presented in this work include the biochar yield for the distinct operating conditions tested and the respective physical-chemical characteristics for some parameters.

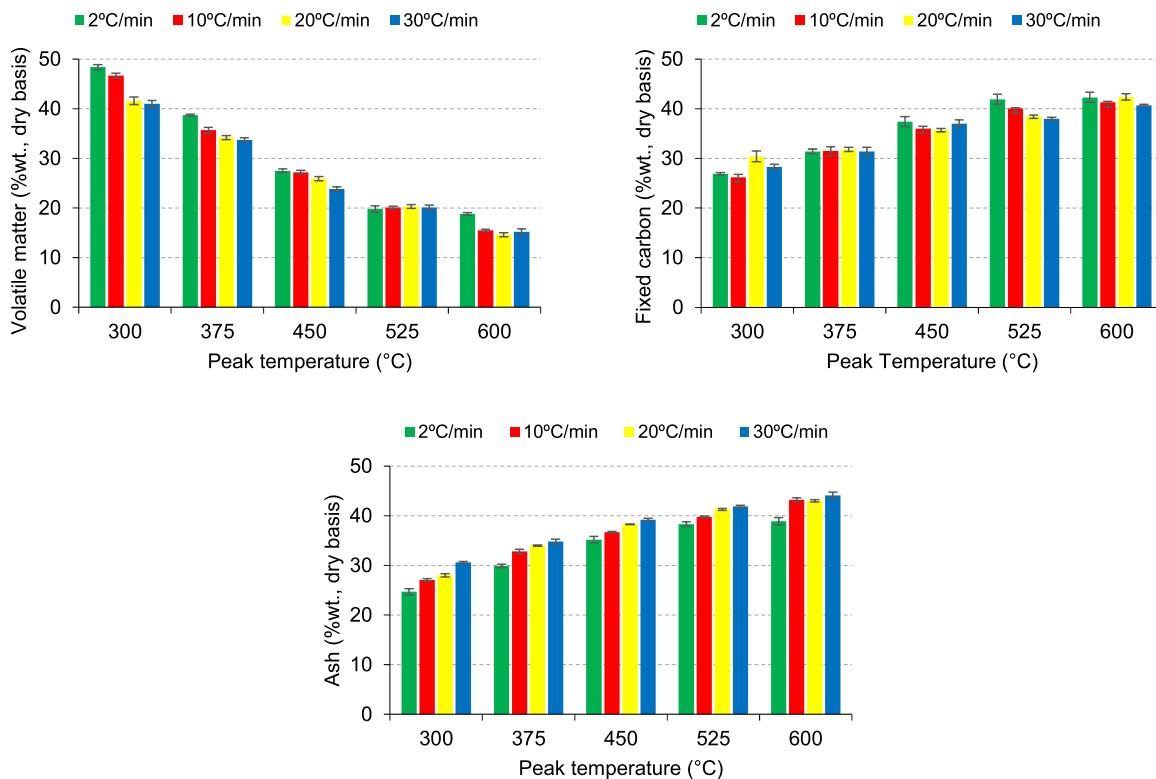
The biochar yield was in the range 0.40 to 0.73 kg/kg dry sludge (Fig. 1). Higher yield of biochar was observed with decreasing peak temperature and heating rate, in accordance with that reported in literature [15,16], and can be explained as resulting from the promotion of the thermal decomposition of biomass with increasing temperature and heating rate.



**Fig. 1.** Mean values of biochar yield (mass of biochar per mass of dry sludge, expressed as percentage) as a function of pyrolysis heating rate (°C/min) and peak temperature (°C).

The proximate analysis of the biochar produced is shown in Fig. 2, with the values shown in dry basis (db). It is observed that both the increase in peak temperature and heating rate promote the decrease in volatile matter content, with values between 14.4%wt. (db), observed at 600 °C and 20 °C/min, and 48.4%wt. (db) at 300 °C and 2 °C/min. Otherwise, the ash content of the biochar increases with peak temperature and heating rate, with the minimum value of 24.7%wt. (db) observed for 300 °C and 2 °C/min, and the maximum value of 44.1%wt. (db) observed for 600 °C and 30 °C/min. The increase in ash content with the increase in the temperature and heating rate is a consequence of the higher thermal decomposition of the organic fraction of the solid biomass with the increase in the severity of the thermal process, which has as consequence the enrichment in inorganic (the ash) elements in the biochar. This enrichment in inorganics (ash) in the biochar is of the order of 1.4 to 2.4 times the value of ash present in the raw sludge (db). The relevance of this inorganic fraction of the biochar in the context of the further environmental applications, e.g., as soil amendment, must be further evaluated considering its chemical composition (e.g., in alkalis and metals with environmental relevance, namely the potential toxic elements). The fixed carbon content, determined by difference between the total mass of biochar and its volatiles and ash content, has a minimum value of 26.2 wt% (db) at 300 °C and 2 °C/min, and a maximum value of 42.4%wt. (db) at 600 °C and 20 °C/min. A direct relation between the increase in peak temperature and the increase in the fixed carbon content of the biochar is observed, but there is not a clear effect of the heating rate; in fact, a decrease, an increase or almost no effect of heating rate on the fixed carbon content of the biochar can be observed, depending on the peak temperature (Fig. 2). There is also a decrease in the organic matter content of the biochar with increasing peak temperature, with the lowest value of 55.9%wt. (db) observed at 600 °C and 30 °C/min, and the highest value of 75.3%wt. (db) observed at 300 °C and 2 °C/min.

The carbon concentration in the biochar is in the range 42.8 to 47.0%wt. (db), with the lower value observed at 450 °C and 30 °C/min and the higher value observed at 525 °C and 2 °C/min (Fig. 3). For each heating rate,

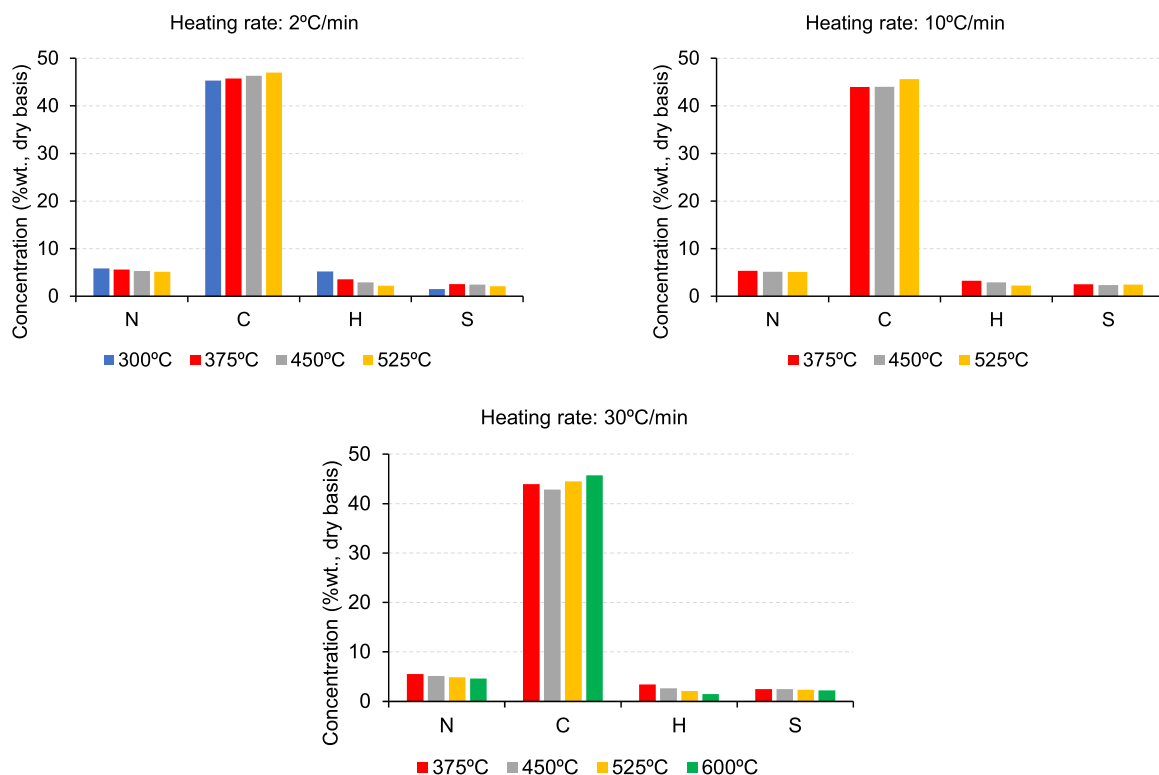


**Fig. 2.** Proximate analysis (volatile matter, fixed carbon and ash content, expressed as %wt. of dry matter) of the biochar produced at distinct heating rate (°C/min) and peak temperature (°C).

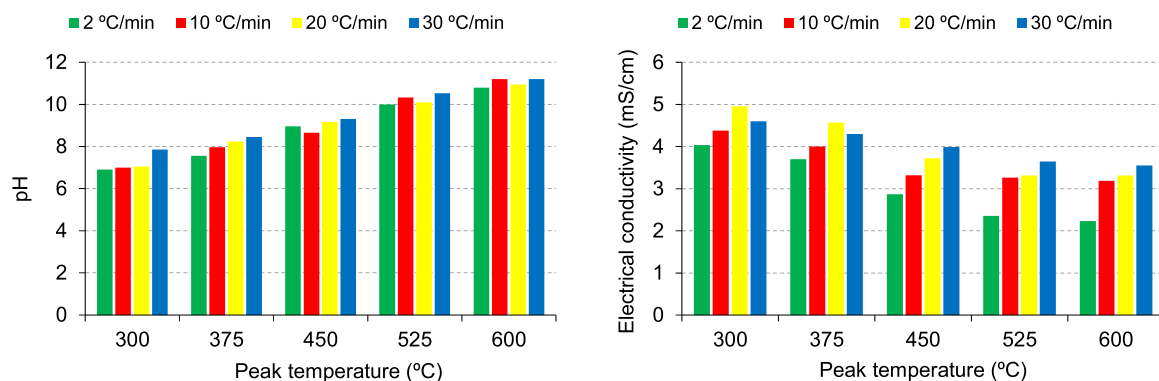
the carbon concentration increases with increasing peak temperature, and for each peak temperature the general trend is a decrease in the carbon concentration with increasing heating rate (Fig. 3). The hydrogen concentration in the biochar is in the range 1.5 to 5.2%wt. (db), with the lower value observed at 600 °C and 30 °C/min and the higher value observed at 300 °C and 2 °C/min. For each heating rate, the hydrogen concentration decreases with increasing peak temperature, and for each peak temperature there is a minor influence of heating rate, although a slight trend to a lower hydrogen concentration in the biochar is observed at higher heating rate (Fig. 3).

The nitrogen concentration in the biochar is in the range 4.6 to 5.9%wt. (db), with the lower value observed at 600 °C and 30 °C/min and the higher value observed at 300 °C and 2 °C/min. For each heating rate, the nitrogen concentration decreases with increasing peak temperature, and for each peak temperature there is a minor influence of the heating rate, although a slight general trend to a decrease in nitrogen concentration with increasing heating rate is observed (Fig. 3). The concentration of sulfur in the biochar is in the range 1.53 to 2.54%wt. (db), with the lower value observed at 300 °C and 2 °C/min and the higher value observed at 375 °C and 2 °C/min. There is a minor influence of peak temperature and heating rate on the sulfur concentration in the biochar produced; nevertheless, with exception of the lowest sulfur concentration observed in the biochar produced at 300 °C and 2 °C/min, it is possible to identify a trend for a slight lower sulfur concentration in the biochar produced at higher temperatures (Fig. 3).

The biochar pH is in the range 6.9 to 11.2, with the lower value observed at 300 °C and 2 °C/min and the higher value observed at 600 °C and 30 °C/min. For each heating rate, the biochar pH increases with peak temperature, and for each peak temperature the general trend is an increase of pH with the heating rate, although some exceptions can be observed (Fig. 4). The electrical conductivity (EC) of biochar is in the range 2.2 to 5.0 mS/cm, with the lower value observed at 600 °C and 2 °C/min and the higher value observed at 300 °C and 20 °C/min. For each heating rate, the EC decreases with the peak temperature, and for each peak temperature the general trend of EC is to increase with heating rate, although for the lower peak temperatures of 300 °C and 375 °C there is a decrease of EC when increasing the heating rate from 20 °C/min to 30 °C/min (Fig. 4).



**Fig. 3.** Mean values for the concentration of chemical elements CHNS (expressed as %wt. of dry matter) of the biochar produced at distinct heating rate ( $^{\circ}\text{C}/\text{min}$ ) and peak temperature ( $^{\circ}\text{C}$ ).



**Fig. 4.** Mean values of pH and electrical conductivity (mS/cm) of the biochar produced at distinct heating rate ( $^{\circ}\text{C}/\text{min}$ ) and peak temperature ( $^{\circ}\text{C}$ ).

#### 4. Conclusion

Biological sludge from wastewater treatment from pulp and paper industry was used to produce biochar by pyrolysis process in a bench-scale fixed-bed reactor using distinct operating conditions of heating rate (2, 10, 20 and 30  $^{\circ}\text{C}/\text{min}$ ) and peak temperature (300, 375, 450, 525, and 600  $^{\circ}\text{C}$ ). The biochar yield is in range 0.40 to 0.73 kg/kg dry sludge, and decreases with increasing peak temperature and heating rate. The organic matter content of the biochar is in the range 55.9 to 75.3%wt. (dry basis). Both the temperature increase and the heating rate increase promote the decrease of biochar volatile matter content within values between 14.4 and 48.4%wt. (dry basis). The biochar ash content increases with peak temperature and heating rate, with values in the range 24.7

to 44.1%wt. (dry basis). The corresponding fixed carbon content is between 26.2 and 42.4%wt. (dry basis), and increases with an increase in the peak temperature. The carbon concentration of biochar is in the range 42.8 to 47.0%wt. (dry basis). For each heating rate, the carbon concentration increases with increasing peak temperature, and for each peak temperature the general trend is a decrease in the carbon concentration with increasing heating rate. The biochar pH is in the range 6.9 to 11.2, and the electrical conductivity (EC) is in the range 2.2 to 5.0 mS/cm. Several of these properties of the biochar produced comply with international standards for biochar, but further complementary analysis are needed to verify the suitability of the biochar produced to be used in environmental applications, e.g., as soil amendment.

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