Hydrothermal carbonization of sewage sludge under different reaction conditions: Biodegradability and biomethane potential of the generated liquid fraction

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Introduction

The management of sewage sludge represents a significant environmental and logistical challenge for modern wastewater treatment plants (WWTPs). As urbanization and industrial activities continue to grow, the volume of sewage sludge produced globally is rising, placing considerable pressure on existing disposal and treatment methods. Traditional approaches, such as landfilling or incineration, are increasingly restricted due to stringent environmental regulations and public opposition. Furthermore, these methods often fail to capitalize on the potential value embedded in sewage sludge, such as its organic and nutrient content. Innovative and sustainable solutions are therefore imperative to address the dual objectives of reducing environmental impact and extracting value from this waste stream (Bagheri *et al*., 2023).

Hydrothermal carbonization (HTC) has emerged as a promising technology for the treatment and valorization of wet biomass, including sewage sludge (Kossińska *et al*., 2023). By subjecting the material to moderate temperatures (180–300°C) and autogenous pressures in an aqueous environment, HTC mimics natural coalification processes, producing three main fractions: syngas, a solid hydrochar, and a liquid phase. Each of these fractions has distinct characteristics and potential applications. The syngas can serve as a renewable energy source, while the solid hydrochar is a valuable material that can be used as a fuel, soil amendment, or precursor for advanced carbon materials. However, the liquid fraction generated during HTC has historically been regarded as a less valuable byproduct. This aqueous phase typically contains a complex mixture of soluble organic compounds, including carboxylic acids, phenols, and other oxygenated hydrocarbons. While its direct disposal poses environmental risks, its composition suggests significant potential for anaerobic digestion as a carbon source for biogas production.

This study focuses on optimizing HTC process conditions to maximize syngas and/or high-carbon-content hydrochar production while simultaneously assessing how these conditions influence the biodegradability of the liquid fraction. By exploring the interplay between HTC operating parameters, such as temperature, reaction time, and initial pH, and the characteristics of the liquid phase, this work aims to establish a comprehensive framework for the sustainable and integrated valorization of sewage sludge. The findings of this research will contribute to advancing HTC as a dual-purpose technology that not only produces renewable energy carriers but also facilitates the generation of biogas from its liquid byproduct.

Experimental conditions

HTC experiments were conducted using a laboratory-scale reactor with a working volume of 0.34 L (Figure 1a). This reactor allows precise control over temperature, pressure, and reaction time, ensuring consistent and reproducible conditions. The experimental design followed a Taguchi approach to optimize process parameters and analyze their influence on the resulting liquid fraction. Nine distinct sets of experimental conditions were applied, varying the temperature (180–300°C), reaction time (1–6 hours), and initial pH (2–10), to generate liquid fractions with diverse characteristics. The detailed operational conditions are summarized in Table 1.

Table 1. Experimental conditions for HTC processes.

Experiment:	1	2	3	4	5	6	7	8	9
Temperature (°C)	180	180	180	220	220	220	300	300	300
Time (h)	1	3	6	1	3	6	1	3	6
Initial pH	2	7	10	7	10	2	10	2	7

The raw sludge (Figure 1b), sourced from the primary settler of a municipal WWTP, is characterized by high moisture content (78%), typical of such residues, and a significant organic fraction, with 56.5% volatile matter on a dry basis. Fixed carbon accounts for 33.5%, while ash content is 9.9%, indicating a moderate inorganic component suitable for hydrothermal carbonization processes.

The liquid fractions obtained from these HTC processes were analyzed by GC/MS (Agilent 5977B) to identify organic compounds. Additionally, elemental analysis (LECO CHN828), solids content (total and volatile), and chemical oxygen demand (COD) were measured to provide a comprehensive characterization of these samples. Following these analyses, the fractions were subjected to anaerobic biodegradability tests. The tests were carried out in 1 L stainless steel reactors with a working liquid volume of 500 mL (Figure 1c). The inoculum used was digestate from an anaerobic reactor operating at a municipal WWTP, pre-incubated for 72 hours at 35°C to eliminate residual organic substances. A solution of 10 g/L glucose was prepared, and the liquid samples from the HTC process were mixed to contribute 25% of the organic matter to be digested, while the remaining 75% was provided by the glucose solution. Additionally, 1 mL of nutrient solution was added to each reactor. The nutrient solution composition (in g/L) was: NH4Cl 170, KH2PO4 38, CaCl2·2H2O 8, MgSO4·4H2O 9, FeCl3·4H2O 2, CoCl2·6H2O 2, MnCl2·4H2O 0.5, CuCl2·2H2O 0.03, ZnCl2 0.05, H3BO3 0.05, (NH4)6Mo7O24 0.09, Na2SeO3·5H2O 0.1, NiCl2·6H2O 0.05, EDTA 1, and Resorcinol 0.5. Substrate-to-inoculum ratios were set at 2.0 ± 0.01 gCOD/gVS. Experiments were performed under controlled conditions (34 ± 1°C) with constant agitation. Biogas production was monitored using pressure sensors, and gas composition was analyzed using a Varian CP-4900 Micro-GC equipped with thermal conductivity detectors.

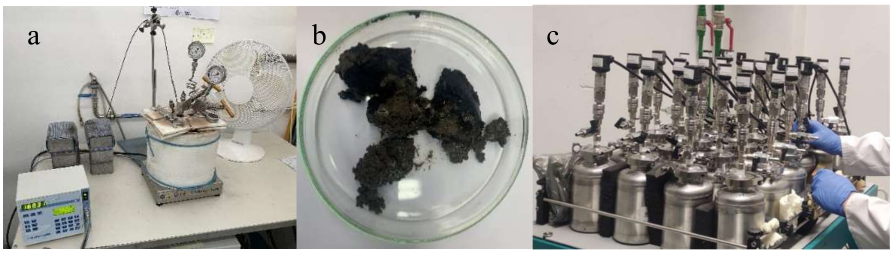

Figure 1: a) HTC lab-scale reactor; b) Sewage sludge entering the HTC; c) Anaerobic digestion test.

Preliminary results

Table 2 summarizes the characterization of the liquid phase obtained from each HTC experiment. Key parameters were analyzed to assess their potential impact on biogas production during subsequent anaerobic digestion.

Table 2. Characterization of the liquid phase from HTC experiments under varying conditions

Experiment:	1	2	3	4	5	6	7	8	9
pH	4.74	7.52	8.05	7.81	7.95	6.91	8.18	7.57	7.89
COD (mg/L)	102058	69953	78294	57757	635001	85484	46882	42491	70032
Total Carbon (%)	4.7	3.4	4.1	2.5	3.6	4.1	2.6	3.1	2.1
Total Solids (%)	10.7	9.3	12	4.8	8.5	10.1	5.1	5.4	1.8
Volatile Solids (%)	9.4	6.6	8.7	4.3	5.5	9.1	2.3	4.9	1.3

The pH of the liquid phase ranges from acidic (pH 4.74 in experiment 1) to slightly alkaline (pH 8.18 in experiment 7). Acidic conditions, observed in experiments with lower pH, may inhibit microbial activity, while neutral or slightly alkaline pH, such as in experiments 2, 3, or 5, are more favorable for anaerobic digestion processes. High COD values, such as those in experiments 1 (102,058 mg/L) and 6 (85,484 mg/L), suggest a substantial presence of biodegradable organic matter, which can enhance methane production. However, excessively high organic loads might require careful management to prevent microbial inhibition. The total carbon and volatile solids content also vary significantly, with experiment 1 showing higher values (4.7% and 9.4%, respectively). These results indicate a greater availability of easily degradable substrates in experiments conducted under milder HTC conditions. Conversely, experiments with more severe conditions, such as experiment 9, show reduced volatile solids (1.3%) and total carbon (2.1%), likely due to the breakdown of organic compounds into smaller, less complex molecules.

Preliminary results from anaerobic digestion tests suggest that milder HTC conditions (e.g., lower temperature, shorter reaction times) tend to produce liquid fractions with higher biodegradability and methane potential. This is likely due to the preservation of easily degradable organic compounds in these conditions, as opposed to harsher conditions where more recalcitrant byproducts may dominate the liquid phase. Further testing will refine these observations and help establish the parameters for large-scale applications.

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References

- Bagheri, M., Bauer, T., Burgman, L. E., & Wetterlund, E. (2023). Fifty years of sewage sludge management research: Mapping researchers' motivations and concerns. Journal of Environmental Management, 325, 116412.

- Kossińska, N., Krzyżyńska, R., Ghazal, H., & Jouhara, H. (2023). Hydrothermal carbonisation of sewage sludge and resulting biofuels as a sustainable energy source. Energy, 275, 127337.