Biochar production from sewage sludge and microalgae mixtures: properties, sustainability and possible role in circular economy

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Abstract
Possible destination for sewage sludge sustainable disposal is its transformation in biochar, achieved by post-processing of the sludge itself through pyrolysis. Biochar from sludge is considered one of the most interesting final products in wastewater-based circular economy, as proven by the multitude of its possible uses tested so far in different areas. Recently, combined activated sludge (AS)-microalgae systems have been proposed to simultaneously remove both carbon and nutrients from wastewaters, as alternative to conventional technologies such as those based on AS. Such innovation could be efficient from the point of view of removal of regulated components from effluents, but it adds potential issues to solid residue disposal practices, as algae normally respond poorly to traditional, mechanical drying processes. In this study, a disposal solution was investigated, consisting of pyrolysation of a mixed sludge/bioalgal matrix under different conditions: in such way, not only landfilled residuals are practically eliminated, but a material with multiple possible beneficial end uses is generated. Initial materials (algae, sludge and
combinations thereof) and end-products (biochar and bio-oil) were physically and chemically characterized after pyrolysis under different conditions. Algae alone were also subject to preliminary solvent oil extraction to assess whether increased biochar production would result from this process modification (which did, increasing biochar production by 25-33%). A comprehensive discussion on properties of end products as function of process design, possible applications in a circular economy cycle, and advantages of co-pyrolysis follows.

Keywords
Slow pyrolysis – microalgae – Chlorella – Biochar analysis – Bio-oil – Sewage sludge disposal

Introduction
Increasing industrialization, demographic expansion and expansion of the transportation and mobility sector worldwide, and especially in developing countries, are the cause of excessive conventional fossil fuels exploitation, leading not only to repeated energy shortages worldwide, but also to increasing global levels of greenhouse gases emissions [1]. Renewable feedstocks and energy sources are thus being investigated to face the demand for cleaner energy alternatives, in order to fulfil growing energy demands. Moreover, increasing carbon dioxide and greenhouse gases emissions into the atmosphere have prompted the ethical obligation to investigate more sustainable and environmentally neutral energy sources [2,3]. A current area of intense investigation is the exploitation of biomasses for energy production [4,5]. Amongst them sewage sludge, the final residue of wastewater treatment in the integrated water cycle, is getting increasing attention as not only it normally requires additional expensive treatment and disposal costs by generating utilities, but it is also targeted for sustainable recovery of materials and energy, in compliance with increasingly ambitious EU objectives of generating circular economy cycles from waste streams [6] in accordance to new paradigms in urban water management [7]. Cost of sludge disposal has been estimated at around 50% of the total cost of wastewater treatment [8] while, at the same time, disposal alternatives under current strategies are getting increasingly limited, since accumulation of heavy metals, organic pollutants and pathogenic organisms in the sludge narrow its continued use in commonly adopted practices, such as direct land disposal and composting [9]. Among possible alternatives, incineration would significantly reduce the quantity of waste to be disposed of, allowing energy cogeneration at the same time [10]. However, this involves high costs for effluent gas treatment, which may contain metals, acidic components and dioxins, in addition it generates
residual ashes considered hazardous waste, and may be poorly accepted, or outright opposed by public opinion. Therefore, researchers’ interest has switched to non-combustion, more environmentally sustainable technologies such as gasification and pyrolysis. Pyrolysis is the thermal degradation of biomass in the absence of oxygen, resulting in the production of liquid (bio-oil) and solid (biochar) residues, and gaseous products (py-gas), effectively transforming wastes into valuable products [11,12,13,14]. These show different possible applications, in particular biochar has proven multiple uses as solid fuel, soil conditioner for agricultural land, and industrial applications in flue gas cleaning, as building material, or aid in contaminated sites remediation [15]. Also, high process temperatures, favour increased stabilization of metals, that concentrate in sewage sludge, into the carbonaceous char matrix, considerably reducing the possibility of their release into soil, and ultimately into the food chain [12,16]. Depending on heating velocity and residence time of the process, pyrolysis can be broadly classified as slow (conventional), or fast. Slow pyrolysis maximises solid fraction (biochar) production, and occurs at long residence times and slow heating rates, while liquid and gaseous energy-rich products (bio-oil or py-gas) fractions are increased during fast pyrolysis [17]. An increase of pyrolysis temperature generally maximizes the gaseous fraction, minimizing the solid yield [18]. Properties of the solid residue (biochar) also vary in terms of carbon content and composition. Concerning energetic aspects, bio-oil and biochar could be used as fuels, meeting increasing needs for energy from non-fossil fuels sources [19,20]. However, biochar derived from sewage sludge generally presents high ash content and lower heating value, diminishing its energetic worth [11].

For this reason, an interesting opportunity could consist in the application of co-pyrolysis of sludge with microalgae, which have been recently investigated both as a wastewater treatment process and potential energy feedstock [21]. Microalgae are unicellular photosynthetic microorganisms capable of fixing carbon dioxide by photosynthesis, with several characteristics that make them suitable for energy recovery [22]. These include: (i) absence of competition with food supply, (ii) high productivity with reduced cultivation areas (oil yield of about 70% by weight of dried biomass, with area requirement of just 0.1 m²/year per kg extracted), (iii) growth possibility on areas not suitable for other crops, without subtraction of soil from food crops cultivation, (iv) production in most types of water (fresh, brackish and waste water), with minimal or positive impact on water resources use [23]. Microalgae present positive impact also on carbon dioxide emissions, in fact they contain about 50% C over dry weight derived mainly from atmospheric CO₂, therefore, production of 100 tons of microalgae allows fixation of about 183 tons of carbon dioxide [24]. High growth rate, cultivation ease, high lipid and low ash contents makes microalgae highly appealing, compared to other biomasses, with high yields in terms of both bio-oil and biochar [25],
as determined with satisfactory results by numerous studies [26–28]. Growth and productivity of microalgae are strongly influenced by environmental and physiological factors, such as temperature, pH, light intensity and nutrient availability [29]. Microalgal biochar has lower carbon content than biochar from other feedstocks, lower surface area, and lower cation exchange capacity, while pH, ash and nitrogen contents and extractable inorganic nutrients are high. These properties make it a useful additive to enhance soils characteristics and improve crop productivity, particularly for acidic soils [12].

Recently, combined activated sludge (AS)-microalgae wastewater treatment systems have been proposed to remove simultaneously both carbon and nutrients from liquid streams, as a more energy sustainable and economic alternative to conventional technologies (e.g. AS with nitrification and denitrification). The cultivation of microalgae in wastewater allows direct removal of nitrogen and phosphorus contained within, producing up to 1 kg of dry biomass per m$^3$ of wastewater [30]. In this alternative to conventional AS processes, bacteria oxidize the organic substance in wastewater to inorganic compounds consuming oxygen, while microalgae use sunlight to absorb inorganic nutrients released by bacteria, including CO$_2$, producing oxygen subsequently used by bacteria for oxidation. Although efficient for liquid streams treatment, such systems generate a residue that is more difficult to handle, as algae normally respond poorly to traditional sludge mechanical separation and drying processes. In fact, algal cells are small (2–20 μm), with density similar to that of water, and rather low (0.5–0.3 g L$^{-1}$) concentration in wastewater [31]. Purpose of this paper is to evaluate biochar and bio-oil production through thermal pyrolysis processes starting from these initial residues (microalgae and AS waste sludge) and their combination, and to determine which conditions are more favourable to optimal recovery of valuable by-products.

2. Materials and methods

Three different materials were tested, characterized and pyrolyzed at two different temperatures throughout the following experiments. Both initial materials and final products were characterised using thermogravimetric analysis (TGA) and infrared spectroscopy (IR). HHV (higher heating value) in recovered biochar samples was also evaluated.

2.1 Samples preparation

A mixed culture of microalgae *Chlorella* was cultivated in four lab-scale open reactors (0.35-0.20-0.10 cm, constant water depth 3 cm) in BG-11 medium (Table 1)
Table 1. Chemical composition of the BG-11 medium

| Compound                        | Concentration (mg L⁻¹) |
|---------------------------------|------------------------|
| NaNO₃                           | 1500                   |
| MgSO₄·7H₂O                       | 75                     |
| K₂HPO₄                          | 40                     |
| CaCl₂·2H₂O                      | 36                     |
| Na₂CO₃                          | 20                     |
| Citric acid                     | 6                      |
| Ferric ammonium citrate         | 6                      |
| H₃BO₃                           | 2.86                   |
| MnCl₂·4H₂O                      | 1.81                   |
| EDTA (disodium salt)            | 1                      |
| NaMoO₄·2H₂O                     | 0.39                   |
| ZnSO₄·7H₂O                      | 0.222                  |
| CuSO₄·5H₂O                      | 0.079                  |
| Co(NO₃)₂·6H₂O                   | 0.049                  |

A domestic aquarium aerator provided air bubble agitation to keep microalgae in suspension, light was provided by a conventional warm light LED bulb (40 W) under a 16:8 light:dark sequence. Once the culture reached stable growth, microalgae were harvested, dried on nylon filters (⌀ = 0.25 μm) for 12 h, and pulverized to uniform size in a mortar. Sewage sludge (mixture of primary and secondary sludge) was collected from a nearby wastewater treatment plant and dried at 100°C for 12 hours (reaching humidity content below 10%). The third material tested was a mixture of sludge and microalgae with high humidity content, collected from a phytoremediation plant in Spain (kindly supplied by FCC Aqualia S.A.). Fresh material was distributed in 2 cm layers in a crystallizer, and then dried at 100°C for 12 hours to reduce humidity below 10%. Subsequently, dried material was shredded, to obtain a resulting grain size as uniform as possible.

2.2 Oil extraction from microalgae

Previous studies assessed that preliminary oil extraction from dried microalgae samples lead to enhanced bio-oil and biochar recovery yields from a subsequent thermal processing. Combination of a two-step lipid extraction and slow pyrolysis processing regime may in fact yield an oil product high in valuable fatty acids, with no variation on its quality, compared to the one-step process, with overall increased yields of liquid and solid fractions over the gaseous one [32,33]. Therefore, preliminary microalgae solvent oil extraction was performed using a chloroform-methanol ratio 2:1, as described in [29]. From a fraction of the two algae-containing materials described in the previous section, 1 g of dried sample was immersed in 20 mL of solvent solution in a flat-bottomed pyrex glass flask, stirred for 25 minutes, then centrifuged for 20 mins at 4000 rpm. The liquid fractions
were then filtered and evaporated in a rotary evaporator (Rotovapor, Buchi) to remove solvent and determine the weight of the extracted oil.

2.3 Thermogravimetric analysis (TGA) and infrared spectroscopy (IR)

Aliquots (20 g each) of the initial and processed materials (sludge, algae and sludge mix, powdered algae) were subject to thermogravimetric analysis (TGA, 25–800 °C, heating speed 20 °C min⁻¹, with TGA1 Star System, Mettler Toledo). TGA analysis weights any changes in samples as a function of increasing temperatures. Thermal degradation of samples occurs in multiple stages between initial and final temperature settings. TGA was first conducted under nitrogen (nitrogen-TGA) atmosphere (0.4 L min⁻¹) to identify the temperature at which pyrolysis process began, later under air (air-TGA), to determine samples’ ash and inorganic material content. Both nitrogen- and air-TGAs were subsequently carried out also on solid residue samples deriving from pyrolysis, to assess the characteristics of processed materials, and compare their ash content. Subsequently, a nitrogen-TGA analysis was carried out on residues of microalgae subject to solvent oil extraction. Infrared spectroscopy (IR) was also used to characterize initial materials, liquid and solid residues from pyrolysis, and to detect any presence of water in liquid samples.

2.4 Pyrolysis process and products recovery

Initial substrates were pyrolyzed in a thermostatic sand bath S-70 (FALC instruments) during the experiments. Process equipment is schematized in Figure 1. A flat-bottomed pyrex glass flask containing 20 g of sample was immersed within the heating sand medium in contact with its bottom. The absence of oxygen was ensured by continuous flow of nitrogen blown directly inside the reactor. A three-way glass fitting was connected by silicone tubing to a solvent trap containing acetone, and immersed in crushed ice, for recovery of the oily fraction. Py-gas thus flowed through the tubing, entering the trap where it condensed. The non-condensable py-gas was not further characterized and eliminated from the system. Experiments were conducted at 500°C and 350°C temperatures for each sample. In tests at 500 °C the oven was kept operating at maximum temperature, monitoring the temperature curve with a thermocouple inserted in the sand bath. Once the desired set-point was reached, temperature was kept constant for 30 minutes before switching off the heating device. As for the remaining tests, temperature was monitored with the thermocouple until reaching 350°C, manually maintaining this value for about 30 minutes by acting on the oven’s thermoregulator. After cooling, the process’ solid and liquid products were recovered.
All tests were conducted in triplicate. Table 2 summarizes samples analyses throughout the experiment.

![Schematic of the pyrolysis equipment.](image)

**Figure 1** – Schematic of the pyrolysis equipment. 1) Carrier gas tank (N\textsubscript{2}); 2) flowmeter; 3) Erlenmeyer flask containing sample; 4) sand bath; 5) thermocouple; 6) scrubber with solvent trap

**Table 2** – Tests summary

| Sample ID | Substrate                  | Temperature |
|-----------|----------------------------|-------------|
| 1         | Microalgae *Chlorella*     | 500 °C      |
| 2         | Microalgae *Chlorella*     | 350 °C      |
| 3         | Sludge from WWTP           | 500 °C      |
| 4         | Sludge from WWTP           | 350 °C      |
| 5         | Mix Algae +Sludge         | 500 °C      |
| 6         | Mix Algae+Sludge          | 350 °C      |

Solid (biochar) and liquid (bio-oil) product fractions were recovered from each test, while the uncondensed gas fraction was considered irrelevant for purposes of this work, and only estimated through mass balance. After completion of each pyrolysis test, all glassware and tubing were washed with acetone to remove all residual solid and oil particles still contained therein. This resulted in a mixture of biochar, bio-oil, acetone and water, subjected to further treatment for components separation. For the solid fraction, filtration with Buchner funnel, with weight determination before and after filtration to quantify the separated fraction was performed. The liquid fraction (a mixture of acetone and oil) was transferred into a balloon flask, and vacuum evaporated using Rotavapor R-100 (BUCHI) to remove the solvent, weighting the flask before and after the process. In case water were detected in the sample during IR analysis, anhydrous Na\textsubscript{2}SO\textsubscript{4} was added to the solution, that was then filtrated and evaporated.

Yields of biochar and bio-oil recovered were calculated as follows (Eqs. (1) and (2), respectively):
\[ y_{\text{char}} = \frac{W_{\text{biochar}}}{W_i - W_{H_2O}} \cdot 100 \]  
(1)

where \( W_{\text{biochar}} \) is the weight of biochar recovered, \( W_i \) is the initial sample weight (20 g) and \( W_{H_2O} \) is the water weight in the initial sample, as determined from TGA analysis, and

\[ y_{\text{oil}} = \frac{W_{\text{bio-oil}}}{W_i - W_{H_2O}} \cdot 100 \]  
(2)

where \( W_{\text{bio-oil}} \) is the weight of bio-oil recovered, \( W_i \) is the initial sample weight (20 g) and \( W_{H_2O} \) is the water weight in the initial sample, as before.

2.5 Biochar thermal properties

The calorific value (HHV - higher heating value) of recovered biochar samples was measured with adiabatic calorimeter IKA C6000 Global Standard, in accordance with UNI EN 14918:2010.

3. Results
3.1 Initial materials characterization

TGA was carried out on each initial sample to determine its thermal degradation behaviour. Each material was characterized by both air-TGA (oxidative environment, reproducing a combustion process) and nitrogen-TGA (inert environment), between temperatures of 25 - 800°C.

An oxidative environment allows the ash content of the tested material to be evaluated. TGA in inert atmosphere was also needed to determine the temperature range suitable to pyrolyzation of the samples being tested. The thermochemical process in absence of oxygen leads to degradation of volatile substances in the sample, leaving char as residue. Results of the TGA in both air and nitrogen are summarized in Table 3. According to derivative thermogravimetry (DGT) analyses, thermal degradation of microalgae takes place in one single stage, as reported in previous studies [34], while that of mixed sludge and algal samples occurs in two distinct phases. It should be highlighted that the temperature range 200-500°C includes the highest degradation peaks for all samples (Figure 2). These are generally associated with carbohydrate and protein de-volatilization [35]. In mixed samples a second peak between 600-700°C also appears, corresponding to degradation of lipids and solid residues [36].
Table 3 – Amount of ashes (%) in the three samples based on TGA analyses.

| Substrate          | % ashes (800 °C) | % residues (char+ashes, 800°C) |
|--------------------|------------------|-------------------------------|
| Microalgae Chlorella | 13.7 ± 2.6       | 25.1 ± 1.4                    |
| Sludge WWTP        | 30.2 ± 1.8       | 36.2 ± 2.1                    |
| Mix A+S            | 24.4 ± 3.1       | 38.7 ± 1.9                    |

Based on ash fractions obtained from TGA analyses, composition of mixed microalgae and sludge from the phytoremediation plant sample was confirmed as 15% and 85% of each, respectively. Ash content in WWTP sludge sample was higher (30.2 ± 1.8%) than in those containing microalgae, meaning that adding even a small amount (15%) of microalgae to the mix positively contributes to the reduction of the ash quantity in residues, improving their energy quality. As for nitrogen-TGA results, it is relevant to see that the quantity of solid residues from the sludge-microalgae mix, is higher than that produced by the single-sludge matrix, leading to increased yield in solid material recovery.

Figure 2 – TG and DTG thermograms of the initial materials (microalgae (A), sludge (S), and mix microalgae and sludge (A+S))
3.2 Biochar production and characterization

Resulting pyrolysis products from tests at 350°C and 500°C were solid (biochar) and liquid (bio-oil) residues. After recovering and separating solid and liquid particles remained in the testing equipment, biochar was weighed directly.

Figure 3 represents the product fractions obtained from tests. For all matrixes examined, pyrolysis at 350°C produced the greatest amount of solid residue (biochar), while higher temperatures (500 °C) generally yielded higher production of bio-oil. Considering only the production yield of biochar, WWTP sludge processed at 350°C gave higher values (82.0 ± 4.4 %) along with the mixed sample at the same temperature (82.7 ± 2.1%). As for liquid residues (bio-oil) yields, higher temperatures usually originate higher fractions than those obtained in the present work [37], nevertheless, all samples processed at 500°C produced 13±3% of bio-oil, a fraction higher than at lower temperature.

Figure 3 – Pyrolysis products: biochar (black), bio-oil (yellow) and gas (light blue, estimated). Error bars represent variability of results between triplicates.
Due to the focus of the present work, only the solid residue was fully characterized. Biochar samples from pyrolysis tests were subject to TGA, IR analysis and HHV (High Heating Value, UNI EN 14918:2010). Under visual analysis, all samples appeared different from each other, with appearance changing according to process temperature and initial material. Samples 2 and 4 from tests at 350°C (Figure 5 e, f) presented fairer color (brownish), compared to all others (black or blackish). Among microalgae-derived biochar samples 1 and 2 (Figure 5 a, d, respectively) no colour differences were detected, but they significantly differed in consistence: sample 2 (Figure 5 d) had a dusty structure, while sample 1 was mostly solid (Figure 5 a). Air-TGA analyses were performed to evaluate ash content of the biochar samples, while nitrogen-TGA was used to evaluate the efficiency of the pyrolysis process (Figure 4), by assessing their supplemental weight loss.

**Figure 4** – TGA and DTG thermograms of biochars from pyrolysis at different temperatures. Left: 500°C; right: 350°C. Heating speed constant for all processes (20°C min⁻¹).
Figure 5 – Upper: samples from pyrolysis at 500°C a) microalgae *Chlorella*; b) sludge from WWTP; c) Mix M+S. Lower: samples from pyrolysis at 350°C: d) microalgae *Chlorella*; e) sludge from WWTP; f) Mix M+S.

IR analysis was performed before and after pyrolysis to evaluate variation of internal material bonds induced by the process (Figure 6), by determining functional groups and bonds within samples. The most significant information in the graphs are contained in the wavelengths representing water and carboxyl groups (between 3600-2500 cm\(^{-1}\)), C-C and C-H bonds (3300 cm\(^{-1}\)); esters and fatty acids (1700 cm\(^{-1}\)), and Si-O bonds in inorganic material (1100 cm\(^{-1}\)). By comparing the different spectra, all samples before pyrolysis appear very similar to each other, although some relationships between components vary. Pyrolyzed samples (only one sample is reported in the figure) show removal of water and organic acids during the process, and reduction of many of the functional groups present. This corresponds to formation of compounds with high carbon content, even if some C-C and C-H bonds are still present. Obviously, Si-O bonds are preserved, as not involved in pyrolysis reactions. Further increasing time of pyrolysis process and temperature would lead to formation of a graphitic carbon, with absence of IR bands detected.
Figure 6 – IR analyses results. Absorbance curves for initial materials and for biochar from Mix A+S at 350°C are shown. Arrows show the relevant sections.

HHV analysis shows that microalgae-derived biochar has higher heating value (samples 1 and 2) than others, decreasing with decreasing process temperature. HHVs of remaining samples, are lower, suggesting that thermal uses might not be indicated as the main final application of these biochars. Significant results are summarized in Table 4.

Table 4 – Amount of ashes detected by air-TGA, weight loss (incomplete pyrolysis) from nitrogen-TGA analysis, and HHV value of biochars obtained in tests (1-6).

| Sample | Pyrolysis temperature [°C] | Ashes [%] | Weight loss [%] | HHV [kJ kg⁻¹] |
|--------|-----------------------------|-----------|-----------------|---------------|
| 1      | 500                         | 41.6 ± 2.3| 16.8            | 29091         |
| 2      | 350                         | 31.5 ± 1.7| 67.5            | 26951         |
| 3      | 500                         | 50.1 ± 2.2| 23.9            | 16629         |
| 4      | 350                         | 37.0 ± 1.9| 46.2            | 15648         |
| 5      | 500                         | 44.3 ± 2.7| 26.8            | 16245         |
| 6      | 350                         | 34.5 ± 3.0| 49.3            | 16671         |

To assess the effect of solvent oil pre-extraction from microalgae on biochar production yield, as suggested in previous studies [32, 33], solid residues after this pretreatment were subject to
nitrogen-TGA, comparing the results with those on raw materials. These samples showed significantly better results, than initial ones: biochar production yield after pre-extraction increased from 25% to 33% in microalgae-only samples. However, no benefits were detected from such preliminary oil extraction in the mixed samples (microalgae and sludge), with 38% biochar yield in both cases.

4. Discussion

This work aimed to assess potential advantages in terms of biochar production and characteristics of the combination of sewage sludge and microalgae as feedstock in pyrolysis processes, with a view to improve the final use value of recovered resources. Product analysis was not limited at observing mass weight obtainable from each matrix, but was extended to determine ash fractions in the final products, and their quality. Alternatives for coupling the two matrixes in one feedstock are feasible: one option could consist of separate microalgae production with direct addition to sludge at the time of pyrolysis. However, this strategy would be of small benefit compared to the direct use of a microalgae-sludge mix originated by a wastewater treatment facility of new conception. This novel type of process, in fact, in addition to allowing simultaneous nutrients removal from wastewater by microalgae, without costly bio-denitrification processes, produces a mixed biomass (sludge and microalgae), originating a solid residue with excellent characteristics after thermal treatment, as reported.

4.1 Comparative analysis

Observed product yields were compared with those obtained by other authors, to validate present results (Table 5). Sewage sludge biochar was obtained by slow pyrolysis in helium atmosphere using a quartz tubular reactor containing 30 g sludge samples by Sanchez et al. [38]. In this study the original matrix had ash content of 3.4% by weight. Tests were conducted at 350, 450, 550 and 950°C, with the largest amount of biochar (52%) produced at the lower temperature of 350 °C, in accordance with the present study.

Microalgae-derived biochar was obtained by Gong et al. [35] using a quartz, fixed-bed reactor under inert (N₂) gas flow, testing 1 g samples at temperatures between 300 and 700°C, with heating rate of 10°C min⁻¹. The study showed that bio-oil fraction increased with temperature from 30.9% (at 300°C) to a maximum of 60.7% (at 500°C), decreasing afterwards to 48.1% (at 700°C). As for biochar yield, the highest amount was obtained at 300°C (57%), decreasing with temperature to a minimum of 25.5%. HHV of the char also decreased with temperature (from 22.3 to 16.4 MJ kg⁻¹),
while gas yield increased along with temperature (from 0.4 to 15.5%). Compared to the results of this study, char production yield from the Chlorella culture was higher, as well as the product HHV.

Results from microalgae and sewage sludge mixtures in this study could not be compared due to the lack of similar literature data concerning these feedstocks co-pyrolysis. The highest productions of biochar were detected in pyrolysis of microalgae alone, while intermediate results were obtained from co-pyrolysis of sewage sludge and microalgae, as expected by preliminary information reported in other studies on co-pyrolysis of microalgae with other, non-sludge matrixes [12].

Table 5 – Product yields of microalgae and sewage sludge pyrolysis.

| Feedstock [Reference] | Pyrolysis type | Temperature [°C] | % biochar | % bio-oil | % gas | HHV [MJ kg⁻¹] |
|-----------------------|----------------|------------------|-----------|-----------|-------|---------------|
| Sewage sludge [38]    | Slow           | 350              | 52        | 10        | 20    | -             |
| Sewage sludge (this study) | Slow     | 350              | 74.3      | 11.5      | 14.2  | 15.6          |
| C. vulgaris [34]       | Slow           | 500              | 31.5      | 49.2      | 4.6   | 19.3          |
| C. vulgaris [36]       | Fast           | 500              | 34.0      | 41.5      | 24.5  | -             |
| C. vulgaris residues [39] | Fast   | 500              | 31.0      | 53.0      | 11.0  | 19.4          |
| Chlorella (this study) | Slow           | 350              | 78.9      | 6.0       | 15.1* | 26.9          |
| Chlorella (this study) | Slow           | 500              | 58.8      | 10.2      | 31.0* | 29.1          |

* gas value estimated

4.2 Possible beneficial applications of biochar

Pyrolysis operating conditions are paramount to determine optimal final uses of derived biochar, since these factors directly contribute to the development of different intrinsic characteristics of the product [40]. It is therefore important to analyse feedstock materials before thermal processing, in order to establish a priori the best application for the biochar that will be obtained under given operating conditions. Results obtained in this study from HHV analysis on obtained biochars, compared with HHV of hard coal (around 30 MJ / kg), prove that biochar from microalgae could in fact be used as fuel (HHVs of 29.1 and 26.9 MJ/kg, not dissimilar from coal’s value). As biochar is the product of renewable feedstock, this would substitute the caloric equivalent amount of fossil fuels, offsetting related GHG emissions. However, other alternative uses of this product are known, a more interesting one being its use in agriculture as soil enhancement or in wastewater or contaminated site remediation as pollutants adsorbent, either a use with greater added value compared to outright combustion. Agricultural use will effectively work as long-term carbon sequestration (also valuable under current policies), uses as adsorbent will substitute other commercial products, after which the spent biochar could be sent to controlled combustion, that would simultaneously serve as final contaminants destruction and exploitation of the char energy content.
The most interesting outcomes for these products, regardless of original feedstock, are in fact considered to be those related to the possibilities of their re-use and valorisation, from an urban (wastewater) based circular economy perspective. An appealing use of biochar is that of soil improver in agriculture, that has shown to allow increase in crop productivity, but also to reduce soil pollution by adsorbing metals and other solute contaminants in groundwater [41]. Biochar in fact has excellent adsorbent capacities for both organic and inorganic pollutants, and by virtue of its C content, also acts as a long-term carbon sink. For proper agricultural use, biochar carbon content must be greater than 50% (dry mass), N and P content should be between 1 and 45%, pH should not exceed 10, and particles’ specific surface should be greater than 150 m²g⁻¹ [42, 43]. Biochars derived from bagasse and vegetal biomass feedstocks generally fit these specifications, and some studies confirmed that also microalgal biochar presented compatible characteristics [44, 45]. Effects of biochar on physical-chemical improvement of soils also depend strongly on the original soil characteristics and on feedstock used for its production [46].

A recent study from Oliveira and co-workers [47] showed that low pyrolysis temperatures (<500°C) favour partial carbonization, producing biochar with smaller pores and reduced surface area, while increasing the presence of oxygen-containing functional groups, making it ideally suitable for removal of inorganic pollutants. On the contrary, biochar produced at high temperatures (> 500°C) could be applied for adsorption of organics, due to higher specific surface area, making it highly suitable for environmental bioremediation of organic pollution and for wastewater treatment applications, specifically for removal of toxic compounds, instead of activated carbon (AC) [48]. In that respect, Alhashimi and Aktas [49] performed a LCA (life cycle assessment) analysis evaluating the relative economic and environmental performance of biochar as adsorbent, compared to AC. Environmental impact was evaluated in terms of energy demand and GWP (Global Warming Potential) for their production. GWP of biochar generation is usually negative (~0.9 kgCO₂eq kg⁻¹), against an average 6.6 kgCO₂eq kg⁻¹ of commonly used AC. Energy demand for biochar production is lower than that required for AC by one order of magnitude (1.1 ÷ 16 MJ kg⁻¹ for biochar, 44 ÷ 170 MJ kg⁻¹ for activated carbon). However, it has to be considered that spent AC is usually not discarded immediately, but regenerated for reuse, while spent biochar is usually destroyed after its first use. As for economic aspects, biochar and AC industrial production costs are comparable, estimated as $5 kg⁻¹ and $5.6 kg⁻¹, but this does not factor in the missed high costs for the original sewage sludge disposal that would otherwise be needed. Some drawbacks of biochar as adsorbent must also be considered, such as less controllable quality and fluctuating efficiency, longer time needed for absorption of certain contaminants, differences in performance of products from different feedstocks. However, environmental advantages are obvious and with adequate
optimization biochar may be considered suitable for most adsorption applications. Finally, due to its high carbon content, biochar has found other applications, for example for use as electrode material in bioelectrochemical systems (BES) in lieu of granular graphite or AC, and many others [42].

4.3 Implications for a biochar-based Circular Economy

All the above mentioned and other additional applications of biochar will gradually be investigated and validated as circular economy becomes an effective part of new economic paradigms. In order to encourage the development of a biochar-based circular economy, attempts at certification of biochar are being carried out. Biochar at the moment is defined according to guidelines from the International Biochar Initiative (IBI Biochar Standards) [50] and the European Biochar Foundation [51]. The former concerns the use of biochar uses in soil, the latter consists of guidelines for sustainable production of biochar. Both these guidelines define biochar as material produced by pyrolysis of biomass under low oxygen conditions, without limitations to the origin of the biomass, therefore both sewage sludge and algae fall under this definition. Both guidelines include specifications about maximum toxicants assessment, and their maximum allowed thresholds. Product certification, although at present existing only for a restricted range of applications, is an important step for setting up reliable and lasting circular economy circuits. While circular economy strategies centered on wastewater treatment by-products in the EU generally postulate their direct re-use in energy production, and alternative could be based on their transformation into new products, not necessarily limited to agricultural use. In order to fulfil future certification and regulation requirements for these products, the next challenge for research and development of biochar-based products lies in achieving a greater understanding and control of pyrolysis processes staring with feedstock pretreatment, additives addition, effect of process operating parameters, process yield in terms of specific product properties, such as heavy metal immobilization, specific surface area, elemental analysis, phosphorus and micropollutants contents.

Decentralized biochar production units would constitute the most efficient way to meet local by-products demand with specific characteristics by using homogeneous site-produced feedstock under purpose-designed process conditions, avoiding the economic and environmental impacts of long-range transportation, promoting local business and employment and locally improving resource efficiency and synergistic opportunities for various local sectors in the transition to circular economy paradigms.

5. Conclusions
This study aimed at assessing the effects of adopting mixtures of sewage sludge and microalgae as feedstock in terms of these residuals’ pyrolysis disposal processes, and specifically of possible improvements of biochar production quantity and quality. Final product analysis was not limited at the determination of relative mass produced from each matrix, but also went further to determine the ash fractions, carbon and energy properties of each final product. Results showed that slow pyrolysis of mixed feedstock (85 and 15% sludge and algae respectively) at temperature of 350°C, yielded 80% of the initial sample by weight as biochar, of which only 24% as ash. Comparing this result to the data from pyrolysis of WWTP sludge at the same temperature, biochar extracted was 74% of the initial sample weight, but with 30% ash content. Therefore, co-pyrolysis of sewage sludge and microalgae yielded a more valuable product, with multiple possible applications. This solution could contribute to the reduction of problems deriving from expensive and/or inappropriate disposal of wastewater treatment residuals.

Various possibilities in terms of implementation of productive biochar reuse have been described. Within a wastewater-based circular economy cycle, biochar is a very valuable material, with multiple possible interesting outlets that need further careful evaluation beyond currently known applications. Standardization and certification of final products characteristics are the keys to a successful circular economy implementation. Some attempts in this sense have been already developed for specific biochar applications. Decentralization of biochar production from local feedstock sources would be the most logical and effective way to implement efficient biochar-based circular economy. Such systems would benefit from more homogeneous feedstock characteristics and the possibility to custom-define and design the required final products characteristics according to local applications, and minimize additional environmental impact.

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