# CO-HYDROTHERMAL CARBONIZATION OF NON-DEWATERED SEWAGE SLUDGE AND LIGNOCELLULOSIC WASTE – HYDROCHAR AS A POTENTIAL SOLID BIOFUEL

Matheus Cavali[1*], Nelson Libardi Jr.[1], Boram Kim[2], Hassen Benbelkacem[2], Rémy Bayard[2], Adenise L. Woiciechowski[3] & Armando B. de Castilhos Jr.[1]

[1] *Graduate Program in Sanitary and Environmental Engineering, Federal University of Santa Catarina, Florianópolis, Brazil.*
[2] *DEEP (Déchets Eaux Environnement Pollutions) Laboratory, Lyon National Institute of Applied Sciences, Villeurbanne, France.*
[3] *Graduate Program in Bioprocess Engineering and Biotechnology, Federal University of Paraná, Curitiba, Brazil.*
** Corresponding author's email address: cavali.matheus@gmail.com*

## ABSTRACT

Waste valorization is a crucial aspect of implementing a circular economy. Thus, searching for processes that convert wastes into sustainable and marketable products, such as biofuels, is imperative. Co-hydrothermal carbonization (Co-HTC), for instance, is a thermochemical process that can convert wastes into a carbon-rich material named hydrochar, which can be used as solid biofuel. Accordingly, this work produced hydrochar from sawdust (SD) and non-dewatered sewage sludge (NDSS) through Co-HTC and evaluated its potential as a solid biofuel. Both wastes were submitted to Co-HTC at 240 °C using an SD/NDSS ratio of 1/15 for 2.5 h. The hydrochar obtained was evaluated regarding its yield, composition (proximate analysis – C, N, H, S, and O content – and ultimate analysis – moisture, volatile matter, ashes, and fixed carbon content), and thermochemical behavior to verify its potential as a solid biofuel. The hydrochar yield was 58.1% ± 2.6%, presenting a higher heating value (HHV) of around 21 MJ·kg$^{-1}$. In a coal range, the hydrochar remained between lignite and sub-bituminous coal. Therefore, the hydrochar from Co-HTC of SD and NDSS could be used as a solid biofuel, highlighting the potential of this process to promote waste valorization and the development of a circular economy.

**Keywords:** Thermochemical process. Waste valorization. Biochar. Biofuel. Circular economy.

## 1 INTRODUCTION

The increasing waste generation has put pressure on the development of alternatives to reuse residues as inputs for other processes. In this context, the circular economy concept can be brought to light. The circular economy model emphasizes economic growth and activities that are detached from the consumption of finite resources and minimize system wastes [1]. Therefore, waste valorization processes, such as converting residues into biofuels, can contribute to waste management while also avoiding the use of fossil fuels and promoting the development of a circular economy.

Hydrothermal carbonization (HTC) is a thermochemical process that converts organic wastes into hydrochar, a solid material with the potential to be used as biofuel. Hydrochar is a type of biochar with distinct physicochemical characteristics compared to those produced by pyrolysis and gasification. The HTC process is carried out in a liquid medium at temperatures from 180 to 350 °C under autogenous pressure conditions in sealed reactors [2]. Water between 100 and 374 °C becomes subcritical, acting not only as a solvent but also as a catalyst [3]. This makes HTC suitable for wet waste that would otherwise require a drying step if either pyrolysis or gasification were used. In addition, HTC has the advantage of operating at lower temperatures than these other thermochemical processes [4]. When two or more wastes are combined in HTC, this process is then named Co-HTC [5]. From Co-HTC, it is possible to obtain a hydrochar with better physicochemical characteristics than that produced from conventional HTC. For instance, hydrochar derived from sludge typically exhibits low calorific value, low surface area, poor dehydration capacity, and a high concentration of heavy metals. However, Co-CHT can enhance these properties by blending sludge with other waste materials, such as lignocellulosic biomass [6, 7]. Furthermore, Co-HTC requires less water addition than conventional HTC when combining high-moisture (e.g., non-dewatered sewage sludge – NDSS) with low-moisture (e.g., sawdust – SD) wastes [8].

Accordingly, this work aimed to produce hydrochar from SD and NDSS through Co-HTC and evaluate its potential as a solid biofuel. SD and NDSS are abundantly generated in sawmills and municipal wastewater treatment plants, respectively, requiring proper final disposal. Thus, as a step towards the development of a circular economy, the approach proposed here is in line with waste management and valorization.

## 2 MATERIAL & METHODS

The Co-HTC of SD and NDSS was carried out in a stirred reactor (Parr® - Series 4530, Parr Instrument Company) at 240 °C using an SD/NDSS ratio of 1/15 for 2.5 h. The reactor was loaded with a total mass of 400 g that was stirred at 130 ± 4 rpm. The reaction time was considered after reaching 240 °C. After Co-HTC, hydrochar was separated from the effluent by vacuum filtration, dried at 105 ± 5 °C for 24 h, weighed, and stored for further analysis. Hydrochar yield (HY) was obtained with Equation (1), where $m_{hydrochar}$ is the mass of dried solids after Co-HTC and $m_{solids}$ is the mass of input solids in the Co-HTC process.

$$HY\ (\%) = \left(\frac{m_{hydrochar}}{m_{solids}}\right) \cdot 100 \tag{1}$$

Ultimate and proximate analyses were utilized for hydrochar characterization. The ultimate analysis – C, N, H, S, and O content – was obtained with an elemental analyzer (FlashSmart, Thermo Scientific), in which the hydrochar sample undergoes catalytic combustion (dynamic flash combustion at 950 °C in the presence of Sn and $O_2$) for the elements C, H, N, and S. The O content is determined by catalytic pyrolysis at 1065 °C. The proximate analysis – moisture, volatile matter (VM), ashes, and fixed carbon (FC) – was performed according to the ASTM D1762-84 procedure [9]. Based on ultimate and proximate analyses, the higher heating value (HHV) of the hydrochar produced was estimated with Equations 2 and 3, respectively [10].

$$HHV = 0.3491 \cdot C + 1.1783 \cdot H + 0.1005 \cdot S - 0.1034 \cdot O - 0151 \cdot N - 0.0211 \cdot Ashes \tag{2}$$

$$HHV = 0.1934 \cdot VM + 0.4108 \cdot FC - 0.0211 \cdot Ashes \tag{3}$$

To evaluate the thermal degradation of the hydrochar, it was used a thermogravimetric analyzer (TGA/DSC 2 $STAR^e$ System, Mettler Toledo), under an air atmosphere from 30 to 900 °C with a heating rate of 10 °C $min^{-1}$ and a gas flow of 50 mL $min^{-1}$.

## 3 RESULTS & DISCUSSION

The hydrochar yield obtained at 240 °C with an SD/NDSS ratio of 1/15 for 2.5 h was 58.1% ± 2.6%. Figure 1a presents the contents of C, O, H, and N, which were around 55.2%, 18.4%, 4.4%, and 1.4%, respectively. The S content was lower than 0.04%. In Figure 1b, the proximate analysis indicated that the hydrochar composition is 62.7% VM, 15.9% ashes, and 21.3% FC. The FC/VM ratio is called the "fuel ratio"; the higher the fuel ratio, the better the combustion performance of the hydrochar [11, 12]. Since the fixed carbon of SD and NDSS is 15.5% and 1.3%, respectively [8], it is possible to confirm that hydrochar has a higher combustibility than the wastes used in its production. For comparison, Table 1 presents the proximate and ultimate analyses of other hydrochars from similar wastes.

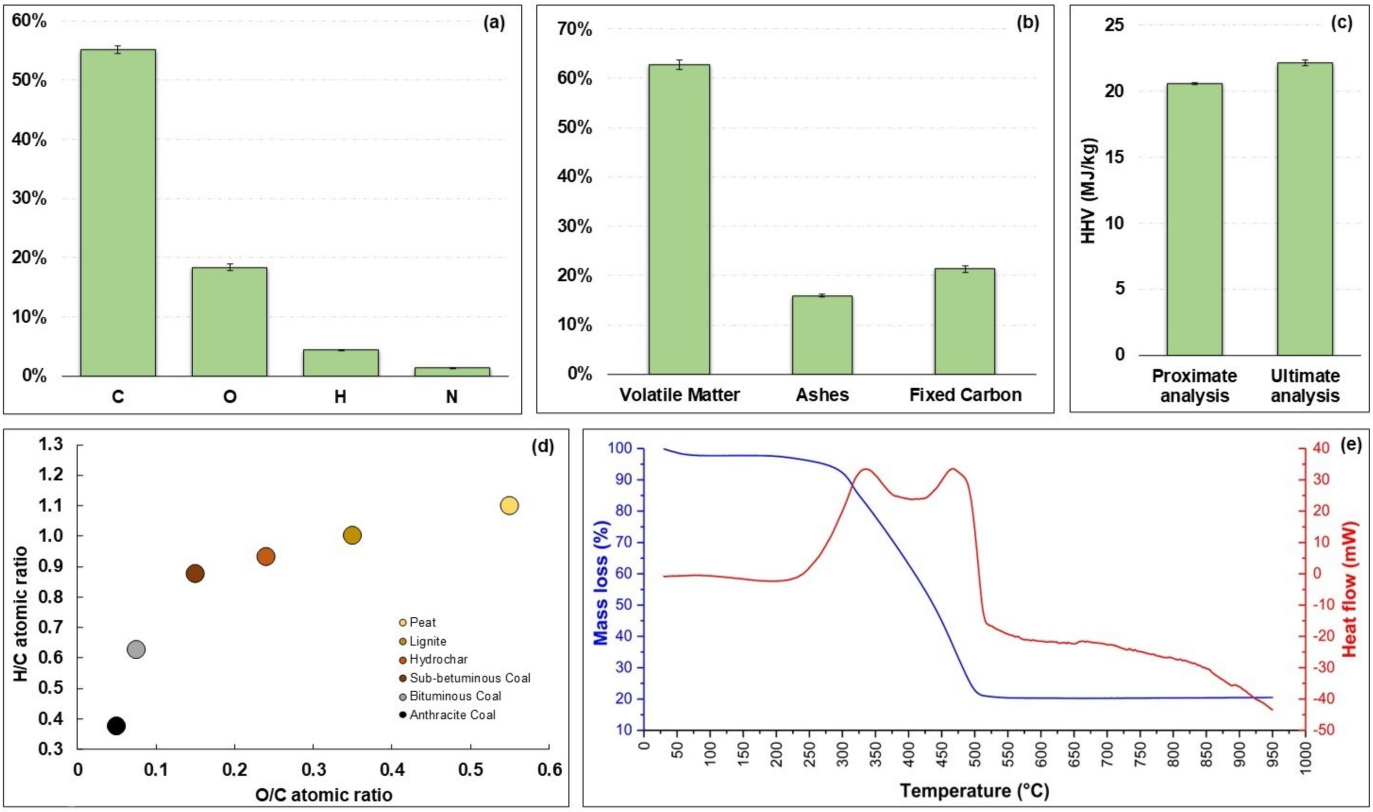

**Figure 1** Proximate analysis (a), ultimate analysis (b), higher heating value (c), Van Krevelen diagram (d), and thermogravimetric analysis (e).

From ultimate and proximate analyses, the HHV was estimated at 20.6 and 22.2 MJ·$kg^{-1}$, respectively, as shown in Figure 1c. For instance, sawdust has an HHV of approximately 18 MJ·kg-1, while sewage sludge can have values ranging from 5 to 15 MJ·$kg^{-1}$ [13, 14]. The H/C and O/C atomic ratios were used to plot the Van Krevelen diagram (Figure 1d), from which it is possible to remark that, in a coal range, hydrochar is between lignite (brown coal) and sub-bituminous coal. This implies, therefore, the coalification of the wastes utilized. Indeed, the Co-HTC process imitates the natural coalification of biomass, but unlike natural coalification which takes millions of years, Co-HTC occurs in just a few hours [15].

**Table 1** Yield and proximate and ultimate analyses of different hydrochars from co-hydrothermal carbonization (Co-HTC) of sewage sludge and sawdust.

| Wastes | Waste A to Waste B ratio (dry basis) | Yield (%) | Proximate Analysis | | | Ultimate Analysis | | | | Ref. |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | VM (%) | Ash (%) | FC (%) | C (%) | H (%) | O (%) | N (%) | |
| Non-dewatered sewage sludge (A)<br>Pine residual sawdust (B) | 1/7 | 58.1 | 62.7 | 15.9 | 21.3 | 55.2 | 4.4 | 18.4 | 1.4 | *This study* |
| Dewatered sewage sludge (A)<br>Sawdust (B) | 3/1, 1/1, 1/3 | 49.7-65.6 | 57.5-71.0 | 4.4-22.7 | 19.8-24.6 | 46.9-54.1 | 5.4-5.7 | 20.8-33.4 | 1.7-3.3 | *16* |
| Dried sewage sludge (A)<br>Sawdust (B) | 1/3, 1/1, 3/1 | 59.4-62.9 | 46.2-65.0 | 13.8-41.0 | 12.8-21.2 | 33.3-49.2 | 3.6-5.4 | 19.0-29.7 | 1.8-2.7 | *17* |
| Dried sewage sludge (A)<br>Sawdust (B) | 1/1 | 48.8-51.9 | 33.2-58.2 | 27.2-50.1 | 14.6-16.6 | 38.4-41.7 | 3.2-4.2 | 2.4-26.5 | 2.1-3.0 | *7* |
| Dried sewage sludge (A)<br>Sawdust (B) | 1/3 | 65.3 | 40.5 | 34.3 | 25.2 | 50.3 | 4.3 | 8.4 | 2.4 | *18* |

According to the thermogravimetric analysis of the hydrochar (Figure 1e), three zones can be noticed in the mass loss profile, which agrees with other works that carried out Co-HTC of similar wastes [17, 19]. Below 250 °C, it occurs the dehydration and release of volatile compounds. Between 250 and 500 ºC, it takes place the combustion of hydrochar, presenting the highest mass loss and heat release. The significant heat release starting around 250 ºC could suggest the zone of the hydrochar ignition temperature. From 500 ºC onwards, the mass loss stagnates, and any heat release occurs after 500 °C, which might indicate the zone of the hydrocar burnout temperature.

## 4 CONCLUSION

Co-HTC of SD and NDSS is a promising thermochemical process to convert these wastes into solid biofuel. The hydrochar, whose yield was 58.1% ± 2.6%, presented a superior HHV (around 21 MJ·kg$^{-1}$) than the untreated wastes. It indicates, therefore, that Co-HTC was effective in concentrating carbon. The FC content of hydrochar was higher than those of SD and NDSS. The content of C, O, and H in hydrochar categorized this material between lignite and sub-bituminous coal in the Van Krevelen diagram, which suggests hydrochar suitability as a solid biofuel. However, future research is required to evaluate the feasibility of this process from an economic perspective since different scenarios could be designed for the Co-HTC of different wastes.

## REFERENCES

[1] TAN, E. C. D., LAMERS, P. 2021. Front. Sustain. 2:701509
[2] PARSHETTI, G.K., CHOWDHURY, S., BALASUBRAMANIAN, R. 2014. Bioresour. Technol. 161:310–319
[3] ZHAO, K., LI, Y., ZHOU, Y., GUO, W., JIANG, H., XU, Q. 2018. Bioresour. Technol. 267:9–16.
[4] CAVALI, M., LIBARDI JUNIOR, N., MOHEDANO, R. de A., BELLI FILHO, P., DA COSTA, R. H., CASTILHOS JUNIOR, A. B. de. 2022. Scienc. of the Tot. Environ. 822:153614.
[5] WANG Q., WU S., CUI D., ZHOU, H., WU, D., SHOU, P., XU, F., WANG, Z. 2022. Scienc. of the Tot. Environ. 850: 158034.
[6] BARDHAN, M., NOVERA, T. M., TABASSUM, M., ISLAM, M. A., ISLAM, M. A., HAMEED, B. H. 2021. J. Clean. Prod. 298: 126734
[7] ZHAI, Y., PENG, C., XU, B., WANG, T., LI, C., ZENG, G., ZHU, Y. 2017. Energy. 127:167-174.
[8] CAVALI, M., BENBELKACEM, H., KIM, B., BAYARD, R., LIBARDI JUNIOR, N., DOMINGOS, D. G., WOICIECHOWSKI, A. L., CASTILHOS JUNIOR, A. B. de. 2023. 340:117994.
[9] AMERICAN SOCIETY FOR TESTING AND MATERIALS. 2021. ASTM D1762 – 84.
[10] KIESELER, S., NEUBAUER, Y., ZOBEL, N. 2013. Energy and Fuels 27:908–918.
[11] HE, C., GIANNIS, A., WANG, J. Y. 2013. Appl Energy 111:257–266.
[12] MA, Q., HAN, L., HUANG, G. 2018. Bioresour. Technol. 269:96–103.
[13] LUNGULEASA, A., AYRILMIS, N., SPIRCHEZ, C., CROITORU, C. 2019. *BioRes*. 14(4), 7821-7839.
[14] YANG, X., LI, H., WANG, Y., QU, L. 2023. *Water.* 2023. *15*(4), 674.
[15] YUSUF, I., FLAGIELLO, F., WARD, N. I., ARELLANO-GARCÍA, H., AVIGNONE-ROSSA, C., FELIPE-SOTELO, M. 2020. 12:100582.
[16] ZHANG, X., ZHANG, L., LI, A. 2017. J. Environ. Manage. 201:52–62.
[17] MA, J., CHEN, M., YANG, T., LIU, Z., JIAO, W., LI, D., GAI, C. 2019. Energy. 173:732-739.
[18] LI, Y., YANG, X., ZHU, M., DONG, L., JIANG, H., XU, Q., ZHOU, H., HAN, Y., FENG, L., LI, C. 2022. Scienc. of the Tot. Environ. 825:153854.
[19] MA, J., LUO, H., LI, Y., LIU, Z., LI, D., GAI, C., JIAO, W. 2019. Bioresour. Technol. 282:133-141.

## ACKNOWLEDGEMENTS

The authors thank the Brazilian foundation Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES) for funding this study (Finance Code 001), the laboratory of the graduate program in Bioprocess Engineering and Biotechnology of the Federal University of Paraná and the DEEP (Déchets Eaux Environnement Pollutions) Laboratory of the Lyon National Institute of Applied Sciences (INSA Lyon) for the supervision and the analyses carried out.