Thermal Science and Engineering Progress 61 (2025) 103461

Contents lists available at ScienceDirect

Thermal Science and Engineering Progress

journal homepage: www.sciencedirect.com/journal/thermal-science-and-engineering-progress

Hydrothermal carbonisation products energy properties: The role of digested sludge type and operating conditions

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ARTICLE INFO

Keywords:
Hydrothermal carbonisation
Wastewater treatment plant
Digested sludge
Process parameters
Biomethane potential tests

ABSTRACT

Hydrothermal carbonization (HTC) is a promising alternative to conventional sludge drying, enhancing energy recovery in wastewater treatment plants (WWTPs). This study examines how temperature, residence time, and sludge collection point influence HTC product properties. Experiments were conducted at 200–250 °C for 30–120 min using digested sludge collected before filtration, after thickening, and after dewatering. Results show that sludge collection point strongly affects hydrochar's higher heating value (HHV), while temperature and residence time influence the biomethane potential (BMP) of HTC liquids. The highest HHV (16.31 MJ/kg) was obtained from dewatered sludge (19.8 % TS) at 250 °C, 75 min, while the highest BMP (506 mlCH_4/g NPOC) was observed from HTC liquids of thickened sludge (11.1 % TS) at 200 °C, 30 min. Findings highlight that sludge pretreatment (thickening, dewatering) plays a crucial role in HTC efficiency, influencing both solid and liquid fractions. From a WWTP perspective, dewatered sludge processed under mild HTC conditions provides the best trade-off between hydrochar quality, HTC liquid valorization, and operational costs. These insights support the optimization of sludge-to-energy strategies, essential for implementing HTC in WWTPs.

1. Introduction

One of the biggest challenges of wastewater treatment plants (WWTPs) is the efficient and environmentally safe disposal of the main by-products of wastewater treatment, known as sewage sludge (SS). The commonly recommended method for stabilising and recovering energy from SS is anaerobic digestion (AD), with the recommended pathway for their further management being agriculture [1]. However, increasing urbanisation and industrialisation are resulting in stricter requirements for increasing primary effluent volumes and secondary effluent quality, which in turn contributes to a continuous increase in SS production, especially for larger WWTPs [2]. AD processes for large facilities are often insufficient and additional digested sludge (DS) mass reduction solutions are required to reduce transport costs. The implementation of thermal processes, such as dryers, is justified as long as the DS residue is used as a fuel in incineration or co-incineration, as the concentrations of heavy metals and organic pollutants in the sludge after drying may continue to pose a threat in the agricultural sector [3,4]. Moreover, drying processes are often energy-intensive, and the relatively low energy quality of dried digested sludge and the efficiency of its use as fuel are important challenges in the industry [5].

Recently, a high-pressure thermochemical process called hydrothermal carbonisation (HTC) is being considered for combination with AD systems to replace drying processes at WWTPs [5–8]. The

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Abbreviations: AD, Anaerobic digestion; ADS, Anaerobic digestion sludge; BMP, Biomethane potential; COD, Chemical Oxygen Demand; DDS, Dewatered digested sludge; DS, Digested sludge/ Digestate; F, Severity factor; FC, Fixed carbon; HHV, Higher heating value; HTC, Hydrothermal carbonisation; NPOC, Non-Purgeable Organic Carb; THDS, Thickened digested sludge; WWTP, Wastewater treatment plant; SS, Sewage sludge; TS, Total solid; DM, Dry matter; VM, Volatile matter; VFA, Volatile fatty acids.

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https://doi.org/10.1016/j.tsep.2025.103461
Received 2 July 2024; Received in revised form 31 January 2025; Accepted 28 February 2025

advantages of this process are the possibility of using wet digested sludge without pre-treatment, the relatively low-temperature conversion process (180–250 °C), the exothermicity of the HTC system and limited waste gas emissions (mainly in CO_2 but also CH_4, CO, H_2S and trace organics) [8] compared to other thermochemical processes. Moreover, this combined process has the possibility of recovering organic matter from DS in liquid form which may have the potential to produce biogas in anaerobic co-digestion with sewage sludge in biogas plants in situ. [5,9–11]. The solid products of the HTC process called hydrochars have interesting properties in both agricultural and energy applications. For agricultural applications, hydrochars from digested sludge have lower organic micropollutant content [12] and a more stable chemical structure (in terms of gas emissions) compared to feedstock [13]. HTC processes can also promote phosphorus bonding in hydrochars, as phosphate forms stable associations with iron and aluminium, leading to its immobilization in the hydrochar. [14] Hydrochars also contain nitrogen, mainly in organic form [15]. However, due to the potential immobilization and concentration of heavy metals in hydrochar, there may be limitations to agricultural use [16]. Therefore various methods of recovering phosphorus from hydrochar are being considered, e.g., with the addition of organic acids such as citric acid [14]. Hydrochars, on the other hand, when considered as a solid fuel, show higher thermal stability compared to feedstock [5], is more hydrophobic [17] easier to dewater [16] and palletize [18]. Lower nitrogen content compared to feedstock [15] may be more favourable in terms of gaseous pollutants. Nevertheless, there is still a major weakness of using hydrochars from DS as potential fuels, namely, the high content of ash and heavy metals as well a low calorific value [19].

The composition of hydrochar is related to the initial composition of the digested sludge [5] and its properties, such as pH [20] and initial moisture content [21]. Numerous studies show that operating conditions such as temperature and HTC process time closely affect the ash content and organic fraction of hydrochar, which affects its energy properties [21–28]. Some studies indicate that higher temperature and longer residence time in the reactor increase the higher heating value (HHV) of hydrochar [22–24], but other reports are contradictory – some show a minimal effect [19,25,26] or even a decrease in heating value after the HTC process [21,27,28]. These discrepancies may be due to differences in the composition of the digested sludge, particularly the presence of conditioning agents such as dewatering polymers [27]. We hypothesize that the type of digested sludge used as an input to the HTC process (before filtration, after thickening, or after dewatering) influences the energy properties of the hydrochar and may affect the methane potential (BMP) of the HTC liquid.

The objective of this study is to determine the effect of temperature and HTC residence time on the quality of products obtained from various types of digested sludge. In particular, we analyze: 1) Differences in the composition of sludge taken from different points at the sludge dewatering site and their effect on the hydrochar properties. 2) The relationship between the initial moisture content of the sludge and the energy quality of the hydrochar (HHV, ash content). 3) Effect of HTC process parameters on biomethane potential (BMP) of HTC liquids from different types of sludge. Previous studies have analyzed the effect of HTC process parameters, but few have compared the effect of sludge intake at different collection points in a WWTPs on hydrochar quality and HTC liquid composition. [19,27,29] Studies by Aragón-Briceño *et al.* [29] showed that initial dry matter content affects HHV, but used sludge before dewatering as a reference. Merzali *et al.* [27], on the other hand, observed significant differences in the properties of feedstock before dewatering 2.9 % w/w and after dewatering 25 % w/w, while Hämäläinen *et al.* [19] for dewatering sludge 25.6 % w/w and diluted to 14 % w/w emphasizing the influence of industrial filtration processes and conditioning agents used. This study will identify and compare the three types of sludge that were most commonly considered in the research, and determine how sludge type affects the properties of HTC products, especially in terms of their suitability as fuel and biogas feedstock. The results may provide important information for wastewater treatment plants that are considering using HTC as a method for treating digested sludge.

2. Materials and methods

2.1. Materials/sample collection and preparation

Digested sludge was collected from WWTP in Ireland with a population equivalent (PE) value of approximately 168,000. Two types of sludge were sampled in large quantities – active digested sludge (ADS) collected before dewatering on the filter press (Fig. 1, sampling point A) and dewatered digested sludge (DDS) collected after the filter press (Fig. 1, sampling point B). Thickened digested sludge (THDS), was obtained by mixing ADS and DDS in a 1:1 mass ratio. Following collection, The samples were transferred to the laboratory and stored at 4 °C. Particular attention was paid to maintaining a stable dry matter content associated with a stable ADS organic fraction, since changes in this parameter over time can have a significant impact on mass balance calculations and product characteristics. To minimize the loss of organic matter during the experiments, the ADS was initially stored in a closed container in the refrigerator for a week. After this period, the sludge was degassed (dry matter loss of 5 % to 2.4 %) and transferred to separate containers. It was found that the sludge, after reaching 2.4 %, significantly reduced the rate of dry matter loss, allowing the ADS samples to remain stable for up to two weeks. DDS, on the other hand, showed no significant change in dry matter content during the same storage period. Prior to conducting biochemical methane potential (BMP) tests, the ADS called also inoculum was pre-incubated at 36 °C to remove residual methane production potential (degassing). This degassing process lasted five days to ensure that methane generation from the inoculum itself was minimized before the experiment.

2.2. Design HTC experiments

The tests were carried out at temperatures of 200–250 °C. The choice of the lower temperature limit was related to the source of sludge, as the digested sludge contains biologically resistant components remaining after the AD process (e.g., crystalline cellulose, some proteins, extracellular polymeric substances (EPS), lignin, humic substances), requiring higher temperatures to initiate hydrothermal conversion processes [5]. In turn, the upper limit of the temperature range was related to the final temperature of HTC and the initial temperature of HTL (hydrothermal liquefaction) [30]. The experiments were conducted for a residence time of 30–120 min. Residence times below 30 min have been rarely considered in the research literature, while times above 120 min were not justified, due to the large amount of heat required and the lack of significant impact as compared to temperature changes.

All of the digested sludge samples were treated with HTC in a 1-litre pressure reactor equipped with a stirrer and an electric heating jacket from PARR Instrument Company (model 4523, USA). All HTC experiments were carried out three times. The initial mass of all sludge samples for HTC tests was 300 g, while the stirrer speed was 100 RPM. The heating time depended on the initial moisture content of the sludge (different the specific heat) and varied from 50 to 63 min. When the reactor reached the set process temperature, it was maintained at this temperature for the selected residence time (30–120 min), and then the electric heating was turned off, the reactor cooled and opened under atmospheric conditions. A vacuum filtration kit and filter paper (Whatman Cat No 1004 110, 20–25 μm) were used to separate the suspension into hydrochar and liquid HTC. The filtration time for all experiments was set at 15 min. The average mass balance from the three replicates of the experiment was prepared based on the following measurements: the initial mass of the feedstock (ADS, THDS, DDS), mass of the filter paper, the mass of the slurry after the HTC process, the mass of the hydrochars after 15-minute filtration including the mass of the

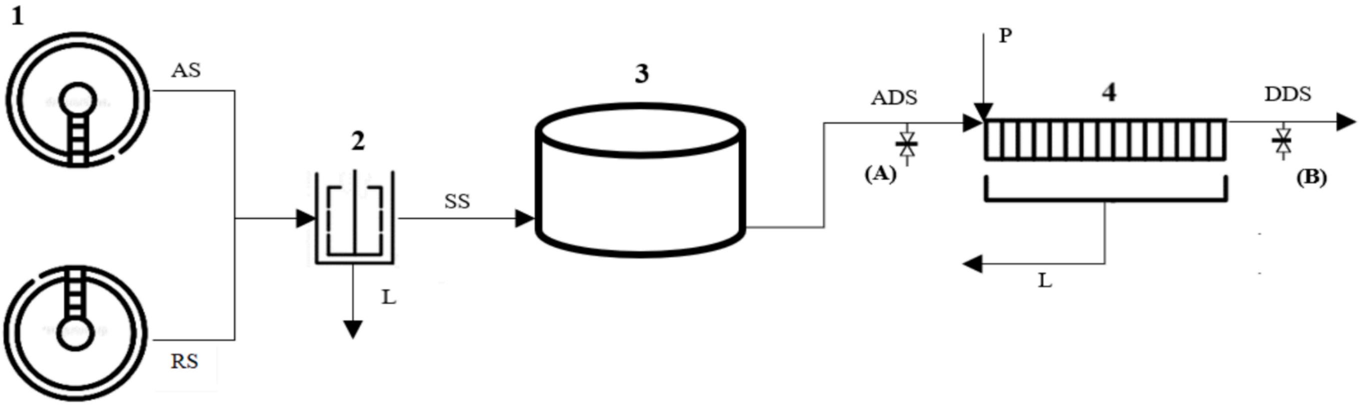

Fig. 1. Diagram of the WWTP and sampling location points. Legend: (1) Dorr type settling tank (2) Thickener to SS (3) Biogas plant (4) Press filter, (AS) – Active sludge (RS) – Raw sludge (L) – Leachates, (SS) – Sewage sludge (ADS) – Active digested sludge (DDS) – Dewatered digested sludge, (P) – Polyelectrolytes/Polymers.

filter paper, and the mass of the HTC liquids after filtration. The quantity of process gases was obtained from the difference of the initial mass of sludge and the mass of the HTC slurry, while the mass loss of the slurry after 15 min separation was obtained from the difference of the initial mass of the slurry and the mass of hydrochars and HTC liquid.

2.3. Property analysis

2.3.1. Digested sludge and hydrochars

Determinations of the dry matter called also total solid (TS) of digested sludge and hydrochar were carried out according to PN-EN ISO 18134–3:2015–11. The materials used for further analysis were dried for several days at 45 °C to avoid reducing the nitrogen content. Proximate analysis was used to determine the percentage of ash content using the ISO 21656:2021 method, as well as the volatile matter (VM) content using the ISO 22167:2021 method in specially designed cylindrical porcelain crucibles with a lid. The ultimate analysis of C%, H%, N%, and S% was performed using an 828 series elemental analyser (LECO Corporation ISO-9001:2015). The higher heating value (HHV MJ/kg) was measured using a calorimetric bomb (6200 Isoperibol) Parr Instrument Company according to PN-ISO 1928:2002. Inductively coupled plasma optical emission spectroscopy (ICP-OES, Agilent 5100 with SPS4 autosampler) was used to determine the heavy metal content of HTC products. Prior to ICP-OES, ISO 21656:2021 was used to obtain ash, followed by a mixture of hydrogen peroxide, nitric acid, and hydrofluoric acid to digest the sample in a microwave oven (Mars 6, CEM) according to ISO 16967 and 16968.

2.3.2. HTC liquid analysis

Biomethane potential (BMP) tests were carried out using the AMPTS II automated methane potential testing system (Bioprocess Control AB, Lund, Sweden). Batch anaerobic digestion experiments were conducted in 500 ml bottles at 37 °C. The working volume of each bottle was adjusted to 400 ml. The main parameters affecting the results of the anaerobic tests, namely the feedstock/inoculum (F/I) ratio (also referred to in the literature as substrate/inoculum (S/I) ratio or inoculum/substrate (I/S) ratio), were calculated by dividing NPOC [g] (non-purgeable organic carbon) of feed substrate by NPOC [g] of inoculum. In this study, the F/I ratio was maintained at 1:2 in the digesters according to the recommendation of Villamil *et al.* [31]. The laboratory tests were based on the modified methodology contained in DIN 38414-S8 and VDI 4630. The minimum test duration was 24 days. The criterion for termination of the test was achieved when the daily volume of biogas for three consecutive days was less than 0.5 % of the total volume of biogas produced up to that time. Standard methods according to APHA (American Public Health Association, Washington, DC (1999)) were used to measure pH (Cole Parmer pH-meter Model No. 59002–00, UK), alkalinity (Cole Parmer pH meter Model No. 59002–00, UK), total volatile fatty acids (VFA) (steam distillation, BÜCHI K-355, Switzerland) and ammonia ion concentration (N-NH_4^+) (steam distillation, BÜCHI K-355, Switzerland). NPOC was determined using a multi-N/C 3100 TOC analyser from Analytik Jena GmbH + Co.

2.3.3. Model design

To facilitate the graphical interpretation of the experimental results in 2D, which depended on three process variables, a model was developed linking temperature and residence time to biomass degradation in the HTC process, referred to and commonly used during statistical analysis as the severity factor (f) [16,21,32]. This model was proposed by Ruyter et al. in 1982 (eq.1), and its prototype is the Arrhenius equation [33,34]. The researchers linked the severity factor (HTC conversion) to the loss of oxygen content in the final solid product (eq.2). In turn, Funke et al [35] correlated oxygen conversion with a change in the degree of carbonisation of lignocellulosic biomass. Due to the different sources of the biomass, the use of this model should be adjusted based on individual experimental results (eq. 3) with the assumption $f_1 = f_2$ [36]. Determination of the model coefficients (a, b, c) is possible through the regression method. The results of the response severity factor (f) obtained are shown in Tables 1 and 2, while the values of a, b, c were calculated in excel using the solver tool. **(Table S-1, S-2, S-3 Supplementary material)**

$$f = 50 \bullet t^{0.2} \bullet e^{\frac{-3500}{T}} \tag{1}$$

$$f_1 = \frac{\Delta O}{\Delta O_{max}} = \frac{O_{biomass} - O_{hydrochars(t)}}{O_{biomass} - O_{theoretical(min)}} \tag{2}$$

$$f_2 = a \bullet t^b \bullet e^{-\frac{c}{T(K)}} \tag{3}$$

where T is temperature [K], t – time [s], $O_{biomass}$ – initial oxygen feedstock content, $O_{hydrochars(t)}$ – oxygen content of the sample after the HTC process, $O_{theoretical\ (min)}$ = theoretical minimum oxygen content = 6 %

3. Results and discussion

3.1. Mass balance

The mass balance values of ADS, THDS and DDS substrates, HTC decomposition products, as well as mass losses are presented in **Table S-4 (Supplementary Material)** and shown in Fig. 2. The increase in the initial TS% content had a effect on the increase in hydrochar production from 3.85 to 59.19 % of the total mass and the decrease in the liquid fraction from 90.31 to 32.5 % in the range of 2.4–19.8 % TS. Also, a slight increase in gas production was observed for DDS compared to ADS

Table 1
Characteristics of digested sludge and hydrochars produced at different operational conditions.

Material	Process parameter			Proximate analysis					Energy properties		Ultimate analysis					
TS	T	t	f	TS[a]	Yields[b]	Ash	VM	FC[c]	HHV (exp)	ED[d]	C	H	N	S	O[e]	HHV[f] (teor)
%	°C	min	–	[%]	[%]	[%]	[%]	[%]	[MJ/kg]	–	[%]	[%]	[%]	[%]	[%]	[MJ/kg]
ADS	–	–	0.00	2.4 ± 0.03	–	37.8 ± 0.06	55.8 ± 1.0	6.5 ± 0.9	12.20 ± 0.01	–	27.77 ± 0.06	4.66 ± 0.06	4.24 ± 0.01	1.32 ± 0.11	23.92 ± 0.21	12.78
2.4	200	30	0.51	21.2 ± 6.5	36.3 ± 0.9	54.5 ± 0.3	43.4 ± 0.5	2.1 ± 0.2	12.63 ± 0.04	1.03	27.03 ± 0.04	4.55 ± 0.02	2.10 ± 0.02	0.80 ± 0.12	14.81 ± 0.13	13.28
	200	75	0.55	18.0 ± 1.3	63.4 ± 7.2	54.8 ± 1.9	44.3 ± 0.2	1.3 ± 0.3	11.92 ± 0.30	0.98	26.49 ± 0.23	4.08 ± 0.01	2.16 ± 0.01	0.90 ± 0.16	14.08 ± 0.91	12.62
	225	30	0.84	19.7 ± 1.5	57.9 ± 2.6	56.7 ± 0.4	40.8 ± 0.1	2.5 ± 0.5	11.75 ± 0.94	0.96	27.31 ± 0.05	3.85 ± 0.10	2.07 ± 0.01	1.13 ± 0.01	8.94 ± 0.82	13.19
	225	120	0.87	21.5 ± 0.6	35.2 ± 1.6	56.5 ± 2.9	42.9 ± 0.4	0.6 ± 0.4	11.14 ± 0.27	0.91	25.81 ± 0.32	3.61 ± 0.01	1.73 ± 0.02	1.02 ± 0.52	8.41 ± 1.00	12.47
	250	75	0.92	28.3 ± 0.6	47.2 ± 0.9	58.7 ± 1.0	40.0 ± 1.8	1.3 ± 0.2	11.39 ± 0.30	0.93	25.73 ± 0.41	3.73 ± 0.11	2.63 ± 0.10	1.56 ± 0.55	7.52 ± 0.21	12.72
THDS	–	–	0.00	11.1 ± 0.4	–	34.6 ± 0.04	58.6 ± 0.3	6.8 ± 0.1	14.34 ± 0.32	–	31.17 ± 0.20	5.16 ± 0.17	4.91 ± 0.11	1.51 ± 0.21	22.67 ± 0.03	14.70
11.1	200	30	0.51	22.6 ± 3.3	64.3 ± 3.3	46.5 ± 0.6	48.7 ± 0.4	4.8 ± 0.2	13.50 ± 0.19	0.94	29.85 ± 0.06	4.33 ± 0.01	3.57 ± 0.01	1.65 ± 0.52	14.16 ± 0.24	14.17
	200	120	0.63	23.9 ± 0.4	66.4 ± 1.4	47.9 ± 1.1	46.7 ± 0.1	5.4 ± 1.0	13.81 ± 0.03	0.96	30.47 ± 0.21	4.40 ± 0.06	3.40 ± 0.12	1.55 ± 0.00	12.24 ± 0.51	14.66
	225	75	0.81	24.7 ± 2.2	63.7 ± 2.5	51.7 ± 1.6	44.9 ± 0.8	3.4 ± 1.7	14.01 ± 0.14	0.98	30.36 ± 0.22	4.13 ± 0.02	3.14 ± 0.03	1.62 ± 0.00	9.10 ± 0.02	14.64
	250	30	0.88	26.5 ± 3.4	58.6 ± 3.1	52.7 ± 1.9	42.1 ± 0.3	5.2 ± 1.2	14.02 ± 0.26	0.98	30.55 ± 0.21	4.00 ± 0.10	3.07 ± 0.03	1.67 ± 0.32	7.98 ± 0.17	14.64
	250	120	1.04	26.6 ± 2.8	58.0 ± 4.6	55.7 ± 0.8	39.8 ± 0.4	4.4 ± 1.1	13.99 ± 0.27	0.98	30.52 ± 0.01	3.95 ± 0.01	2.78 ± 0.01	1.72 ± 0.11	5.28 ± 0.03	14.90
DDS	–	–	0.00	19.8 ± 0.1	–	34.3 ± 0.4	60.4 ± 0.5	5.3 ± 0.7	14.02 ± 0.10	–	30.81 ± 0.08	5.21 ± 0.01	4.76 ± 0.02	1.60 ± 0.54	23.33 ± 0.01	14.58
19.8	200	30	0.59	26.4 ± 1.4	74.8 ± 3.6	43.8 ± 0.8	51.7 ± 0.9	4.5 ± 0.1	14.97 ± 0.02	1.07	32.35 ± 0.64	4.70 ± 0.12	4.41 ± 0.01	1.69 ± 0.00	13.07 ± 1.21	15.58
	200	75	0.60	26.0 ± 1.2	76.8 ± 1.0	44.6 ± 0.6	50.1 ± 0.8	5.1 ± 0.3	15.15 ± 0.05	1.08	31.98 ± 0.09	4.49 ± 0.17	4.12 ± 0.08	1.80 ± 0.00	13.03 ± 0.82	15.53
	200	120	0.67	26.8 ± 0.9	75.3 ± 3.0	45.4 ± 0.6	49.5 ± 0.1	5.1 ± 0.5	14.75 ± 0.22	1.05	32.48 ± 0.32	4.51 ± 0.05	4.11 ± 0.02	1.71 ± 0.00	11.80 ± 0.73	15.16
	225	30	0.80	27.4 ± 4.0	73.2 ± 2.2	48.5 ± 0.7	47.0 ± 0.2	4.9 ± 0.2	15.01 ± 0.03	1.07	32.24 ± 0.21	4.17 ± 0.02	3.84 ± 0.01	1.84 ± 0.11	9.40 ± 0.08	15.28
	225	120	0.86	27.0 ± 0.9	68.4 ± 2.2	49.5 ± 0.3	45.5 ± 0.5	5.0 ± 0.2	15.17 ± 0.22	1.08	32.29 ± 0.28	4.16 ± 0.02	3.63 ± 0.03	1.97 ± 0.17	8.43 ± 0.12	15.44
	250	75	1.04	27.6 ± 2.0	66.3 ± 1.7	51.4 ± 0.5	42.8 ± 0.8	5.8 ± 1.3	16.31 ± 0.31	1.16	32.60 ± 0.12	4.32 ± 0.05	4.38 ± 0.02	1.97 ± 0.01	5.39 ± 0.01	16.04

[a] After 15 min vacuum filtration

[b] Yields $= \frac{TS_{hydrochar} \bullet M_{hydrochar}}{TS_{Feedstock} \bullet M_{Feedstock}} \bullet 100\ \%$, where $TS_{feedstock}$ – total solid/dry matter (w/w) of feedstock, $TS_{hydrochar}$ – total solid/dry matter (w/w) of hydrochar after 15 min filtration, $M_{feedstock}$ – mass of feedstock (300 g), $M_{hydrochar}$ – mass of weighed hydrochar after 15 min filtration

[c] FC (db) = 100 % − Ash% − VM%.

[d] Energy Densification (ED). $= \frac{HHVofproduct}{HHVoffeedstock}$

[e] Calculated by difference: O% = 100 % − C% − H% − N% − S% − ash%.

[f] $HHV_{(teor)} = 0.3491C + 1.1783H + 0.1005S - 0.1034O - 0.0151\ N - 0.021ash$[40].

and THDS. Similar trends and observations were obtained by Briceno et al [29] from 2.5 − 30 TS% and Hämäläinen et al [19] from 14.5 − 25. 6 TS%. In contrast to TS%, an increase in the severity factor f had an effect on the increase in liquid production due to an increase in the solubility of the solid fraction in the liquid (at the expense of a decrease in the hydrochar yield), which has been widely discussed in the literature for different types of biomasses [22,37,38].

3.2. Hydrochar characteristics

3.2.1. Technical analyses

One of the fundamental parameters determining the utility of hydrochars as fuels is TS content. The TS value of hydrochars depended on both the initial TS of the feedstock and severity factors (Fig. 3a, Table 1). The higher the initial TS and f, the higher the TS of the hydrochar. In general, the values obtained were low, as TS was measured after 15-minute vacuum filtration under laboratory conditions to further determine and compare the yields of the resulting hydrochar. Due to the hydrophobic nature of the material, a significant improvement in the TS of the hydrochars was observed after a few days. In this case, the hydrochars showed an inverse trend depending on the initial TS of the feedstocks, as DDS reached 65 % w/w, for THDS it reached 72 % w/w, while for ADS it even reached 97 % w/w. Process yields showed the initial trend of increasing and then decreasing with severity intensity for all three materials (Fig. 3b). The same decreasing trends with increasing temperature and time were observed in other studies [19,26,27,29,39]. The highest hydrochar yields were obtained for the highest TS (19.8 % w/w), while the lowest yields were obtained for TS 2.4 % w/w, which was also observed by Aragón-Briceño's study [29].

HTC processes cause a significant increase in the ash fraction in hydrochar, which generates problems from an energy perspective due to faster fuel consumption, deterioration of flame stability or slagging. The reason is the thermal degradation of the organic fraction of the digested sludge into liquid. Thus, the increase in the intensity of the reaction

Table 2
Characteristics of inoculum and HTC liquid produced at different operational conditions.

Material	Process parameter				Liquids properties				Biological responses
TS	T	t	f	F/I[a]	NPOC[b]	N-NH_4^+	VFA	pH	BMP[c,d]
w/w	°C	min	-	-	g/l	g/l	g/l	-	$mlCH_4/gNPOC$
2.4%	200	30	0.51	1/2	3.03±0.04	1.06±0.04	1.20±0.18	8.23±0.51	416.8
	200	75	0.55		4.08±0.34	0.96±0.04	1.20±0.21	7.63±0.45	447.9
	225	30	0.84		4.48±0.25	1.08±0.02	1.46±0.07	8.30±0.16	323.6
	225	120	0.87		4.12±0.48	1.08±0.04	1.36±0.17	8.52±0.09	333.6
	250	75	0.92		3.21±0.23	1.10±0.03	1.17±0.22	8.55±0.05	315.1
11.1%	200	30	0.51		15.98±1.15	2.14±0.02	2.79±0.06	7.36±0.11	506.5
	200	120	0.63		15.68±0.28	2.41±0.00	3.88±0.03	7.62±0.09	369.9
	225	75	0.81		16.09±0.42	2.73±0.02	4.64±0.10	8.32±0.04	357.8
	250	30	0.88		14.39±0.86	3.01±0.02	4.49±0.18	8.46±0.06	391.0
	250	120	1.04		13.24±1.21	3.46±0.02	4.92±0.24	8.52±0.23	310.4
19.8%	200	30	0.59		27.21±0.06	3.42±0.04	2.72±0.04	7.44±0.04	404.1
	200	75	0.60		27.32±1.60	3.62±0.03	3.27±0.60	7.67±0.26	342.9
	200	120	0.67		28.12±1.20	4.02±0.02	5.24±0.23	7.72±0.21	328.3
	225	30	0.80		26.89±0.63	4.07±0.04	5.60±0.27	8.33±0.14	337.0
	225	120	0.86		26.69±0.11	4.77±0.22	5.98±0.07	8.55±0.01	303.1
	250	75	1.04		24.67±0.04	5.59±0.02	7.15±0.65	8.70±0.06	307.2

[a] Feedstock/Inoculum.

[b] NPOC = Non-Purgeable Organic Carbon as TOC (Total Organic Carbon).

[c] Average value of two BMP series.

[d] $BMP = \frac{V_{CH_4} - V_{CH_{4(inoculum)}}}{gNPOC}$ where: V_{CH_4} - Volume of methane produced in the bottle (ml), $V_{CH_{4(control)}}$ = Volume (ml) of methane produced in inoculum (pre-incubation of digested sludge).

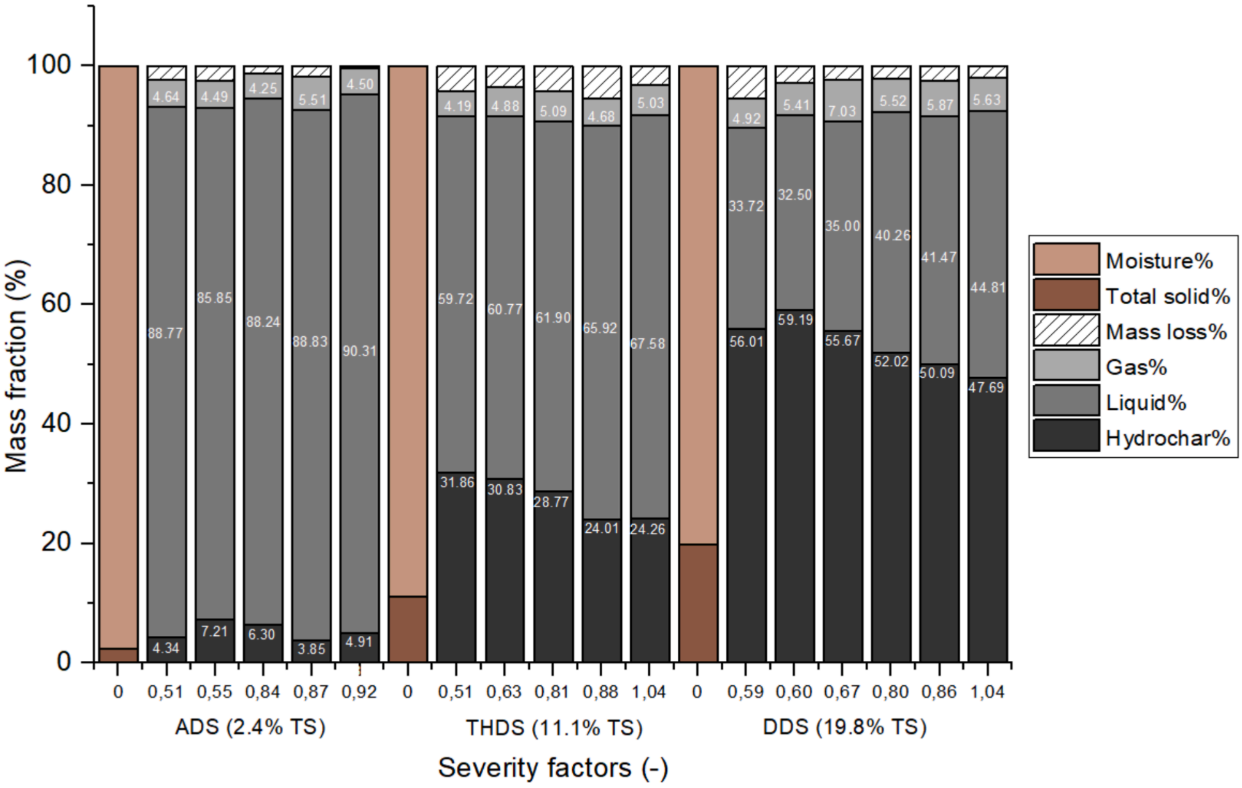

Fig. 2. Mass balance of feedstocks and HTC products obtained after 15 min of separation at different operating conditions.

affects the increase in the ash content of the hydrochar (Fig. 3c), and thus the successive increase in the coalification of the liquid fraction, which is consistent with other studies [19,26,27,39]. As shown in Fig. 3c, the lower the TS% of the feedstock, the higher the ash content of the hydrochar. The reason could be the enhanced hydrolysis of organic compounds into liquids by the higher proportion of water under subcritical conditions. The difference in ash content between the feedstocks was also noted by the Merzari et al. study [27] and the Aragón-Briceno's study [29]. The above observations are correlated with the successive loss of volatile matter with increasing severity factors (Fig. 3d), [19,26,27] where the lowest VM% in the hydrochar is observed for the lowest TS (2.4 %), and the highest for 19.8 %. This difference could also be due to the different initial VM% in active digested sludge and dewatering sludges, which may be due to the

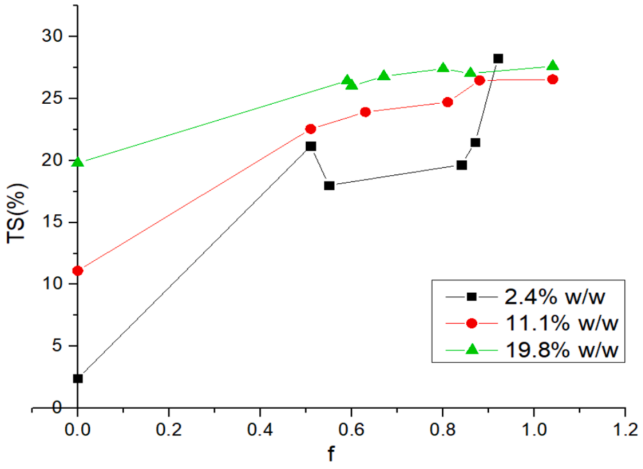

Fig. 3a. Relationship between severity factor and TS% value in hydrochar. The green line shows the feedstock after dewatering, the red line shows feedstock after thickening, and the black line shows feedstock before dewatering.

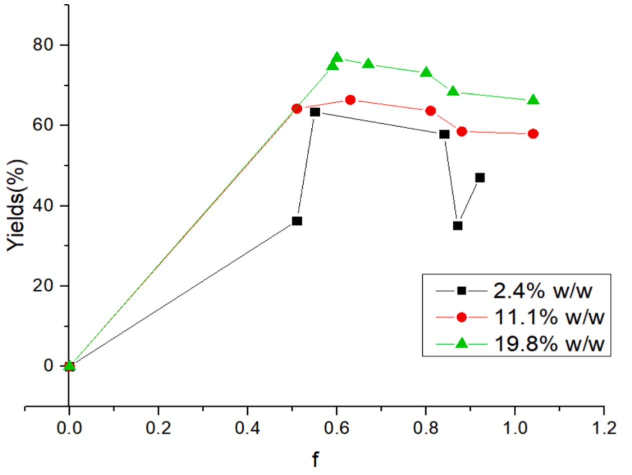

Fig. 3b. Relationship between severity factor and Yields% value in hydrochar. The green line shows the feedstock after dewatering, the red line shows feedstock after thickening, and the black line shows feedstock before dewatering.

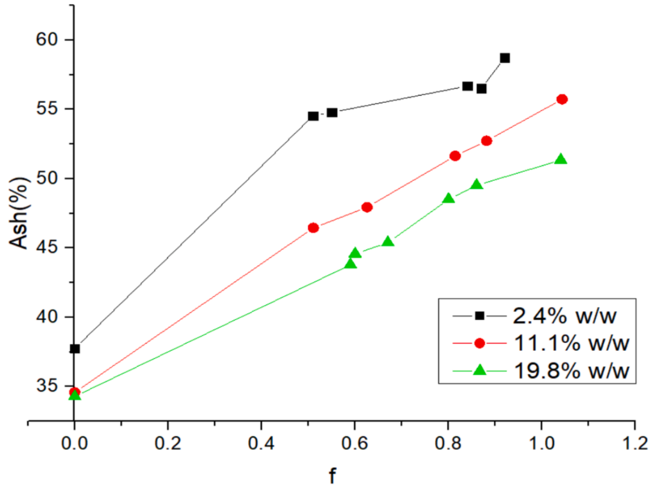

Fig. 3c. Relationship between severity factor and Ash% value in hydrochar. The green line shows the feedstock after dewatering, the red line shows feedstock after thickening, and the black line shows feedstock before dewatering.

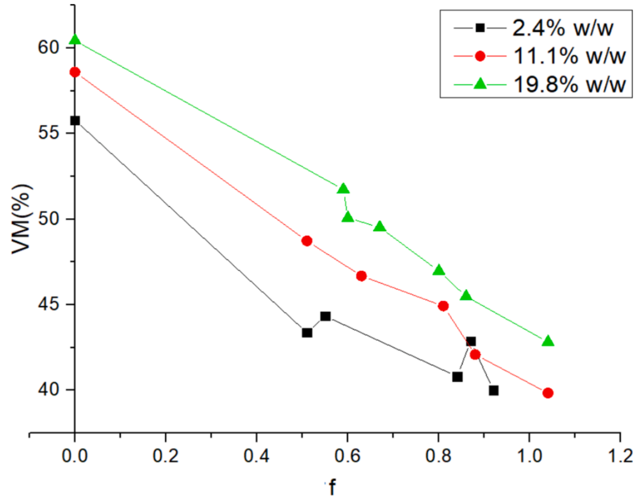

Fig. 3d. Relationship between severity factor and VM% value in hydrochar. The green line shows the feedstock after dewatering, the red line shows feedstock after thickening, and the black line shows feedstock before dewatering.

addition of organic polyelectrolytes in the filtration processes [27].

The content of fixed carbon (FC) (Fig. 3e) i.e., the solid combustible parts of the material, was lower in the hydrochar than in the feedstock, except for the hydrochar obtained from DDS at the highest reaction severity (Table 1). Despite the irregularity of the results obtained, it can be noted that the hydrochars obtained from THDS and DDS had higher FC contents compared to the hydrochars from ADS, which was also observed in other studies [27,29]. Moreover, one could see a favourable effect of residence time on the formation of the FC% fraction in the hydrochar from THDS and DDS.

Hydrochars prepared from DDS had the lowest Ash%, the highest VM % and relatively constant FC %, which could positively affect their final energy values. According to the results, the HHV values of the hydrochars were higher than those of the feedstock (DDS) and improved successively from 14.97 MJ/kg to 16.31 MJ/kg as the reaction intensified, increasing the energy density from 1.07 to 1.16 (Fig. 3f). In contrast, no significant improvement in HHV values was observed for THDS (14.36 MJ/kg), but rather an initial decrease to 13.50 MJ/kg, followed by an increase to 14.02 MJ/kg under 250 °C/30 min conditions (Table 1). Similar trends were observed by Hämäläinen et al. [19], for which HHV values obtained under mild conditions were lower than

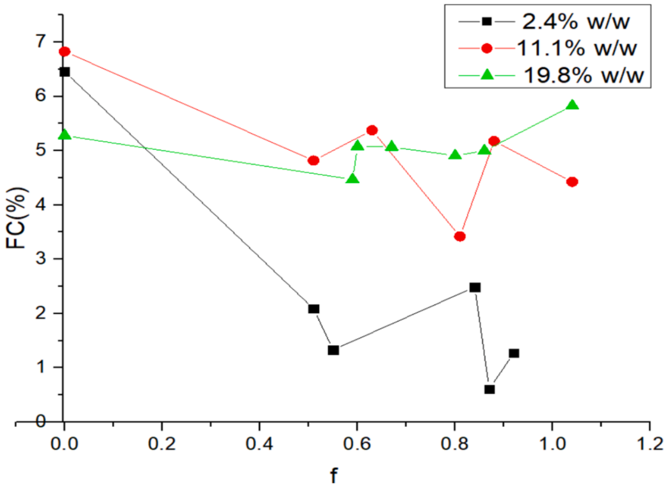

Fig. 3e. Relationship between severity factor and FC% value in hydrochar. The green line shows the feedstock after dewatering, the red line shows feedstock after thickening, and the black line shows feedstock before dewatering.

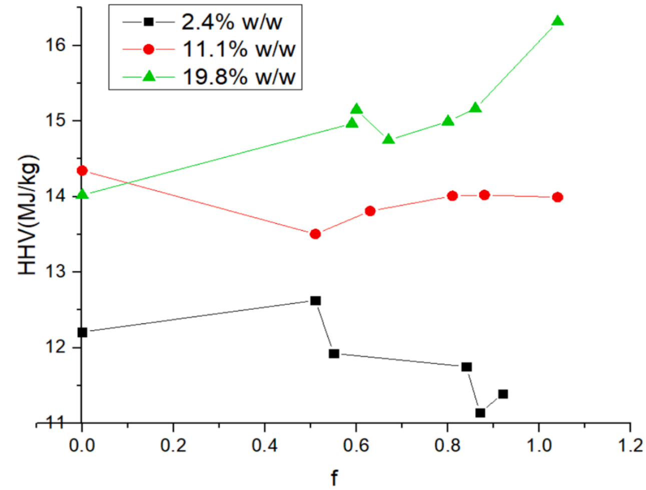

Fig. 3f. Relationship between severity factor and HHV [MJ/kg] value in hydrochar. The green line shows the feedstock after dewatering, the red line shows feedstock after thickening, and the black line shows feedstock before dewatering.

those for the feedstock, and then increased as the reaction intensified. In the present study, the HHV values of hydrochars from ADS (12.21 MJ/kg), under the mildest conditions, were higher (12.63 MJ/kg), and then decreased with intensification of the reaction to 11.39 MJ/kg, probably due to increased degradation of organic fractions in the liquid. A similar case was obtained by Merzari et al [27], examining ADS before the filter press (10.66 MJ/kg), but in this case a decrease with the intensification of the reaction was obtained to as low as 7.86 MJ/kg. On the other hand, for DDS collected after the filter press (16.02MJ/kg), a slight decreasing trend with the intensity of the reaction was also observed (to 15.33 MJ/kg), indicating an adverse effect of HTC treatment, regardless of the sampling location.

3.2.2. *Ultimate analyses*

3.2.2.1. Carbon distribution. In the present study, the elemental carbon content increased with the intensity of the reaction from 30.8 to 32.6C% for DDS, decreased for ADS sludge in the range of 27.8–25.7C% and slightly decreased for THDS in the range of 31.2–30.5C%, which was consistent with the HHV_{exp} trends shown in subsection 3.2.1 (Fig. 4).

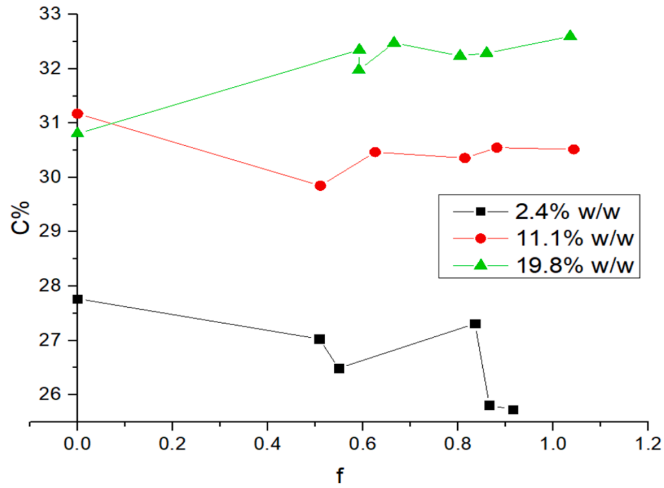

Fig. 4. Relationship between severity factor and C% value in hydrochar. The green line shows the feedstock after dewatering, the red line shows feedstock after thickening, and the black line shows feedstock before dewatering.

Aragón-Briceño et al. [29] obtained similar results which showed that the C% content of the feedstock only improved for materials with an initial TS content between 20 % – 30 %. In turn, for TS% in the range 2.5 % w/w to 17.5 % w/w, the C% content was lower than the feedstock but had an increasing trend, as well as THDS (Table 2). The lack of significant carbonisation and the same observations are also confirmed by another study [26] but for initial 16.5 % TS, which observed an initial decrease in C% under mild conditions and a slight increase with increasing severity factor. In contrast, Hämäläinen et al [19] observed a slight improvement in C% for both dewatered material (25 % TS) and diluted digestate (15 % TS) as the reaction intensified. On the other hand, Marzari et al [27] examined active digested sludge with before filtration (2.9 % TS) and after filtration (25 % TS) and noticed a decrease in carbon content in both cases, which was correlated with a decrease in HHV content.

3.2.2.2. Van Krevelen interpretation. HTC processes change the elemental composition of biomass, which is also reflected in a decrease in the oxygen and hydrogen content as a result of dehydration and decarboxylation reactions. Interpretations of the effect of process conditions on HTC products can be represented by the Van Krevelen diagram (Fig. 5). Better quality fuels were obtained as the severity of the reaction increased, but also as initial TS% increased under the same process conditions (e.g., 200 °C, 30 min). The relative decrease in the molar ratio of O/C was more significant compared to H/C and depended mainly on the severity of the reaction **(Table S-5 Supplementary Material)**, thus decarboxylation processes, i.e., processes of elimination of carboxyl groups, could be mainly responsible for the significant reduction of oxygen in the feedstock. Similar behaviour was observed by Gaur et al [22]. According to the composition of the digested sludge and the reaction mechanisms described in our previous review [5], decarboxylation processes can occur during the decomposition of amino acids derived from proteins – towards amines and CO_2, decomposition of esters derived from non-biodegradable lipids – to ketones, aldehydes and CO_2, while parallel dehydration processes could be involved in the decomposition of glucose/fructose derived from bio-resistant crystalline cellulose – to aldehydes and organic acids.

3.2.2.3 Nitrogen and sulphur distribution

The decrease in N% in the feedstock was mainly related to the decomposition of proteins or dissolution of other N-organic or N-inorganic fractions in the liquid during HTC processes [5] (Fig. 6a). An increase in the intensity of the reaction resulted in a decrease in the N% content of the hydrochar up to a certain point, which was consistent with numerous studies [22,26,39]. In turn, the higher TS% of feedstock, the higher the N% of the hydrochars. During HTC ADS, THDS and DDW, an increase in reaction intensity resulted in a decrease in N%, except for conditions of 250 °C and 75 min for ADS and DDW, where an increase in N% content was observed. Other studies of sludge with 10 % TS [22], and 15 % TS [19], also revealed that the nitrogen content initially decreased, and then increased under conditions of 250 °C and 120 min. The increase in nitrogen content of the hydrochar could be linked to an increase in some heterocyclic forms of N, due to polymerization or coexisting Maillard reactions, which formed polyaromatic forms of the hydrochar as they reached sufficient activation energy to initiate the processes [32].

In this study, an increase in sulfur content was observed with an increase in reaction intensity and a decrease in the efficiency of hydrochars obtained from THDS and DDS (Fig. 6b). This phenomenon was unfavorable from the point of view of the release of gaseous pollutants during hydrochar combustion. A similar trend could be observed for dewatered 25 %TS and thickened sludge 15 %TS [19], however, for this type of case there was an initial decrease in sulfur% and then an increase in the range of 210–250 °C. In our study, the HTC THDS and DDS process increased sulphur content in the hydrochar compared to the feedstock, while in the study by Hämäläinen et al [19] the sulfur %

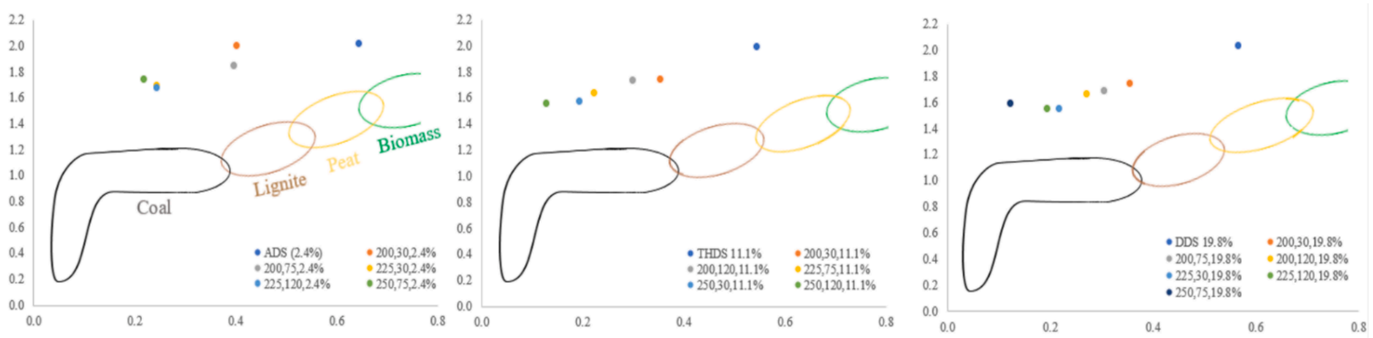

Fig. 5. Van Krevelan interpretation of ADS, THDS, DDS and HTC sample.

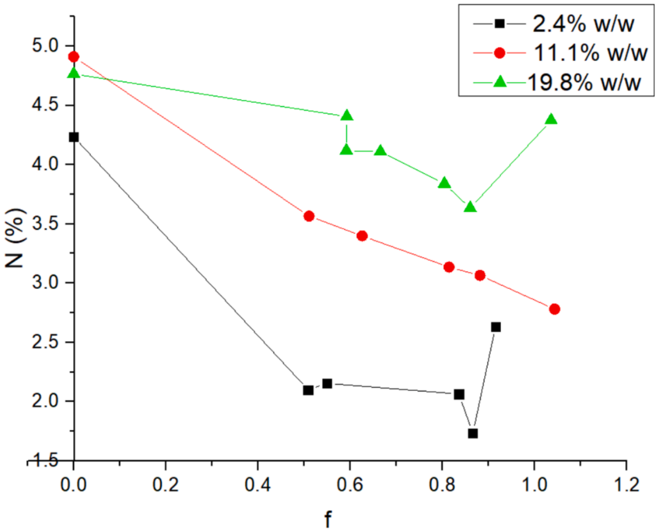

Fig. 6a. Relationship between severity factor and N% value in hydrochar. The green line shows the feedstock after dewatering, the red line shows feedstock after thickening, and the black line shows feedstock before dewatering.

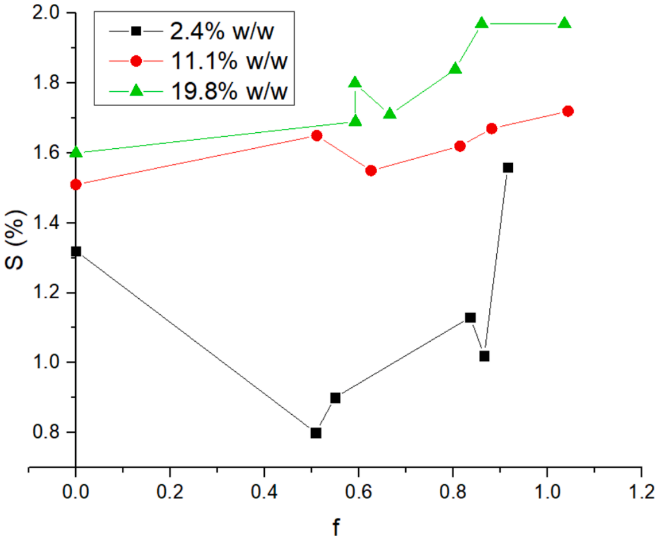

Fig. 6b. Relationship between severity factor and S% value in hydrochar. The green line shows the feedstock after dewatering, the red line shows feedstock after thickening, and the black line shows feedstock before dewatering.

content did not exceed the original amount contained in the feedstock. Moreover, our study observed an increase in sulfur% with increasing TS% of sludge, while [19] obtained lower sulphur content in the HTC process for higher TS% of sludge. In other works [26,41], the sulfur did not change or change slightly as the intensity of the reaction increased, indicating that some sulphur compounds gradually immigrated into the liquid. No change was also observed by [29], where TS% of sludge had only a minor effect on sulphur immobilization In turn, [24] observed a significant decrease in sulfur% with the intensity of the reaction. Differences between studies may have resulted from different sludge compositions (organic and inorganic sulphur compounds) and WWTP operations. For instance, increased doses of coagulants (iron sulphate-based) were used to chemically de-phosphate (reduce phosphorus from effluent) and improve dewatering processes at the wastewater treatment plant. As shown by studies [42] on the fate of impurities of sulfur% compounds contained in SS, during HTC treatment an increase in the inorganic form of sulphur% in hydrochar (from 14 to 20 %), mainly in the form of sulphate, occurs with an increase in temperature from 180 – 240 °C. Such a phenomenon could explain the increase of sulfur% in the hydrochar and the differences between ADS, THDS and DDS (Fig. 6b). In contrast, the content of organic S% initially increases and then degrades as the reaction intensifies. As explained by the researchers [42], the reason could be the transformation of sulphides and mercaptans contained in the sludge into sulfoxide compounds, as well as sulphate compounds, which could further affect the immobilization of these compounds in the hydrochar.

3.3. *Liquid characteristics*

3.3.1. *Biomethane potential test*

Methane production from HTC liquids is an attractive method of utilizing this by-product at WWTPs, due to the possibility of recovering non-biodegradable organic carbon from ADS matrix and producing additional biogas from the AD process. The results of HTC liquids obtained under different process conditions are shown in Table 2 and Fig. 7. The AD process was evaluated on the basis of the maximum amount of CH_4 produced from 1 g of NPOC – which was measured in both the inoculum and filtered HTC liquids, and included biodegradable organic fractions, inert gases, and inhibitors, while suspended solids present in the post-process liquids were not considered, which could adversely affect the evaluation of biogas production from HTC liquids.

No inhibition of anaerobic digestion was observed during the BMP tests, and so the organic F/I ratio was selected accordingly to the quality of HTC liquids obtained under varying operating conditions. The tests were conducted in two measurement series and included pre-incubated sludge, with an average biogas production value of 351.3 $mlCH_4$/g NPOC. Methane production results were positive only for mild HTC reaction conditions for ADS, THDS and DDS samples compared to the inoculum. The highest BMPs (506.5 mlCH4/g NPOC) were obtained at 200 °C, 30 min, 11.1 %TS, while the least favourable results were

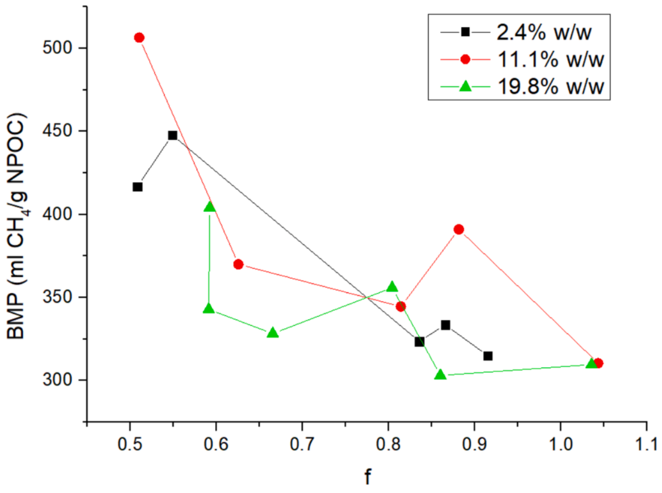

Fig. 7. Relationship between severity factor and BMP test from HTC liquids. The green line (triangle marks) shows the HTC liquid from feedstock after dewatering, the red line (circle marks) shows HTC liquids from feedstock after thickening, and the black line (square marks) shows HTC liquids from feedstock before dewatering.

obtained for the highest severity factor, regardless of initial TS% content, in the range of 303–315 mlCH4/g NPOC. Similar results and trends were observed by Gaur et al. [22], where the highest biomethane yields were obtained at 236 mlCH4/g Chemical Oxygen Demand (COD) under conditions of 200 °C, 30 min, 10 % TS while a decrease was observed with increasing reaction intensity from 115.9 to 68.1 mlCH4/g COD for 250 °C (30 – 120 min). JD Marin-Batista et al. [26] also observed a decrease in biogas production with increasing temperature (180–240 °C), but in this case they obtained the highest values at 180 °C, 60 min, 16.5 % (325 ml CH_4/g Volatile Solid (VS), while the point of disappearance of biogas production was already observed at 240 °C, 60 min, 16.5 %TS. The control sample/inoculum in this case was 150 ml CH_4/g VS, thus the increase in biogas production was significantly higher compared to our best results. On the other hand, Aragón-Briceño et al. [43] tested three temperatures (160, 220, 250 °C) at 30 min and for 4.5 %TS and the highest biogas yields were obtained for 220 °C (277 ml CH_4/g COD) followed by 160 °C (260 ml CH_4/g COD) and 250 °C (225.8 ml CH_4/g COD), respectively. Ahmed et al. [44] studied the specific effect of residence time (30, 60, 120, 180 min) at 190 °C and confirmed that, as residence time increased, biogas production decreased from 235 to 135 ml CH_4/g COD. Parmar et al. [45], in addition to a general study of the effect of temperatures 150, 200 and 250 °C at 60 min, 20 %TS, found that the highest result was obtained at 200 °C (181.7 ml CH_4/g COD), while at 250 °C the figure was 151.9 ml CH_4/g COD and at 150 °C it was 100.2 ml CH_4/g COD. They also studied the effect of initial TS%: 10 %, 20 % and 30 % at 200 °C – 250 °C. Their results showed a positive effect of increasing TS% on increasing biogas production for both temperatures, with the highest BMPs obtained for the sample 200 °C, 30 min, 30 %TS. Such a trend was not observed in our study. The only conditions that could be compared (Table 2) for ADS, THDS and DDS materials were 200 °C and 30 min, for which the highest results were observed for 11.1 %TS (506 ml), followed by 2.4 % TS (416 ml) and 19.8 % TS (404 ml) Our results were similar to those of Aragón-Briceño et al. [29] for comparable TS% content. The highest biogas production rate was obtained for 10 %TS (325.6 ml), followed by 20 %TS (302.1 ml) and 2.5 % TS (301.5 ml). A review of studies shows that, in most cases, there is an initial increase in biogas with the severity of the reaction for temperatures up to about 200 °C and then a decrease for temperatures up to 250 °C, which can also be observed in our research. The reason is the increase in the concentration of inhibitors in the form of refractory compounds with the severity of the reaction [22,26,46,47]. However, some studies were an exception [19], because with the increase in temperature (210–250 °C) for 25.6 %TS, an increase in BMP values was obtained from 183 – 206 ml CH_4/g COD) for 30 min, with values decreasing when increasing only residence time.

3.3.2. AD determinants and inhibitors

The pH value of HTC liquids has a direct impact on microbial growth and enzymatic activity, and so it is important to control this indicator both before and during AD processes. For BMP batch experiments, pH was measured before the process, and the results are shown graphically in Fig. 8a. It is generally known that the most beneficial pH conditions are around 7.0 while the tolerated range is from 6.5 to 8.0 [48]. An increase in pH above neutrality is generally associated with an increase ammonia accumulation, while a decrease in pH values is usually associated with the production and accumulation of VFA (volatile fatty acid) during the second stage of anaerobic digestion – acetogenesis. Thus, excess initial concentrations of N-NH_4^+ and VFA in HTC liquids can adversely affect the AD process. Too high or too low pH can inhibit sensitive methanogens responsible for biogas production during the final stage of methanogenesis. Several studies have noted a slightly alkaline nature or HTC liquids from digested sludge, which was generally due to the higher initial pH of ADS at around 8. Moreover, a generally increasing trend of pH was observed as the severity of the HTC reaction increased [22,26,43]. For example, at 180 °C, the high protein content of HTC liquids was found to decrease with increasing temperature, while pH gradually increased [26]. As explained by Aragón-Briceño et al. [43], proteins mainly derived from bacterial biomass from the anaerobic digestion process, are successively hydrolysed at increased temperature, and then degraded to produce ammonium nitrogen or free ammonia FA in the HTC liquid [46]. An increase in the initial concentration of ammonium nitrogen was observed as the intensity of the reaction increased, with a simultaneous increase in pH (Fig. 8a and Fig. 8b). In particular, these changes were evident at 225 °C, which could be consistent with the successive decomposition of resistant (EPS) fractions in ADS at higher hydrothermal temperatures [49]. Nevertheless, this increase may have negatively affected further AD processes, as the highest methane production was observed for the mildest reaction conditions, and thus the lowest initial pH at 7.36–7.67.

Trends in the content of the soluble organic fraction in HTC liquids (NPOC) depended on both TS% and severity factors (Fig. 8c). With increasing residence time at constant temperature (for 200 °C), a progressive increase in the solubility of the organic fraction in the liquid could be observed for ADS, THDS and DDS. Further increases in

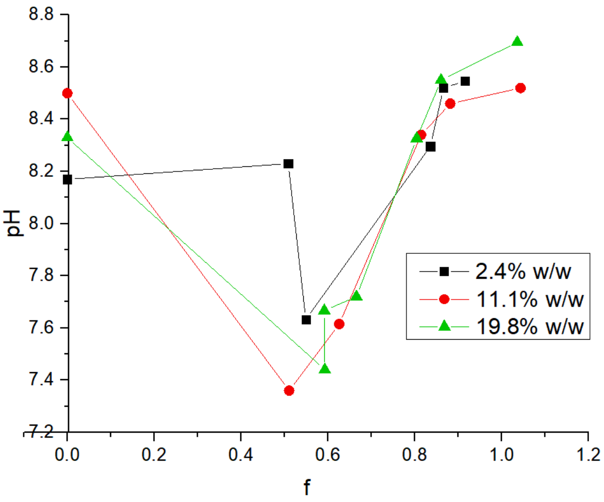

Fig. 8a. Relationship between severity factor and pH value from HTC liquids. The green line shows the HTC liquid from feedstock after dewatering, the red line shows HTC liquids from feedstock after thickening, and the black line shows HTC liquids from feedstock before dewatering.

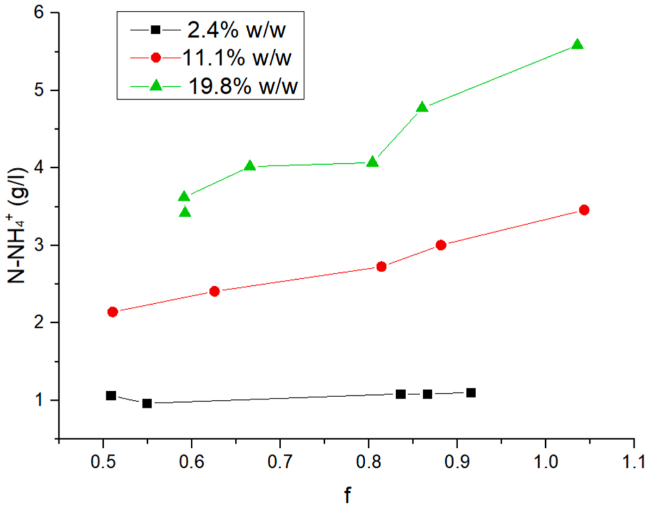

Fig. 8b. Relationship between severity factor and $N\text{-}NH_4^+$ value from HTC liquids. The green line shows the HTC liquid from feedstock after dewatering, the red line shows HTC liquids from feedstock after thickening, and the black line shows HTC liquids from feedstock before dewatering.

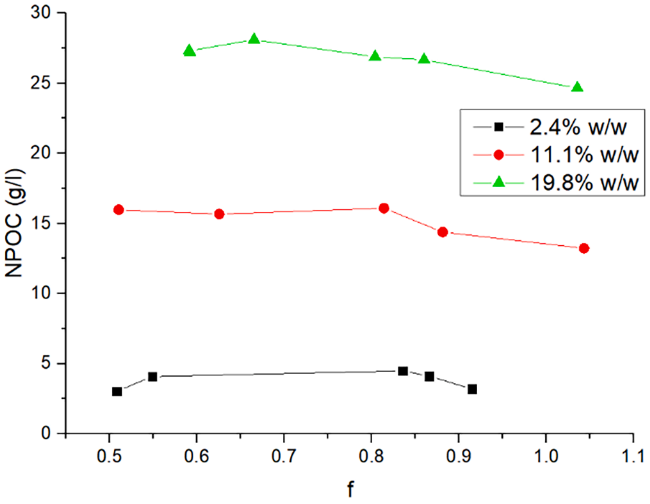

Fig. 8c. Relationship between severity factor and NPOC value from HTC liquids. The green line shows the HTC liquid from feedstock after dewatering, the red line shows HTC liquids from feedstock after thickening, and the black line shows HTC liquids from feedstock before dewatering.

temperature above 200 °C generally resulted in a decrease in NPOC content. A similar trend was observed by Gaur et al. [22] for chemical oxygen demand (COD), which showed an initial increase in these values for 200 °C for residence times from 30 to 60 min and then a decrease as the reaction intensified. Similar results were also obtained by [26], for which COD initially increased from 180 °C to 210 °C and then decreased from 210 °C to 250 °C. It seems that the decrease in both NPOC and COD at higher temperatures is related to the successive degradation of dominant, resistant components such as proteins and some carbohydrates (e.g., cellulose). This can be confirmed by both the increase in $N\text{-}NH_4^+$ (Fig. 8b) and VFA for 11.1 %TS and for 19.8 %TS (Fig. 8d). In addition, polymerization processes of intermediate organic compounds (intermediates) contained in the liquid can occur, forming the secondary structure of hydrochars [5].

3.4. Heavy metals

The monitoring of the heavy metal content of SS is extremely important both from the point of view of application in agriculture (soil reclamation, agricultural, non-agricultural purposes) [50] and also from the point of view of energy due to the control of emissions during combustion processes (e.g. Cd, Pb, Hg) [51]. Fig. 9 shows the results of all regulated heavy metals contained in the feedstocks and hydrochars obtained under the extreme conditions of the HTC reaction, while the values are shown in **Table S-6 (Supplementary material)** The increase in the concentration of heavy metals in the hydrochars (above the feedstock content) with the increase in the intensity of the reaction is due to the reduction of the mass (decrease in yield) and the immobilization of most heavy metals in the hydrochar matrix, which is consistent with the data of Zhang et al [52]. However, the difference between ADS, THDS, DDS materials should be noted, for which the highest concentration of metals was obtained for feedstock collected after filter press DDS (except for arsenic), while the lowest values were for ADS. After the HTC process, the opposite trends were obtained, for the lowest concentrations of heavy metals were obtained in hydrochars from DDS, while the highest concentrations were obtained for hydrochars from ADS. Merzari et al. [27] also obtained, in most cases, lower concentrations of heavy metals and nutrients in hydrochars from dewatered sludge collected after the press filter compared to hydrochars from digested sludge, but nevertheless the initial concentrations for dewatered sludge were also lower, which was not observed in our study.

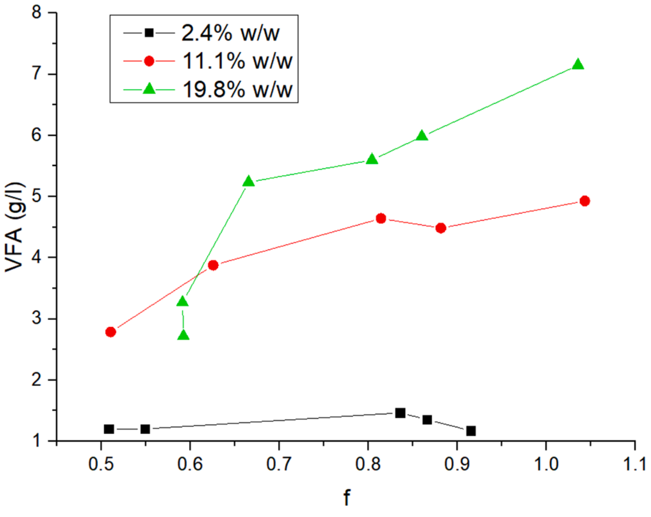

Fig. 8d. Relationship between severity factor and VFA value from HTC liquids. The green line shows the HTC liquid from feedstock after dewatering, the red line shows HTC liquids from feedstock after thickening, and the black line shows HTC liquids from feedstock before dewatering.

4. Summary

Proximate and ultimate analysis showed that an increase in the combustible part consisting of carbon and sulphur compounds in DDS hydrochar, as well as an overall higher VM content and lower Ash content compared to THDS and ADS hydrochars, could affect the overall improvement of HHV after HTC treatment. As previously mentioned, this was most likely due to a modification of the sludge on the filter press and higher concentration of digested sludge. Moreover, the increase in reaction intensity improved the energy value of the hydrochar from DDS (Fig. 3f). Nevertheless, the best compromise between the quality of hydrochar, HTC liquids, and energy consumption seems to be the material after dewatering (properly adjusted), carbonised under mild HTC process conditions. Similar conclusions were reached [26,39 44 46], where also found the temperature range of 180–200 °C/210 °C and short residence times to be the best compromise between biogas production from HTC liquids, energy valorisation and dewatering of hydrochar from digested sludge. Moreover, in addition to technological aspects,

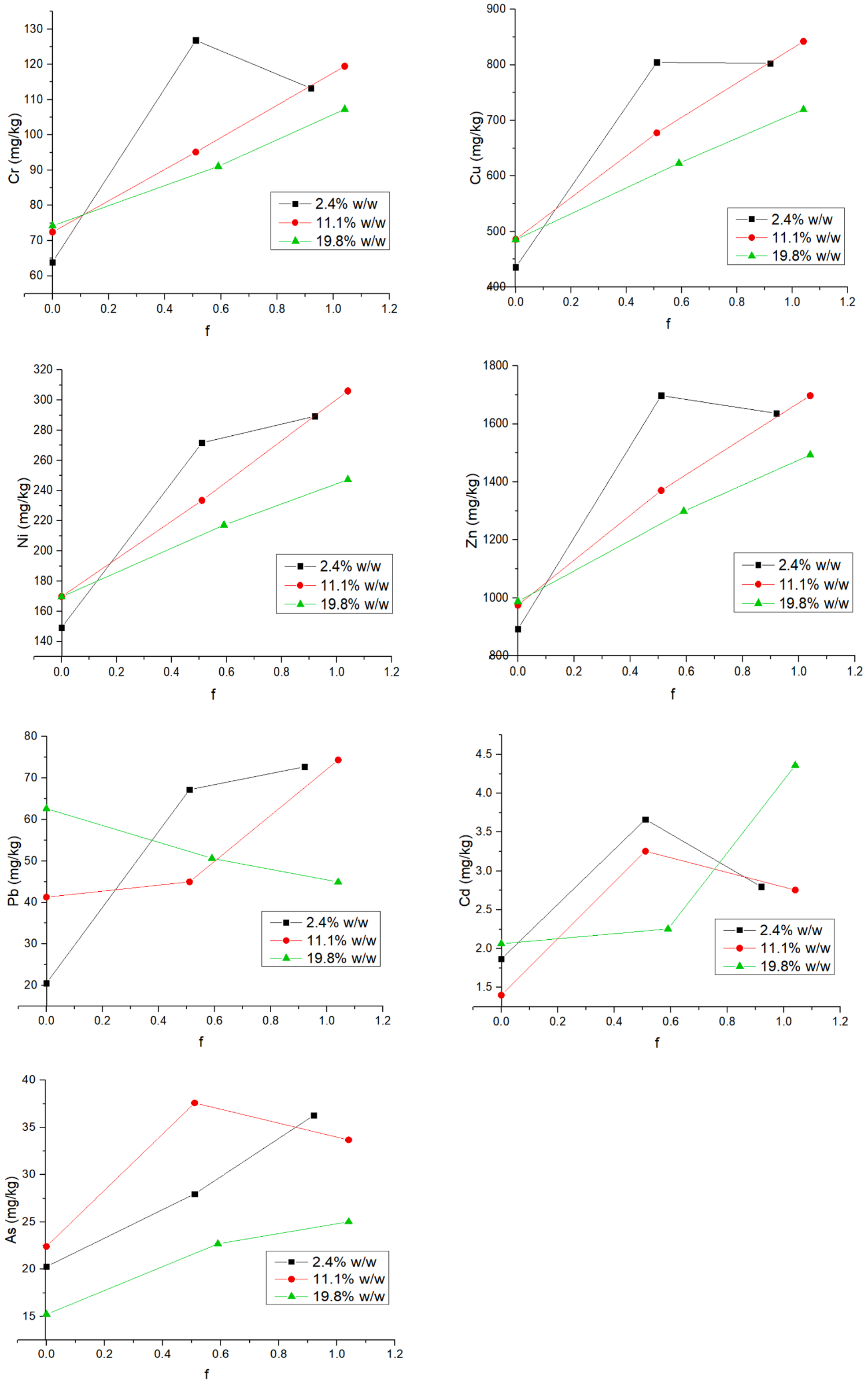

Fig. 9. Relationship between severity factor and heavy metals content in hydrochar. The green line shows the feedstock after dewatering, the red line shows feedstock after thickening, and the black line shows feedstock before dewatering.

technical aspects are important: materials after filtration or thickening have a lower heat capacity, compared to materials with high moisture content [44]. Heating sludge with limited water requires less time and energy during HTC, and smaller working volumes are required to process the larger mass. Thus, from the WWTP point of view, the most favourable results were obtained for dewatered sludge processed under the mildest HTC conditions due to 1) relatively lower system operating costs, 2) lower ash and heavy metal content 3) higher HHV, 4) lower nitrogen and oxygen responsible for NOx pollution compared to the feedstock and ultimately 5) the ability to produce biogas from HTC liquids.

5. Conclusion

The study provides new insights into the effects of HTC conditions on different digested sludge – pre-filtration, thickened or dewatered which is important for the practical application of this technology in wastewater treatment plants. This is especially relevant if the HTC system is run in a continuous process with pumps using thickened sludge or – batch, where dewatered sludge can be used. It has been found that the HTC process conducted under different process conditions does not always improve the energy value of the hydrochar, and strictly depends on the type of sludge taken and prepared, and its hydration. The best results in terms of energy improvement of digested sludge after HTC were obtained for dewatered digested sludge, while the highest energy value ((HHV = 16.31 MJ/kg) was obtained under the highest reaction conditions of 250 °C, 75 min. On the other hand, the highest biogas production in BMP tests was observed for the lowest reaction conditions (200 °C, 30 min) for all sludge types, while the highest biomethane potential was obtained from HTC liquids from thickened sludge (506 mlCH4/g NPOC).

CRediT authorship contribution statement

Nina Kossińska: Writing – original draft, Methodology, Investigation, Conceptualization. **Renata Krzyżyńska:** Writing – review & editing, Supervision. **Anna Grosser:** Formal analysis, Data curation. **Marzena Kwapińska:** Formal analysis, Data curation, Conceptualization. **Heba Ghazal:** Validation, Supervision, Methodology. **Hussam Jouhara:** Supervision. **Witold Kwapiński:** Writing – review & editing, Supervision, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

The study was co-carried out in the framework of the statutory funds for research, co-financed by the Ministry of Science and Higher Education BS/PB-400-301/24.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.tsep.2025.103461.

References

[1] Z. Wang, T. Liu, H. Duan, Y. Song, X. Lu, S. Hu, Z. Yuan, D. Batstone, M. Zheng, Post-treatment options for anaerobically digested sludge: Current status and future prospect, Water Res. 205 (2021) 117665, https://doi.org/10.1016/j.watres.2021.117665.

[2] Council Directive of 21 May 1991 concerning urban wastewater treatment (91/271/EEC), (accessed 8 October 2024).

[3] M.G. Healy, O. Fenton, P.J. Forrestal, M. Danaher, R.B. Brennan, L. Morrison, Metal concentrations in lime stabilised, thermally dried and anaerobically digested sewage sludges, Waste Manag. 48 (2016) 404–408, https://doi.org/10.1016/j.wasman.2015.11.028.

[4] W.A. Ramírez, X. Domene, O. Ortiz, J.M. Alcañiz, Toxic effects of digested, composted and thermally-dried sewage sludge on three plants, Bioresour. Technol. 99 (15) (2008) 7168–7175, https://doi.org/10.1016/j.biortech.2007.12.072.

[5] N. Kossińska, R. Krzyżyńska, H. Ghazal, H. Jouhara, Hydrothermal carbonisation of sewage sludge and resulting biofuels as a sustainable energy source, Energy 275 (2023) 127337, https://doi.org/10.1016/j.energy.2023.127337.

[6] C.I. Aragón-Briceño, A.B. Ross, M.A. Camargo-Valero, Mass and energy integration study of hydrothermal carbonization with anaerobic digestion of sewage sludge, Renew. Energy 167 (2021) 473–483, https://doi.org/10.1016/j.renene.2020.11.103.

[7] E. Medina-Martos, I.R. Istrate, J.A. Villamil, J.L. Gálvez-Martos, J. Dufour, Á. F. Mohedano, Techno-economic and life cycle assessment of an integrated hydrothermal carbonization system for sewage sludge, J. Clean. Prod. 277 (2020) 122930, https://doi.org/10.1016/j.jclepro.2020.122930.

[8] A. Alvarez-Murillo, J.A. Libra, K.S. Ro, Theoretical framework for estimating design reactor pressure for water-based hydrothermal carbonization (HTC) systems, Therm. Sci. Eng. Prog. 30 (2022) 101241, https://doi.org/10.1016/j.tsep.2022.101241.

[9] L.B.S. Thomsen, K. Anastasakis, P. Biller, Wet oxidation of aqueous phase from hydrothermal liquefaction of sewage sludge, Water Res. 209 (2022) 117863, https://doi.org/10.1016/j.watres.2021.117863.

[10] M. Langone, D. Basso, Process waters from hydrothermal carbonization of sludge: characteristics and possible valorization pathways, Int. J. Environ. Res. Public Health 17 (18) (2020) 6618, https://doi.org/10.3390/ijerph17186618.

[11] L. Wang, Y. Chang, A. Li, Hydrothermal carbonisation for energy-efficient processing of sewage sludge: A review, Renew. Sustain. Energy Rev. 108 (2019) 423–440, https://doi.org/10.1016/j.rser.2019.04.011.

[12] M. Alipour, H. Asadi, C. Chen, A.A. Besalatpour, Fate of organic pollutants in sewage sludge during thermal treatments: Elimination of PCBs, PAHs, and PPCPs, Fuel 319 (2022) 123864, https://doi.org/10.1016/j.fuel.2022.123864.

[13] A. Joshi, M. Breulmann, E. Schulz, R. Ruser, Effects of sewage sludge hydrochar on emissions of the climate-relevant trace gases N2O and CO2 from loamy sand soil, Heliyon 8 (10) (2022), https://doi.org/10.1016/j.heliyon.2022.e10855.

[14] G.C. Becker, D. Wüst, H. Köhler, A. Lautenbach, A. Kruse, Novel approach of phosphate-reclamation as struvite from sewage sludge by utilising hydrothermal carbonization, J. Environ. Manage. 238 (2019) 119–125, https://doi.org/10.1016/j.jenvman.2019.02.121.

[15] Z.X. Zhuang Xiu Zheng, H.Y. Huang Yan Qin, S.Y. Song Yan Pei, Z.H. Zhan Hao, Y. X. Yin Xiu Li, W.C. Wu Chuang Zhi, The Transformation Pathways of Nitrogen in Sewage Sludge during Hydrothermal Treatment (2017), https://doi.org/10.1016/j.biortech.2017.08.195.

[16] A.L. Tasca, M. Puccini, R. Gori, I. Corsi, A.M.R. Galletti, S. Vitolo, Hydrothermal carbonization of sewage sludge: A critical analysis of process severity, hydrochar properties and environmental implications, Waste Manag. 93 (2019) 1–13, https://doi.org/10.1016/j.wasman.2019.05.027.

[17] K. Czerwińska, M. Śliz, M. Wilk, Hydrothermal carbonization process: Fundamentals, main parameter characteristics and possible applications including an effective method of SARS-CoV-2 mitigation in sewage sludge. A review, Renew. Sustain. Energy Rev. 154 (2022) 111873, https://doi.org/10.1016/j.rser.2021.111873.

[18] S.K. Hoekman, A. Broch, A. Warren, L. Felix, J. Irvin, Laboratory pelletization of hydrochar from woody biomass, Biofuels 5 (6) (2014) 651–666, https://doi.org/10.1080/17597269.2015.1012693.

[19] A. Hämäläinen, M. Kokko, V. Kinnunen, T. Hilli, J. Rintala, Hydrothermal carbonisation of mechanically dewatered digested sewage sludge—energy and nutrient recovery in centralised biogas plant, Water Res. 201 (2021) 117284, https://doi.org/10.1016/j.watres.2021.117284.

[20] M. Volpe, L. Fiori, F. Merzari, A. Messineo, G. Andreottola, Hydrothermal carbonization as an efficient tool for sewage sludge valorization and phosphorous recovery, Chem. Eng. Trans. 80 (2020) 199–204, https://doi.org/10.3303/CET2080034.

[21] A.L. Tasca, E. Stefanelli, A.M. Raspolli Galletti, R. Gori, G. Mannarino, S. Vitolo, M. Puccini, Hydrothermal carbonization of sewage sludge: analysis of process severity and solid content, Chem. Eng. Technol. 43 (12) (2020) 2382–2392, https://doi.org/10.1002/ceat.202000095.

[22] R.Z. Gaur, O. Khoury, M. Zohar, E. Poverenov, R. Darzi, Y. Laor, R. Posmanik, Hydrothermal carbonization of sewage sludge coupled with anaerobic digestion: Integrated approach for sludge management and energy recycling, Energ. Conver. Manage. 224 (2020) 113353, https://doi.org/10.1016/j.enconman.2020.113353.

[23] A. Petrovič, C. Hochenauer, M. Zazijal, S. Gruber, K. Rola, L. Čuček, D. Goričanec, D. Urbancl, Torrefaction and hydrothermal carbonization of waste from the paper industry: Effects of atmosphere choice and pretreatment with natural acidic reagent on fuel properties, Therm. Sci. Eng. Prog. 51 (2024) 102623, https://doi.org/10.1016/j.tsep.2024.102623.

[24] D. Kim, K. Lee, K.Y. Park, Hydrothermal carbonization of anaerobically digested sludge for solid fuel production and energy recovery, Fuel 130 (2014) 120–125, https://doi.org/10.1016/j.fuel.2014.04.030. ISSN 0016-2361.

[25] C. He, A. Giannis, J.Y. Wang, Conversion of sewage sludge to clean solid fuel using hydrothermal carbonization: Hydrochar fuel characteristics and combustion behavior, Appl. Energy 111 (2013) 257–266, https://doi.org/10.1016/j.apenergy.2013.04.084.

[26] J.D. Marin-Batista, A.F. Mohedano, J.J. Rodríguez, M.A. de la Rubia, Energy and phosphorous recovery through hydrothermal carbonization of digested sewage sludge, Waste Manag. 105 (2020) 566–574, https://doi.org/10.1016/j.wasman.2020.03.004.

[27] F. Merzari, J. Goldfarb, G. Andreottola, T. Mimmo, M. Volpe, L. Fiori, Hydrothermal carbonization as a strategy for sewage sludge management: Influence of process withdrawal point on hydrochar properties, Energies 13 (11) (2020) 2890, https://doi.org/10.3390/en13112890.

[28] J.N. Zvimba, E.V. Musvoto, L. Nhamo, T. Mabhaudhi, I. Nyambiya, L. Chapungu, L. Sawunyama, Energy pathway for transitioning to a circular economy within wastewater services, Case Stud. Chem. Environ. Eng. 4 (2021) 100144, https://doi.org/10.1016/j.cscee.2021.100144.

[29] C.I. Aragón-Briceño, O. Grasham, A.B. Ross, V. Dupont, M.A. Camargo-Valero, Hydrothermal carbonization of sewage digestate at wastewater treatment works: Influence of solid loading on characteristics of hydrochar, process water and plant energetics, Renew. Energy 157 (2020) 959–973, https://doi.org/10.1016/j.renene.2020.05.021.

[30] D. Lachos-Perez, P.C. Torres-Mayanga, E.R. Abaide, G.L. Zabot, F. De Castilhos, Hydrothermal carbonization and Liquefaction: differences, progress, challenges, and opportunities, Bioresour. Technol. 343 (2022) 126084, https://doi.org/10.1016/j.biortech.2021.126084.

[31] J.A. Villamil, A.F. Mohedano, J.J. Rodriguez, M.A. de la Rubia, Valorisation of the liquid fraction from hydrothermal carbonisation of sewage sludge by anaerobic digestion, J. Chem. Technol. Biotechnol. 93 (2) (2018) 450–456, https://doi.org/10.1002/jctb.5375.

[32] L. Wang, Y. Chang, Q. Liu, Fate and distribution of nutrients and heavy metals during hydrothermal carbonization of sewage sludge with implication to land application, J. Clean. Prod. 225 (2019) 972–983, https://doi.org/10.1016/j.jclepro.2019.03.347.

[33] H.P. Ruyter, Coalification model, Fuel 61 (12) (1982) 1182–1187, https://doi.org/10.1016/0016- 2361(82)90017-5.

[34] D. Jung, A. Kruse, Evaluation of Arrhenius-type overall kinetic equations for hydrothermal carbonization, J. Anal. Appl. Pyrol. 127 (2017) 286–291, https://doi.org/10.1016/j.jaap.2017.07.023.

[35] A. Funke, F. Ziegler, Hydrothermal carbonization of biomass: A summary and discussion of chemical mechanisms for process engineering, Biofuels Bioprod. Biorefin. 4 (2) (2010) 160–177, https://doi.org/10.1002/bbb.198.

[36] N. Stobernack, F. Mayer, C. Malek, R. Bhandari, Evaluation of the energetic and environmental potential of the hydrothermal carbonization of biowaste: Modeling of the entire process chain, Bioresour. Technol. 318 (2020) 124038, https://doi.org/10.1016/j.biortech.2020.124038.

[37] M. Heidari, A. Dutta, B. Acharya, S. Mahmud, A review of the current knowledge and challenges of hydrothermal carbonization for biomass conversion, J. Energy Inst. 92 (6) (2019) 1779–1799, https://doi.org/10.1016/j.joei.2018.12.003.

[38] H. Liu, I.A. Basar, A. Nzihou, C. Eskicioglu, Hydrochar derived from municipal sludge through hydrothermal processing: A critical review on its formation, characterization, and valorization, Water Res. 199 (2021) 117186, https://doi.org/10.1016/j.watres.2021.117186.

[39] E. Danso-Boateng, G. Shama, A.D. Wheatley, S.J. Martin, R.G. Holdich, Hydrothermal carbonisation of sewage sludge: effect of process conditions on product characteristics and methane production, Bioresour. Technol. 177 (2015) 318–327, https://doi.org/10.1016/j.biortech.2014.11.096.

[40] Z.C. Zheng Chu Peng, M.X. Ma Xiao Qian, Y.Z. Yao Zhong Liang, C.X. Chen Xin Fei, The Properties and Combustion Behaviors of Hydrochars Derived from Co-Hydrothermal Carbonization of Sewage Sludge and Food Waste (2019), https://doi.org/10.1016/j.biortech.2019.121347.

[41] S.Z. Roslan, S.F. Zainudin, A. Mohd Aris, K.B. Chin, M. Musa, A.R. Mohamad Daud, S.S.A. Syed Hassan, Hydrothermal carbonization of sewage sludge into solid biofuel: influences of process conditions on the energetic properties of hydrochar, Energies 16 (5) (2023) 2483, https://doi.org/10.3390/en16052483.

[42] Z. Wang, Y. Zhai, T. Wang, C. Peng, S. Li, B. Wang, X. Liu, C. Li, Effect of temperature on the sulfur fate during hydrothermal carbonization of sewage sludge, Environ. Pollut. 260 (2020) 114067, https://doi.org/10.1016/j.envpol.2020.114067.

[43] C. Aragón-Briceño, A.B. Ross, M.A. Camargo-Valero, Evaluation and comparison of product yields and bio-methane potential in sewage digestate following hydrothermal treatment, Appl. Energy 208 (2017) 1357–1369, https://doi.org/10.1016/j.apenergy.2017.09.019.

[44] M. Ahmed, G. Andreottola, S. Elagroudy, M.S. Negm, L. Fiori, Coupling hydrothermal carbonization and anaerobic digestion for sewage digestate management: Influence of hydrothermal treatment time on dewaterability and bio-methane production, J. Environ. Manage. 281 (2021) 111910, https://doi.org/10.1016/j.jenvman.2020.111910.

[45] K.R. Parmar, A.B. Ross, Integration of hydrothermal carbonisation with anaerobic digestion opportunities for valorisation of digestate, Energies 12 (9) (2019) 1586, https://doi.org/10.3390/en12091586.

[46] F. Merzari, M. Langone, G. Andreottola, L. Fiori, Methane production from process water of sewage sludge hydrothermal carbonization. A review. Valorising sludge through hydrothermal carbonization, Crit. Rev. Environ. Sci. Technol. 49 (11) (2019) 947–988, https://doi.org/10.1080/10643389.2018.1561104.

[47] K. Zhu, Q. Liu, C. Dang, A. Li, L. Zhang, Valorization of hydrothermal carbonization products by anaerobic digestion: Inhibitor identification, biomethanization potential and process intensification, Bioresour. Technol. 341 (2021) 125752, https://doi.org/10.1016/j.biortech.2021.125752.

[48] A.E. Cioabla, I. Ionel, G.A. Dumitrel, F. Popescu, Comparative study on factors affecting anaerobic digestion of agricultural vegetal residues, Biotechnol. Biofuels 5 (2012) 1–9, https://doi.org/10.1186/1754-6834-5-39.

[49] X.Q. Ma, J.J. Liao, D.B. Chen, Z.X. Xu, Hydrothermal carbonization of sewage sludge: Catalytic effect of Cl− on hydrochars physicochemical properties, Mol. Catal. 513 (2021) 111789, https://doi.org/10.1016/j.mcat.2021.111789.

[50] Council Directive of 12 June 1986 on the protection of the environment, and in particular of the soil, when sewage sludge is used in agriculture (86/278/EEC) https://eur-lex.europa.eu/eli/dir/1986/278/oj/eng (accessed 8 September 2024).

[51] Council Directive Directive 2010/75/EU of the European Parliament and of the Council of 24 November 2010 on industrial emissions (integrated pollution prevention and control) https://eur-lex.europa.eu/eli/dir/2010/75/oj/eng (accessed 8 September 2024).

[52] Z.J. Zhang Jin Hong, L.Q. Lin Qi Mei, Z.X. Zhao Xiao Rong, The Hydrochar Characters of Municipal Sewage Sludge under Different Hydrothermal Temperatures and Durations (2014), https://doi.org/10.1016/S2095-3119(13)60702-9.