energies

Editorial

Recent Advances in Hydrothermal Carbonization of Sewage Sludge

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Abstract: The transition from the use of fossil fuels to renewable and green energy is a worldwide challenge that must be seriously considered in order to ensure sustainable development and the preservation of the environment. The conversion of wet biomasses (i.e., sewage sludge) into energy through thermochemical processes in general and hydrothermal carbonization (HTC) in particular has been pointed out as an interesting and attractive approach for the energetic and agricultural valorization of the produced solid residues, named hydrochars. The success of such valorization options is highly dependent on these hydrochars' physico-chemical and energetic properties that are influenced not only by the type of the sludge (urban or industrial) and its nature (primary, secondary, or digested) but also by the HTC parameters, especially temperature, pressure, and residence time. This editorial provides a summary of the latest studies regarding the impact of the cited above parameters on the properties of the produced hydrochars. The economic and environmental feasibility of this process for sewage sludge management is also presented.

Keywords: sewage sludge; hydrothermal carbonization; hydrochars; characterization; energetic valorization; agricultural use

Citation: Jellali, S.; Zorpas, A.A.; Alhashmi, S.; Jeguirim, M. Recent Advances in Hydrothermal Carbonization of Sewage Sludge. *Energies* **2022**, *15*, 6714. https://doi.org/10.3390/en15186714

Received: 1 September 2022
Accepted: 11 September 2022
Published: 14 September 2022

1. Introduction

Sewage sludge is produced in large amounts all over the world [1,2]. It mainly results from the treatment of urban/industrial wastewater treatment plants (WWTPs). The sustainable management of this sludge represents a global challenge due to its potential negative effects on the environment. At the same time, these materials are rich in organic matter as well as nutrients that could be valorized for renewable energy production and plant growth [3,4]. Recently, various technologies used for the thermochemical conversion of sludge, including pyrolysis, gasification, and hydrothermal carbonization (HTC), have been highlighted as promising methods for renewable energy recovery [5], the production of materials which can be used as effective amendments in agriculture [6], and the removal of various pollutants from urban and industrial wastewaters [7]. Since sewage sludge consists of wet biomasses with very high moisture contents, HTC has been highlighted as the most adapted technology for their thermal conversion into a solid biofuel, named hydrochar. Essentially, HTC is a process that converts wet biomasses in a closed system at temperatures ranging between 180 °C and 260 °C for 0.5 to 24 h and at elevated autogenous pressures (1–20 bars) due to the gaseous compounds formed during the thermal reaction [8–11]. It is considered a cost-effective technology since it does not require the costly step of pre-drying the sludge. The by-products of the HTC process are: a gaseous stream that is mainly formed by CO_2, a liquor containing a mixture of water and oil, and an energy-dense solid named hydrochar [8,10]. The physico-chemical and energetic characteristics of the sludge-derived hydrochars seem to be dependent on the nature and type of the raw sludge and the HTC conditions. These properties will affect the future valorization of the hydrochars in energetic and/or agriculture domains. This editorial aims to give a concise review of the recent works related to the conversion of sludge into useful materials through the hydrothermal carbonization process. Particular attention will be given to the roles of the sludge type and the HTC experimental conditions on the properties of the generated hydrochars.

2. Effect of Sludge Nature and HTC Conditions on Hydrochars Properties

Various studies have focused on the effect of the type of sludge as well as the HTC experimental conditions in the physico-chemical and energetic characteristics of the generated hydrochars. In this context, Martinez et al. [10] studied, at the laboratory scale, the HTC of a primary sludge (PS) and a bio-sludge (BS) generated from a WWTP of a pulp and paper mill in Finland. They characterized the corresponding generated hydrochars and liquors at temperatures of 180 °C, 200 °C, 220 °C, and 240 °C and with a residence time of 3 h. They showed that, according to the van Krevelen diagram, the increase in the HTC temperature resulted in lower H/C and O/C values and made dehydration and demethylation reactions the dominant carbonization pathways. They demonstrated that the generated hydrochars had improved hydrophobicity, heating value, and energy density ratios. For instance, the high heating value (HHV) of the PS and the BS increased with the rise in the HTC temperature by about 1.3 and 4.9 MJ kg dry-1, reaching values of 18.8 and 24.7 MJ/kg of dry matter, respectively. Regarding mineral contents, the experimental results showed that there was no clear followed trend. It appeared that their contents in the hydrochars were dependent on the nature of the mineral, the type of the sludge, and the HTC temperature. For instance, for Si and Cr in PS and for P and Na in both PS and BS, they were concentrated at a temperature of 180 °C before being dissolved in the liquor with the increase in the HTC temperature. On the contrary, for Si, Ni, and Cr in BS and Al in PS, they were initially removed at a temperature of 180 °C, then re-adsorbed by the hydrochars from the liquid phase. On the other hand, the analysis of the produced liquors showed that their chemical oxygen demand (COD) increased with the HTC temperature (from 126 and 24 mg/L at 180 °C to 331 and 81 mg/L at 220 °C for PS and BS, respectively). This is due to the decomposition of organic acidic compounds that significantly contribute to the acidification of this liquor phase (i.e., 4.07 at 220 °C for PS).

In another study [12], the effect of the type of paper mill sludge (six types: primary sludge: PS; deinked primary sludge: DPS; two types of mixture of primary and secondary sludge: PSS1 and PSS2; mixture of primary sludge and fibers reject: PFR; and pre-thickened sludge: PTS) and the HTC temperature (180 °C, 220 °C, and 260 °C) on the energetic properties of the generated hydrochars were investigated at the laboratory scale. The residence time of the HTC operation was fixed at 0.5 h. The experimental results showed that, except for PTS, the HHV values of the produced hydrochars at the HTC temperatures of 180 °C and 220 °C were relatively similar to the raw feedstocks. However, except for the deinked primary sludge, increasing the HTC temperature to 260 °C significantly increased the HHV and energy densification factor (ED: ratio of the hydrochars' and raw feedstocks' HHV). At this temperature, the HHV of the hydrochars produced from the PS, PSS1, PSS2, PFR, and PTS were assessed to 22.8, 27.4, 28.9, 25.2, and 31.5 MJ kg^{-1}, corresponding to energy densification factors of 1.5, 1.3, 1.5, 1.3, and 1.8, respectively. This behavior is mainly due to the important increase in C and decrease in O contents in these hydrochars compared to the raw sludge materials. Compared to the raw sludge, at a fixed HTC temperature of 260 °C, the C contents of the raw sludge increased from about 35% to 44%, 38% to 41%, 43% to 63%, 40% to 58%, and 24% to 40% for PS, PSS1, PSS2, PFR, and PTS, respectively. At the same time, due to the loss of hydroxyl groups (mainly through the dehydration reaction), the oxygen contents in these respective sludge types decreased from 44% to 19%, 30% to 16%, 46% to 25%, 35% to 9%, and 48% to 3%, respectively, after the HTC process.

The van-Krevelen diagram (H/C vs. O/C) of these hydrochars clearly showed that the HTC process made them more similar to bituminous coals, which is a promising result. On the other hand, the produced hydrochars had higher contents of ash and lignin than the raw sludge, due to the concentration of inorganic components and unbroken lignin. Based on the overall characteristics of the hydrochars, the authors concluded that the one resulting from the mixture of primary and secondary sludge (PSS2) could be used as an interesting material and viable option for co-combustion with coal in existing coal-fired power plants.

The effect of endogenous pressures, which are fixed by various filling levels of the HTC reactor (24%; 32%; 40%, and 48%), on the properties of hydrochars generated from wine sludge at a constant temperature of 200 °C and a residence time of 24 h has been studied at lab scale [13]. The experimental results showed that higher HHV values of the produced hydrochars were observed for higher pressures, with a maximum value of 20.4 MJ kg^{-1}. Concerning the generated liquid fractions, increasing the HTC pressure resulted in an increase in chemical oxygen demand (COD) values (from 235 to 281 g L^{-1}) and a decrease in phenolic contents (from 21 to 16 g L^{-1}). For all filling ratios, the pH values were relatively low (4.9–5.1), due to the formation of organic acids (i.e., acetic and propanoic acids).

In the same context, Merzari et al. [14] studied the effect of the nature of sludge sampled from a WWTP in Italy on the properties of the derived hydrochars. They used three samples: (i) a thickened mixture of primary sludge from a settler and a secondary sludge from an MBR system, (ii) digested sludge before dewatering, and (iii) dewatered digested sludge. The HTC of these samples was carried out at three temperatures of 190 °C, 220 °C, and 250 °C and two reaction times of 0.5 and 1 h. The experimental results showed that the properties of hydrochars are highly influenced by the nature of the used sludge and also by the HTC experimental conditions. For all the sludge types, the total COD contents significantly decreased for all the HTC temperatures and contact times used due to the organic matter dissolution into the liquid phase and its conversion into CO_2, CO, and other non-condensable gases. This step also induced a significant increase in the soluble COD contents with the increase in the HTC process severity, especially for the thickened and digested sludge. Similarly, the pH of the hydrochars decreased with the increase in the carbonization severity, showing the dissolution of the acidic groups under the used experimental conditions. For instance, the pH values of the raw, dewatered, digested sludge (7.0) decreased to 6.0 at 250 °C and 0.5 h and 5.5 at 250 °C and 1 h. Regarding the energetic valorization of the produced hydrochars, the highest HHV (20.7 MJ kg^{-1}) was obtained for the hydrochar produced from the thickened sludge at 190 °C and 1 h, having moderate ash (24.4%) and high volatile matter (71.0%) contents. However, the produced hydrochars presented high O/C contents compared to typical coals which would result in a more important thermal reactivity. Regarding the main heavy metals (Ag, V, Cr, Ni, Co, Mo, As, and Pb), all of the produced hydrochars' contents were lower than those fixed by the international biochar initiative (IBI) for agricultural application. Relatively high P, Mg, Ca, and K contents were observed for hydrochars produced from the digested and the dewatered sludge, which indicates that they may be used as soil amendments.

On the other hand, Gerner et al. [15] investigated the recovery of phosphorus from a slurry generated from the HTC of digested sewage sludge (collected from a WWTP, Switzerland) at a temperature of 200 °C and a residence time of 4 h. This P recovery step was carried out through: (i) direct liquid solid/liquid separation without acid addition (control test: HTC-C), (ii) phosphorus stripping (HTC-PS), where sulfuric acid was added to the slurry followed by vacuum filtration, and (iii) phosphorus leaching (HTC-PL) consisting of liquid/solid separation (rapid sedimentation and decantation), followed by sulfuric acid addition to the collected hydrochars. The experimental results showed that, compared to the blank test, sulfuric acid addition reduced the derived hydrochars' ash contents by 14% to 19%, but increased the S contents by about 10%. The HHVs of the produced hydrochars were evaluated to 11.3 and 13.3 MJ kg^{-1} for HTC-PL and HTC-PS, which are comparable to the value assessed for the raw material (12.7 MJ kg^{-1}). On the other hand, the acid addition has significantly increased P recovery (in the liquid phase) from about 2% (blank test) to 84% and 71% for HTC-PS and HTC-PL, respectively. Fortunately, heavy metals (Pb, Cd, Cu, Ni, and Zn) seem to be well retained by the hydrochars since their contents in the liquid phase were lower than the detection limits, except for Cd (0.9 ppm) and Zn (21–43 ppm). In this context, Luca et al. [16] proved that the HTC of sewage sludge collected from six WWTPs (Italy), at 220 °C for 85 min, efficiently immobilized both heavy hydrocarbons and heavy metals (except arsenic). Moreover, the sum of the polychlorinated dibenzo-dioxins (PCDDs) and polychlorinated dibenzo-furans (PCDFs) in the produced hydrochars was lower than 20 ng kg^{-1}.

Similarly, Song et al. [17] investigated the use of three organic acids (oxalic, tartaric, and citric acids) at a concentration of 5% for the removal of phosphorus contained in a sludge-derived hydrochar (SDH). This SDH was produced through the HTC of sewage sludge collected from a domestic WTTP (South Korea) at a temperature of 200 °C and a residence time of 2 h. They showed that the HTC increased the P_2O_5 percentage in the raw sludge ash from 43.7% to more than 48.1% in the generated hydrochar's ash. The experimental results showed that oxalic acid was the most efficient organic acid since it permitted a P_2O_5 removal efficiency from ash of more than 93.5%. This removal capacity was evaluated to be about 86.7% and only 55.6% for tartaric and citric acids, respectively. Phosphorus elimination occurred mainly through the chelation process, where insoluble phosphorus is converted into solubilized forms. At the same time, the treatment with oxalic acid increased the C content and the HHV of the hydrochar from 45.3% to 50.6% and 20.8 to 22.4 MJ kg^{-1}, respectively. This treatment, at the same time, decreased the solid yield and ash contents from 27.6% to 17.3% and from 56.8% to 54.7%, respectively. According to the preliminary results, for larger applications, the authors suggested using oxalic acid at a concentration in the range of 0.5–1% to reduce the acid-consumption-related cost without a significant decrease in the P removal efficiency and the degradation of the quality of the generated hydrochars.

In another study, Lühmann and Wirth [9] investigated the optimization of enhanced dewaterability and phosphorus release into the liquid phase through the HTC of a dewatered digested sludge collected from a domestic WWTP (Germany). For the optimization of this process, they used the response surface methodology approach for the following parameters range: HTC temperature: 160–200 °C; HTC residence time: 0.5–1.5 h; initial pH: 1.9–8.1. They found that the optimal digested sludge dewaterability (48.6% of dry matter content) and phosphorus release in the liquid phase (70.3%) were obtained at low initial pH values (pH = 1.93) and a moderate HTC temperature (170 °C). Under these conditions, the HHV of the produced hydrochar was evaluated to be about 14.0 MJ kg^{-1}, which is comparable to the raw sludge (14.3 MJ kg^{-1}). The residence time variation did not have a significant effect on the chosen variation range. The authors concluded that the low HTC temperature and short residence time are economically attractive, while the required acid consumption to obtain a highly acidic medium is unfavorable.

On the other hand, Meisel et al. [18] investigated the economic and environmental feasibility of using HTC for the management of the produced sludge in typical German WWTPs. They studied twelve different scenarios including the presence/absence of a digestion step, the absence/presence of HTC at two temperatures (170 °C and 210 °C), and two residence times (2 and 10 h) for valorization in agriculture or energy recovery. They reported that the high expenses involved in the HTC process cannot be covered by the additional energy production and agricultural valorization of the hydrochars. However, introducing sludge digestion and water recirculation to the digester could lead to a significant reduction in the GHG emissions of the HTC process. They concluded that when direct agricultural use or direct co-combustion is no longer permitted in Germany (from 2029–2032), the integration of a digestion step as well as an optimized HTC process would be one of the best valorization options in the future.

3. Conclusions

The hydrothermal carbonization of wet sludge can be considered a promising technology for the preservation of the environment as well as the production of useful materials that can be used for renewable energy recovery and agricultural amendment. The physico-chemical and energetic properties of the sludge-derived hydrochars not only depend on the type of the sludge but also on the HTC experimental conditions (mainly temperature). It is recommended to apply the HTC for digested sludge where water recirculation to the digester is performed.

The upcoming research topics, where ENERGIES and MDPI should play a vital role as leading publishers, would concern mainly the optimization of the HTC process, especially the reduction in the cost related to energy consumption. Moreover, more studies, including technical, economic, and environmental feasibility, should be carried out. In this context, the life cycle assessment (LCA) of the overall process, including wastewater treatment and sludge management, should be taken into account.

Author Contributions: Conceptualization, S.J. and M.J.; methodology, S.J. and M.J.; validation, A.A.Z.; formal analysis, S.J. and S.A., investigation, S.J. and M.J.; resources, S.J., A.A.Z., S.A. and M.J.; writing—original draft preparation, S.J. and M.J.; writing—review and editing, A.A.Z. and S.A.; visualization, S.J. and M.J.; supervision, S.J. and M.J., project administration, S.J.; funding acquisition, S.J., A.A.Z. and M.J. All authors have read and agreed to the published version of the manuscript.

Funding: This work was performed in the framework of projects funded by Sultan Qaboos University (RC/RG-DVC/CESR/21/01), the Open University of Cyprus (Cyprus), and the University of Haute Alsace (France).

Acknowledgments: Thanks to all funding institutions. Special thanks go to the ENERGIES editors and team for their outstanding management of the journal.

Conflicts of Interest: The authors declare no conflict of interest.

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