Hydrothermal carbonisation of mechanically dewatered digested sewage sludge—Energy and nutrient recovery in centralised biogas plant

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ABSTRACT

This study aimed to assess the role of hydrothermal carbonisation (HTC) in digestate processing in centralised biogas plants receiving dewatered sludge from regional wastewater treatment plants and producing biomethane and fertilisers. Chemically conditioned and mechanically dewatered sludge was used as such (total solids (TS) 25%) or as diluted (15% TS) with reject water in 30 min or 120 min HTC treatments at 210 °C, 230 °C or 250 °C, and the produced slurry was filtered to produce hydrochars and filtrates. The different hydrochars contributed to 20–55% of the original mass, 72–88% of the TS, 74–87% of the energy content, 71–92% of the carbon, above 86% of phosphorous and 38–64% of the nitrogen present in the original digestates. The hydrochars' energy content (higher heating values were 11.3–12.2 MJ/kg-TS) were similar to that of the digestates, while the ash contents increased (from 43% up to 57%). HTC treatments produced filtrates in volumes of 42–76% of the dewatered digestate, having a soluble chemical oxygen demand (SCOD) of 28–44 g/L, of which volatile fatty acids (VFAs) contributed 10–34%, and methane potentials of 182–206 mL-CH$_4$/g-SCOD without any major indication of inhibition. All 32 pharmaceuticals detected in the digestates were below the detection limit in hydrochars and filtrates, save for ibuprofen and benzotriazole in filtrate, while heavy metals were concentrated in the hydrochars but below the national limits for fertiliser use, save for mercury. The integration of HTC to a centralised biogas plant was extrapolated to enhance the annual biogas production by 5% and ammonium recovery by 25%, and the hydrochar was estimated to produce 83 GJ upon combustion or to direct 350 t phosphorous to agriculture annually.

1. Introduction

Municipal wastewaters are typically treated using an activated sludge process that results in high amounts of sewage sludge, including primary sludge consisting of wastewater solids and biosludge consisting of aerobic microbes. In wastewater treatment plants, sewage sludge is often gravimetrically thickened and then stabilised in anaerobic digestion (AD), which recovers the energy from the process as biogas, which is valued as a renewable energy source. The digestated material is typically mechanically dewatered using polymers into solid fraction and liquid fraction, referred to as reject water. The solid fraction (total solids (TS) 15–30%) with high organic and nutrient content may be composted to be used as soil

amendment or combusted (Alvarenga et al., 2015). The reject water is usually circulated to the wastewater treatment plant.

The sewage sludge energy content recovered in AD has recently been increasingly considered for upgrading into biofuel or gas grid injection to promote energy transition; for economic reasons, centralised biogas plants treating dewatered sludge from several sewage plants are used. Furthermore, the recovery of sewage sludge nutrients and residual carbon, especially that of phosphorous, is of major interest because of diminishing phosphorous resources and to reduce the climate impacts of nitrogen fertilizer production (Becker et al., 2019). However, in practice, the use of sewage sludge digestates in agriculture is a concern because of contaminants; thus, the use of sewage sludge–based nutrients is facing major challenges. The concern is about certain contaminants, such as heavy metals, pharmaceuticals and microplastics, which the biological processes alone are incapable of converting

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into something more harmless and part of which can also end up in the digestate (Alvarenga et al., 2015).

Hence, to harness sewage sludge digestate in a safe manner, an additional post-treatment step needs to be considered. One such recently discussed sludge post-treatment is hydrothermal carbonisation (HTC) (Aragón-Briceño et al., 2017). HTC is a thermal treatment applicable for organic material and is conducted at temperatures of 180–250 °C with residence times from 0.5 to several hours (Libra et al., 2011). Particularly, HTC is considered for moist (TS 10–50%) organic material, which differentiates it from other thermal processes, for example pyrolysis, which typically requires a higher solids content (TS≥90%) (Bridgwater et al., 1999) and utilises comparatively high temperatures (500–800 °C) (Paneque et al., 2017). HTC yields a moist carbonaceous solid fraction that is usually separated into a solid and liquid, i.e. hydrochar and filtrate, respectively. In addition, HTC releases exhaust gas comprising primarily of CO_2 but also of other compounds, such as hydrogen sulphide, nitrogen dioxide, nitric oxide and ammonia, hence requiring further treatment (Berge et al., 2011; Danso-Boateng et al., 2015). The amounts and characteristics of the three fractions are affected by the feedstock (e.g., Berge et al., 2011) and the used HTC conditions, such as temperature and residence time. HTC has been studied for a range of feedstocks to produce hydrochar, which could be used as is or after downstream processing, for example, as a soil amendment (Bargmann et al., 2014), for sequestrating atmospheric carbon to soils (Libra et al., 2011), as an adsorbent (Sun et al., 2011), or for combustion (Smith et al., 2016).

HTC treatment has also been studied for sewage sludge, for example, to screen the effects of HTC on the treatment of sludges from different phases of the plant (Merzari et al., 2020), to compare with different feedstocks, including agricultural waste (He et al., 2019), and to determine the effects of HTC treatment conditions on hydrochar (Danso-Boateng et al., 2015). The AD process affects the characteristics of the sludge in many ways; for example, it lowers the carbon content of the sludge, impacts its sulphur and phosphate chemistry, and increases the ammonium concentration. Thus, the characteristics of the hydrochar and filtrate from the HTC treatment of digestate may differ from those of the HTC-treated raw sewage sludge (Aragón-Briceño et al., 2017). There are several laboratory studies on the HTC treatment of digested sewage sludge that have shown, for example, that the filtrate of HTC-treated digested sewage sludge at 240 °C has a clear inhibition towards methane production (Marin-Batista et al., 2020), whereas at lower temperatures, no clear inhibition has been reported (Aragón-Briceño et al., 2017). Regarding the effects of HTC on digestate phosphorous, Marin-Batista et al. (2020) reported an increase in phosphorous content in the filtrate with increasing HTC temperatures, while Merzari et al. (2020) observed no increase, or even a decrease, in the filtrate's phosphorous content after HTC. However, the studies on sewage sludge digestates differ, for example, in the origin of the digestate (before or after dewatering), in the HTC conditions studied and in the processing of the samples in the laboratory before HTC. For example, Merzari et al. (2020) studied dewatered sewage sludge digestate (TS 25%) that they, however, diluted for the HTC treatment (15 g sludge and 10 g water), resulting in ca. 17% TS digestate. Aragón-Briceño et al. (2020), on the other hand, studied sewage sludge digestate with an original TS of 3% but processed the sample in the laboratory to study HTC at eight different TS contents (2.5–30%). Thus, there is a lack of information on the dewatered digestates representing real conditions. Also, the separation techniques employed to obtain hydrochar and filtrate vary, including filtering through a cellulose filter paper (Merzari et al., 2020), vacuum filtration (0.9 mm) followed by an additional supernatant filtration (0.45 μm) (Marin-Batista et al., 2020) and through glass microfibre filters (Aragón-Briceño et al., 2020).

The current work examined the effects of HTC process parameters on the amounts and characteristics of the hydrochar and filtrate produced from dewatered digested sewage sludge. The studied dewatered digestate was obtained directly from the centralised biogas plant, and it was studied as such (TS of 25%) and after dilution with dewatering reject water to TS of 15%, using temperatures of 210 °C, 230 °C and 250 °C and residence times of 30 or 120 min. The separation of hydrochar and filtrate was conducted at a pilot scale. The energy and nutrient characteristics and recovery of both fractions were determined, and the mass balances were evaluated. Results from the laboratory scale study are needed to assess the technological and economic feasibility of scale-up applications for centralised biogas plants.

2. Materials and methods

2.1. Digestates and reject water

In the HTC experiments, mechanically dewatered digestate from an industrial thermophilic sewage sludge digester was used. Mechanical dewatering of digested sludge was done in the plant with a decanter centrifuge, along with polymer addition. Also, reject water from dewatering was used. The materials were obtained from a centralised biogas plant in Topinoja (Turku, Finland), which treated during the experiments annually 75,000 t (ca. 23% TS, 16,500 t-TS/a) of mechanically dewatered sewage sludge transported from six regional municipal wastewater treatment plants, producing 30,000 t of dewatered digestate (ca. 30% TS, 9000 t-TS/a). For the biomethane potential (BMP) assays, the inoculum was from a mesophilic municipal biowaste digestion facility (Riihimäki, Finland). All samples were anaerobically stored at 4 °C for 1–2 months until used. In the HTC experiments, the digestate was used as such (TS 25%, referred to as digestate) or diluted to 15% TS by adding 400 mL of reject water to 600 g of the digestate (referred to as diluted digestate). The dilutions were performed right before the HTC treatments. The material characteristics are shown in Table 1.

2.2. HTC treatments

The HTC treatment used a two-litre Parr® 4500 pressure reactor with an external circulating cooling water system and internal rotary mixer (initially 40 rpm). The final mixing speed increased as a result of the viscosity decrease of the samples during the treatments (Table 2). The sample wet weight for the experiments was 1 kg, and the treatment temperatures were 210 °C, 230 °C or 250 °C with residence times of 30 or 120 min (Table 2).

The heating of the reactor vessel to the target temperatures was achieved within ca. 90 min. The temperature was manually adjusted using Parr® 4848 reactor controllers. The vessel pressure started to increase after the inside temperature reached 100 °C and then increased to 20 to 40 bar depending on the applied temperature. The vessel was held at the target temperature for the pre-set residence time. The realised temperatures fluctuated but remained within ±9 °C from the targeted temperature (Table 2). The 250 °C runs started when the vessel temperature had reached 245 °C because of difficulties in attaining the targeted temperature within 90 min. In all the runs, after the residence time, the heating was switched off, an arbitrary volume of gas was released, and cooling water circulation was initiated in the water jacket. The gas release reduced the inside pressure and temperature by 2–4 bar and 1–4 °C, respectively, of which purpose was to prevent possible condensation. The water cooling lasted until the vessel temperature had decreased to 40–70 °C, which was achieved within 30–40 min. After the HTC treatments, the whole sample volume was weighed,

Table 1

Material characteristics. Total volatile fatty acids (TVFA) comprise of acetate, propionate, isobutyrate, butyrate, isovalerate and valerate.

	Digestate	Diluted digestate	Reject water	Inoculum
pH	7.5	7.9	8	8.4
Total solids (%)	25.6 ± 0.6	14.5 ± 0.2	n.a.	5.1 ± 0.1
Volatile solids (%)	14.6 ± 0.3	7.7 ± 0.8	n.a.	3.3 ± 0.1
VS/TS (%)	57	53	n.a.	64
Ash at 550 °C (%)	43.0 ± 0.1	43.0 ± 0.4	n.a.	n.a.
Ash at 815 °C (%)	40.9 ± 0.1	41.1 ± 0.2	n.a.	n.a.
SCOD (g/L)	2.1 ± 0.01	7.03 ± 0.1	10.3 ± 0.01	10.1 ± 0.01
TVFA (g/L COD)	0.0 ± 0.0	n.a.	1.4 ± 0.1	0.6 ± 0.1
Total nitrogen (g/kg-TS)	35.2 ± 0.1	31.0 ± 0.4	3.9	n.a.
Ammonium-nitrogen (g/L)	n.a.	n.a.	2.91	n.a.
Total phosphorous (g/kg-TS)	37.2	31.5	2.30[a]	14.1
Phosphate-phosphorous (mg/L)	n.a.	n.a.	58.7	n.a.

n.a. not applicable

[a] calculated (g/L)

Table 2

The target temperatures and realised HTC treatment conditions for digestate and diluted digestate.

Sample	HTC parameters				
	Min. treatment temperature (°C)	Max. treatment temperature (°C)	Max. pressure (bar)	Average treatment pressure (bar)	Final mixing speed (rpm)
Digestate HTC					
210 °C,30min	202	215	29.4	22.7	43
210 °C, 120min	206	214	26.8	20.5	44
230 °C, 30min	229	232	38.8	32.2	45
230 °C, 120min	221	235	34.4	31.0	46
250 °C, 30min	242	251	43.7	42.6	46
250 °C, 120min	243	252	44.5	41.1	46
Diluted digestate HTC					
210 °C, 30min	207	217	25.5	20.8	40
210 °C, 120min	203	214	19.4	23.1	40
230 °C, 30min	227	232	33.1	29.6	46
230 °C, 120min	226	232	30.2	28.2	46
250 °C, 30min	244	252	42.5	40.5	46
250 °C, 120min	243	252	42.7	40.1	46

recovered and stored at 4 °C prior to solid–liquid separation by filtration.

Filtration for the HTC-treated sludges (called slurry) was conducted in a small-scale pressurised filtration unit. The temperature during filtration was ca. 60 °C, which was attained by warming up the samples (ca. 1 kg) in a water bath before filtration. The heated sample was placed onto a filter cloth inside a cylinder. The pressure in the closed cylinder gradually increased: 5 min to 1 bar, 10 min to 4 bar and then to the final pressure of 15 bar. The total pressing time for the digestate samples was about 20 min, whereas for the diluted digestate samples, it was about 30 min. The end-products of filtration are from now on called hydrochar (solid fraction) and filtrate (liquid fraction). The hydrochar product is comprised of both moisture that was not removed by filtration and of dry solids that are obtained after evaporation. The weights of the recovered filtrate and hydrochar were recorded.

2.3. Biomethane potential assays

The BMPs of the filtrates of the HTC-treated digestates were determined in static 37-day long batch assays in triplicate at 35 °C. In all assays, 120 mL serum bottles and 3.4 g (wet weight) of inoculum were used. The SCOD concentration of the filtrate was set to 2 g-SCOD/L. NaHCO₃ (4 g/L) was used as a buffer, and distilled water was added to the bottles to reach the volumes of 64 mL. The initial pH was adjusted between 7 and 8 with HCl (1 M), after which the bottles were closed with rubber stoppers. Anaerobic conditions were created inside by flushing with nitrogen gas for 3 min. Assays containing only water, buffer and inoculum functioned as the control, and their methane production was subtracted from the methane production of the sample assays. The methane concentrations in the BMP determination were measured with a GC-FID (Perkin Elmer Clarus), as described previously (Kinnunen et al., 2015) and the BMPs were calculated as presented in Eq. S1.

2.4. Chemical analysis and calculations

The TS and volatile solids (VS) were gravimetrically determined according to standard methods (APHA 2540). The ash content measurements at 550 °C and 815 °C followed the same gravimetric principle. The pH level was measured with a WTW pH 3210 metre using WTW SenTix® 41 electrode. COD and SCOD were analysed according to Finnish standard methods (SFS 5504). Volatile fatty acids (VFA) were determined with GC-FID, as described previously (Kokko et al., 2018). Prior to the analysis of VFA and SCOD, the samples were filtered through a 0.45 µm filter (Chromafil Xtra PET).

The total nitrogen and soluble ammonium-nitrogen in the liquid phase were analysed using Hach Lange kits (LCK 238, LCK 338, LCK 305 and LCK 303) according to the instructions provided by the company. The other cations than ammonium-nitrogen in the liquid samples were analysed according to the ion chromatography standard SFS-EN ISO 10,304–1 using an ion chromatograph (Dionex DX-120, USA) with AS40 autosampler, IonPac CS12A cation exchange column and CSRS 300 suppressor (4 mm). The eluent contained 2 mM methane sulphonic acid, and the flow rate was 1 mL/min.
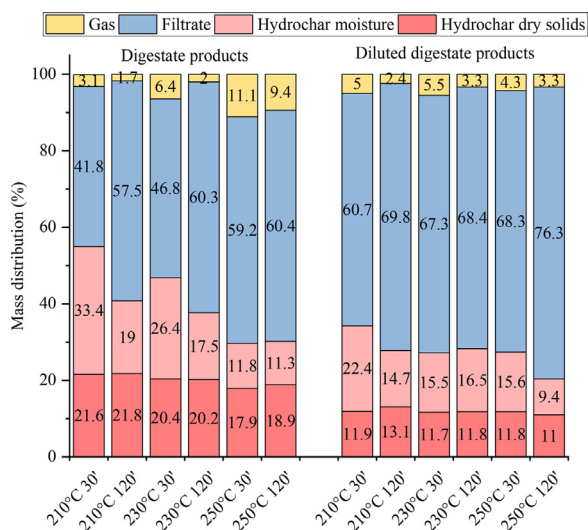
Fig. 1. The mass distribution of digestate and diluted digestate after the HTC treatments at different conditions into hydrochar, filtrate and gas fractions. Hydrochar and filtrate were produced by filtration. The hydrochar mass fraction is expressed as wet weight.

The solid phase total carbon, hydrogen, nitrogen and sulphur were determined by elemental analysis in Thermo Scientific FlashSmart Elemental analyzer (CHNS/O) with TCD (Thermal Conductivity Detector). Before the analysis, samples were properly homogenized; samples were first dried in oven at 100 °C overnight, after which the dry samples were grinded with mortar to obtain fine powder. The samples for CHNS analysis were weighted (2–3 mg) on a microgram balance (Mettler Toledo WXTS Microbalance) in tin cups. Calibration was evaluated analysing BBOT (2,5-Bis(5–tert–butyl–2-benzo-oxazol-2-yl)) as a standard. Gases used were helium as a carrier gas and oxygen as a gas for sample oxidation. The total phosphorous and other elements in the solid and liquid samples were determined with inductively coupled plasma mass spectrometry (ICP-MS). For further details of this analysis, see Supporting Information. The calorific values of the solid samples were determined in duplicate with a Parr® 6725 Semi-micro Oxygen Bomb Calorimeter, according to the ISO 1928 standard. Prior to the analysis, the samples were dried overnight at 100 °C. The sample weight for the analysis was 0.2–0.3 g.

The hydrochar yields (Y), energy densification (E_d) and energy recovery of hydrochar were calculated as described previously (Danso-Boateng et al., 2015). The energy content and energy recoveries of the filtrates were calculated based on the results of the BMP and the mass distribution after different HTC runs. The mass of digestate converted to gas during HTC treatment was calculated by the difference in the masses of the input digestate and the obtained slurry after HTC (Eq. S7). For further details of the calculations, see Supporting Information.

3. Results and discussion

3.1. Mass and TS recoveries

The HTC treatment yielded three fractions, the relative mass yields of which depended on the applied HTC conditions (Fig. 1). The produced hydrochar masses (wet basis) covered 30–55% and 20–34% of the original masses of the digestate and diluted digestate, respectively (Fig. 1). The moisture content of the hydrochars after filtration ranged between 37 and 61% and 46 and 65% for the digestate and diluted digestate, respectively (Table 3). The VS/TS ratio decreased from 57% of the digestates to 43–50% in the hy-

drochars. The hydrochar yields (dry basis) were between 72% and 87% and between 72% and 88% for the digestate and diluted digestate (Table 3), respectively, suggesting that the TS content of the digestate does not affect the recovery of TS in hydrochar. With the digestate, an increased treatment temperature decreased the hydrochar mass and TS yields and increased the yields of the filtrate and gas (Fig. 1), while the effects were not so clear for the diluted digestate. The mass of the filtrate varied between 42% and 60% and between 60% and 76% for the digestate and diluted digested (Fig. 1), respectively. The calculated gas formation ranged from 1 to 11% of the original digestate mass and was larger in the HTC of the digestate than in the HTC of diluted digestate. The highest hydrochar TS yields of 87.6% and 88.3% were obtained at 210 °C for 120 min for the digestate and diluted digestate, respectively, while the residence time had no clear effect on hydrochar TS yield.

The present study and other research (Aragón-Briceño et al., 2017) have shown that in processing mechanically dewatered digestate, HTC treatment with subsequent solids separation can produce hydrochar with recoveries even above 70–85% of the original TS while contributing to around 40–50% of the original mass. The present hydrochar yields on a TS basis (72–88%) are at the upper range of the hydrochar yields of 66–75% (at 220–250 °C) and 67–74% (at 180–210 °C) reported in other HTC studies with digested sewage sludge with a TS content of 17% (Merzari et al., 2020) or 16.5% (Marin-Batista et al., 2020), respectively, with decreased hydrochar yields at increased temperatures, which is also observed in the current study. However, a hydrochar yield of 51% was obtained at 240 °C (Marin-Batista et al., 2020), indicating that the original characteristics of the sewage sludge digestate have a major effect on the product characteristics. In HTC studies conducted with digested sewage sludge at a lower TS content of below 5%, the hydrochar yields on a TS basis have varied from 47% (Berge et al., 2011) to 56–78% (Aragón-Briceño et al., 2017; Merzari et al., 2020) without a clear effect of temperature on hydrochar yield, as what is found at higher digestate TS contents. Thus, the hydrochar TS yield may not be fully deduced from the TS content or the HTC conditions, but also from the chemical characteristics of the sludge (Merzari et al., 2020; Parmar and Ross, 2019). The hydrochar mass yield in the present study (30–55% for digestate and 20–34% for diluted digestate) was considerably lower than the 66–88% obtained for digested sewage sludge with TS content of 17% (Merzari et al., 2020). However, it should be noted that the reported mass and TS yields of hydrochar and filtrate are affected along with the digestate characteristics by the separation technique used to separate the hydrochar and filtrate, which vary by research.

3.2. Energy characteristics

3.2.1. Hydrochar

The energy content and solid fuel properties of the different hydrochars and digestates were assessed using moisture content, heating values, and the ash content, which is responsible for the combustion furnace fouling (Jenkins et al., 1998). The energy content and solid fuel properties of the 12 hydrochars, and the digestate and diluted digestate are presented in Table 3. The HHV of all the hydrochars were of a similar range (11.3–12.2 MJ/kg-TS) as the digestates' HHVs (11.5–11.9 MJ/kg-TS), with energy densification values of 0.95–1.05. The HHV of the digestate hydrochars was 1.2–5.5% higher than the HHV of the digestate after all the treatments, except for the mildest ones conducted at 210 °C. Conversely, the HHV of diluted digestate hydrochar increased by 2.2% from the digestate HHV only in the severest treatment (250 °C, 120 min), while the other treatment conditions decreased the HHV by 0.6–4.9%. The ash content (determined at 550 °C) of the hydrochars increased from 50% to 57% with increasing treatment temperature

Table 3
The characteristics of the digestates and their respective hydrochars.

Sample	Proximate analyses					Heating values				Ultimate analyses				Yield (%)	Energy densification
	Moisture (%)	VS[a] (%)	VS/TS	Ash[a] 550 °C (%)	Ash[a] 815 °C (%)	LHV[a] (MJ/kg)	HHV[a] (MJ/kg)	C (%)[a]	H (%)[a]	N (%)[a]	S (%)[a]	O (%)[b]	P (%)[a]		
Digestate	75.00	14.00	57.00	43.10	40.90	10.60	11.49	30.30	4.40	3.50	2.30	59.50	3.72	n.a.	n.a.
Diluted digestate	85.00	8.0	57.0	42.90	41.00	11.10	11.90	28.60	4.20	3.10	2.30	61.80	3.15	n.a.	n.a.
Hydrochars of HTC treated digestate															
210 °C for 30min	60.70	19.80	50.40	49.60	47.70	10.56	11.33	31.07	3.87	2.54	1.83	60.69	5.33	86.46	0.99
210 °C for 120min	46.60	25.90	48.50	51.80	49.60	10.60	11.38	31.00	3.69	2.57	1.80	60.94	5.11	87.58	0.99
230 °C for 30min	56.40	21.10	48.40	51.60	49.60	10.83	11.63	31.40	4.00	2.70	1.93	59.97	4.65	81.97	1.01
230 °C for 120min	46.30	24.90	46.40	53.70	51.50	11.17	11.89	30.30	3.58	2.40	1.77	61.95	4.73	81.62	1.03
250 °C for 30min	39.80	26.80	44.50	55.50	52.50	11.10	11.85	30.03	3.78	2.26	2.16	61.77	4.94	72.24	1.03
250 °C for 120min	37.30	27.10	43.20	56.70	54.30	11.43	12.12	30.30	3.48	2.15	2.17	61.90	5.67	75.24	1.05
Hydrochars of HTC treated diluted digestate															
210 °C for 30min	65.30	16.70	48.10	51.80	49.50	10.57	11.35	30.41	3.98	2.58	1.91	61.12	4.95	78.65	0.95
210 °C for 120min	52.70	22.60	47.80	52.20	50.20	10.61	11.38	30.01	3.80	2.38	2.00	61.81	3.74	88.29	0.95
230 °C for 30min	57.00	20.40	47.40	52.60	50.30	11.01	11.82	29.72	3.99	2.42	2.10	61.77	5.07	77.40	0.99
230 °C for 120min	58.40	19.20	46.20	53.70	50.90	10.75	11.48	29.59	3.66	2.14	2.18	62.43	4.94	77.65	0.96
250 °C for 30min	56.90	20.00	46.40	54.00	51.60	11.05	11.86	30.41	4.00	2.31	2.23	61.05	4.65	77.58	0.99
250 °C for 120min	46.00	23.20	43.00	57.00	54.20	11.42	12.19	30.38	3.84	2.30	2.19	61.29	5.02	72.00	1.02

VS: volatile solids, TS: total solids, LHV: lower heating value, HHV: higher heating value, C: carbon, H: hydrogen, N: nitrogen, S: sulphur, P: phosphorous.

[a] reported against total solids.

[b] calculated as difference between 100 and total sum of C, H, N and S on dry basis.

and residence time, while the ash contents of both the digestate and diluted digestate were 43%.

Based on the current study and what is reported in the literature, it appears that the effects of HTC treatment on the HHV of the digestate are quite minimal (less than 4.5%). The HHV of the digestates used in the present study (11.5–11.9 MJ/kg-TS) was much lower than reported in other studies with digestate TS content of 16.5% (14.9 MJ/kg-TS; Marin-Batista et al., 2020) or 17% (16.0 MJ/kg-TS; Merzari et al., 2020). A lower HHV of the digestate (10.7 MJ/kg-TS) has been reported with 2.9% TS in the digestate (Merzari et al., 2020). The HHVs of the hydrochars differed less than 2% (Martin-Batista et al., 2020) and less than 5% (Merzari et al., 2020) from the HHVs of the digestates with a TS content above 15%, which is in accordance with the findings of the present study. Higher differences in the HHVs of the digestate and hydrochar of 7.2–26% have been reported for digestates with a lower TS content of 2.9–4.5% (Table 5). While a high ash content of the feedstock is related to decreased HHVs (Zhuang et al., 2018), it does not explain the difference in the observed HHV for the different digestate hydrochars between the present and previous studies (Marin-Batista et al., 2020; Merzari et al., 2020). Thus, it seems that the HHV of the digested sewage sludge hydrochar depends on the HHV of the digestate used as feedstock.

Although the effects of HTC treatment on the HHV are often negligible, HTC treatment results in higher ash content of the hydrochar compared with the original digestate. In the present study, the ash content of the digested sewage sludge increased from 43% to as high as 50–57% on HTC treatment, while with other digested sewage sludge, the ash content increased from 40% to 42–48% (Marin-Batista et al., 2020) and from 28% to 35–43% (Merzari et al., 2020) on HTC treatment of digestates with TS content of 16.5% and 17%, respectively. HTC treatment of digested sewage sludge with a lower TS content of 2.9–3.0% has resulted in an even higher increase in the ash content, from 35% to 55% (Berge et al., 2011) and from 45% to 57–77% (Merzari et al., 2020). Merzari et al. (2020) linked the lower ash content of the dewatered digestate (28.4%) compared with the original digestate (45%) to the removal of inorganic compounds, such as NH_4-N, $CaCO_3$, Mg and Na, that end up in the reject water during conditioning and dewatering.

In terms of fouling, slagging and corrosion, the inorganics contained in the ash influence the fuel behaviour upon combustion, thus affecting the choice of an appropriate combustion technology (Smith et al., 2016). These ash-forming inorganic elements include alkali and earth alkali metals (Na, K, Mg and Ca) as well as P, Fe, Si and S (Smith et al., 2016). In the present study, the increase in the concentrations of calcium with temperature of HTC treatment in the hydrochars were similar for the digestate and diluted digestate (from 22 to 24 to 23.2–35.1 g-Ca/kg-TS), whereas those of sodium and potassium were decreased for diluted digestate (from 6.2 to 3.0–4.2 g-Na/kg-TS and from 2.4 to 1.5–2.0 g-K/kg-TS) and were increased or unaffected for digestate (from 4.25 to 2.8–4.1 g-Na/kg-TS and from 1.7 to 1.6–2.0 g-K/kg-TS) (Table S1). In the case of iron, a larger decrease in concentration from 229 to 165–201 g-Fe/kg-TS was observed with the digestate than with the diluted digestate (from 184 to 133–182 g-Fe/kg-TS), which could be due to the degradation of digestate particles and their extraction into the liquid fraction (Wang et al., 2019). In addition, in the present study, the HTC treatment slightly decreased the sulphur concentrations from 23 g-S/kg-TS of digestates to 18–22 g-S/kg-TS of hydrochars. These concentrations of sulphur were higher than in the digested sewage sludge hydrochars reported elsewhere (maximum sulphur concentration of 12 g-S/kg-TS; Aragón-Briceño et al., 2017; Parmar and Ross, 2019), which was because of their lower initial digestate sulphur concentration when compared with the present digestate. The comparatively high sulphur content in the present digestate may arise from the addition of phosphorous precipitation chemical, Fe(II)SO$_4$, at the WWTP, which is also supported by the high iron concentrations in the hydrochars that are ca. 10-fold higher than that reported for dewatered digestate by Marin-Batista et al. (2020).

3.2.2. Filtrate

The HTC treatment produced filtrates with pH of 8.4–9.0 from the digestate (initial pH 7.5) and with a pH of 9.3–9.7 for the diluted digestate (initial pH 7.9). HTC treatment of digested sewage sludge results in alkaline filtrates (Aragón-Briceño et al., 2017; Marin-Batista et al., 2020), even though the degradation products of hydrolysis generated during HTC often promote acidity rather than alkalinity (Qiao et al., 2011). However, the final pH is also impacted by volatilisation, for example, of ammonia, during HTC treatment (Liu et al., 2019). Even though the pH values of the filtrate are higher than those considered optimum for anaerobic treatment, the treatment of the filtrates in AD may be managed

Table 4

The characteristics of the reject water, filtrate of digestate and filtrates after HTC treatment.

Sample	Energy content				Nutrients			
	SCOD (g/L)	TVFA (g/L COD)	BMP (L CH$_4$/kg SCOD)	pH	N (g/L)	NH$_4$–N (g/L)	P (mg/L)	PO$_4^{2-}$ (mg/L)
Reject water	10.3	1.4	n.a.	8.0	3.7	2.9	n.a.	58.6
Filtrate of digestate	2.1	n.d.	97 ± *n*.a.	8.0	0.3	n.d.	1080	n.d.
Filtrates of HTC treated digestate								
210 °C for 30min	38.9	3.9	183 ± 8.3	8.4	5.4	2.6	700	40
210 °C for 120min	44.4	5.1	126 ± 48.4	8.7	6.1	3.2	810	49
230 °C for 30min	36.8	7.2	195 ± 2.5	8.9	5.3	2.8	590	48
230 °C for 120min	40.3	12.4	191 ± 23	8.9	5.6	3.3	800	99
250 °C for 30min	38.5	11.4	206 ± 8.1	8.9	4.9	2.7	890	67
250 °C for 120min	38.8	12.8	185 ± 18.8	8.9	5.0	2.9	510	68
Filtrates of HTC treated diluted digestate								
210 °C for 30min	30	3.3	n.a.	9.3	4.6	2.3	730	129
210 °C for 120min	31.9	3.5	n.a.	9.4	4.8	2.6	770	97
230 °C for 30min	28	6.7	n.a.	9.6	4.3	2.5	330	87
230 °C for 120min	28.6	7.6	n.a.	9.7	4.6	2.8	1130	88
250 °C for 30min	28.8	6.0	n.a.	9.7	4.3	2.8	550	119
250 °C for 120min	28	9.5	n.a.	9.5	4.3	2.8	680	176

n.a. not analysed, n.d. not detected, SCOD: soluble chemical oxygen demand, TVFA: total volatile fatty acids, BMP: biochemical methane potential.
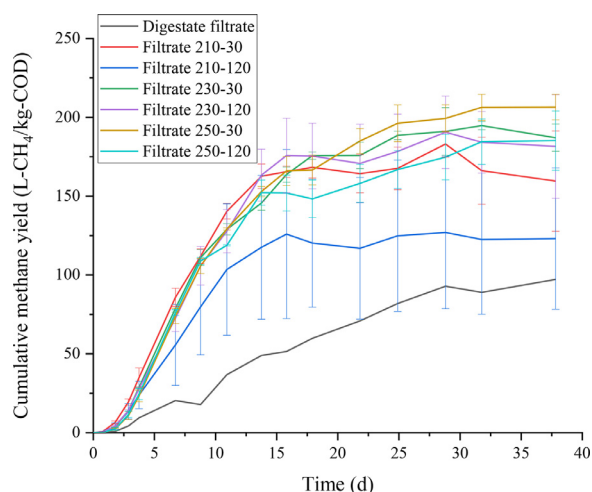

Fig. 2. The cumulative methane production of the filtrates from digestate before (digestate filtrate) and after the HTC treatment (filtrate obtained at HTC temperature between 210 and 250 °C and residence times of 30 or 120 min).

without pH adjustment because the process' operation and co-digestion can be adjusted.

The SCODs of the HTC filtrates ranged from 37 to 44 g/L and from 28 to 32 g/L for the digestate and diluted digestate, respectively, being 10–20 times higher than in the feedstocks. The SCODs were slightly higher at higher HTC treatment temperatures, but no major effects of the HTC conditions were obvious. However, even though the SCOD changed only a little, its composition varied because total VFA contributed ca. 30% of the SCOD at higher temperatures, while at 210 °C TVFAs were ca. 10% of SCOD. The higher treatment temperature especially increased the propionate concentration from around 0.4 g/L at 210 °C to 6.9 g/L at 250 °C, while the changes in other VFA concentrations were low. Increased residence time increased acetate concentration slightly (≤1.8 g/L) at all temperatures. Even though the SCOD composition varied in different filtrates, the cumulative methane production profiles of all the filtrates were almost similar with an initial two-day lag phase (Fig. 2). The resulting BMPs varied from 185 to 206 mL-CH$_4$/g-SCOD with little difference and without a clear impact resulting from the HTC conditions (Table 4). The BMP yields of the HTC filtrates were around two-fold higher compared with the BMP yield of the filtrate of the original digestate.

The present and previous studies have shown that HTC treatment increases the SCOD of the filtrate several fold compared with the SCOD of the sewage sludge digestate, resulting in reported SCOD values ranging from 5.7 g/L up to 72 g/L for HTC filtrates (Table 6). This increase in SCOD is a result from the hydrolysis of fats, carbohydrates and proteins into smaller units, that is, fatty acids, VFAs, sugars and amino acids (Qiao et al., 2011). With a specific feedstock, the feedstock solids content used in the HTC treatment affects the SCOD concentration. For example, HTC treatment (250 °C, 30 min) of sewage sludge digestate increased filtrate SCODs from 9.7 g/L up to 72 g/L when the TS content of the digestate used in HTC treatment was increased from 2.5% to 30% (Aragón-Briceño et al., 2020). Contrary to our study, Aragón-Briceño et al. (2020) reported that HTC treatment decreased the share of VFAs of the SCOD because it was around 15% for the digestate and, at the highest, 10% for HTC filtrate. Furthermore, the share of the VFAs of the SCOD decreased with increasing loading from 10% to ca. 5% of the highest solids loading of 72 g/L (Aragón-Briceño et al., 2020). It should be noted that in HTC treatments, some produced compounds may also volatilise and be discharged in the gas phase.

Based on the current study and the literature, the HTC treatment of digested sewage sludge has resulted in two- to three-fold higher methane production per g-SCOD (Aragón-Briceño et al., 2017) compared with reject water from sewage sludge digestate, even though the effects on SCOD composition vary. The batch assays used to determine methane production have not suggested major inhibition in most of the studies (Aragón-Briceño et al., 2020; Parmar and Ross, 2019). On the other hand, severe inhibition was observed in BMP assays with a 240 °C filtrate (Marin-Batista et al., 2020). However, it should be noted that the methane potential is assayed in specific conditions (e.g., batch, with different substrate dilutions) and care should be taken in practice if an anaerobic process is used for the treatment of filtrates. It should also be noted that the volume of the filtrate may be up to 76% of the digestate and close to the feedstock volume. Furthermore, the introduction of the filtrate into the digestor affects the composition of the reject water, the digestate to be treated in HTC and, subsequently, the filtrate characteristics.

3.2.3. Overall energy balance

The combined energy contents (kWh/kg feed) and recoveries (% of the original feed) of the hydrochars (as HHV) and filtrates (as BMP) were assessed for the digestate and of the hydrochars for
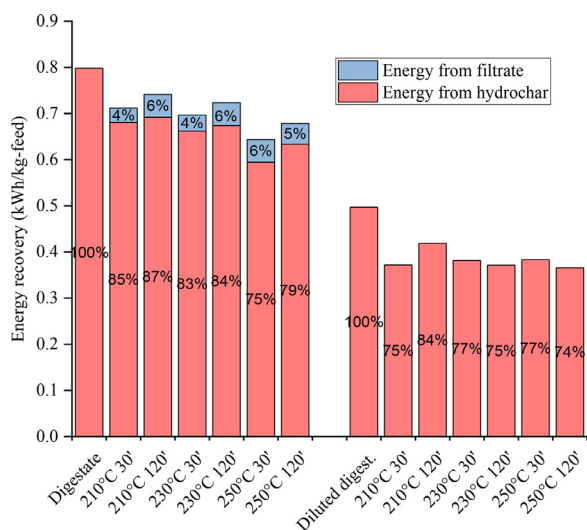
Fig. 3. The energy recovered (as kWh/kg feed) in the hydrochar and filtrate after the HTC treatment of digestate and diluted digestate compared to the energy content of the digestate and diluted digestate, respectively. The energy yields (% of the HTC feed) of the hydrochars are marked on the columns. The energy contents of the filtrates originating from the diluted digestates were not determined.

the diluted digestate (Fig. 3). The values presented do not consider the energy consumed in the HTC. The hydrochars covered 74–87% of the total energy content of the digestate and diluted digestate, while the filtrates covered 4–6% of the total energy content of the digestate. The highest energy contents were obtained in the digestate hydrochars from the treatments at 210 °C and 230 °C (0.66–0.69 kWh/kg feed). Overall, the hydrochar energy content was more influenced by the digestate TS content than the different HTC conditions. It has been observed that the energy recovery in hydrochar decreases with increasing temperature and time (Aragón-Briceño et al., 2017; Danso-Boateng et al., 2015) but, according to the present results, also with the TS content of the original digestate. The energy balance suggests that HTC downgrades the energetic potential of digested sewage sludge by 7–20%. However, the benefit of the HTC treatment may not come from the absolute energy recovery alone but from the improved suitability for combustion, here considering that the moisture content and a favourable ash composition may diminish fouling (Smith et al., 2016).

3.3. Nutrients

To assess the fate of the nutrients present in the dewatered sewage sludge digestate and diluted digestate, the hydrochars' and filtrates' phosphorous and nitrogen contents were analysed for the different HTC conditions studied (Tables 3 and 4).

For the total phosphorus concentrations, HTC showed an increase by 25–52% and 19–61% compared with the original digestate (37.2 g/kg-TS) and diluted digestate (31.5 g/kg-TS), respectively. The filtrates from the digestate and diluted digestate had total phosphorous concentrations of 510–890 mg/L and 330–1130 mg/L and phosphate concentrations of 40–99 mg/L and 87–176 mg/L, respectively. Although phosphate was increasingly formed during the HTC treatments (not detected in the original digestate filtrate), the total phosphorous concentration of the filtrates decreased (1080 mg/L in the original digestate filtrate), indicating that part of the total phosphorous was transferred to the hydrochar fraction.

In the present study, the recovery of phosphorous in the hydrochar was higher or similar, as previously reported, even though the initial phosphorous concentrations were at a lower range.

Much like in our study, an increase in phosphorous concentrations from 45.8 g/kg-TS to 52.8–63.0 g/kg-TS (with an increase of 15–38%) and from 9.2 g/kg-TS to 9.2–10.9 g/kg-TS (with an increase of 0–18%) have been shown to occur with digestate TS contents of 16.5% and 17%, respectively (Marin-Batista et al., 2020; Merzari et al., 2020). The phosphorous content (g/kg-TS) of the hydrochar has been increased with increasing HTC treatment temperature and residence time (Marin-Batista et al., 2020; Merzari et al., 2020), as also reported in the current study. The difference in the phosphorous concentrations in the hydrochars in different studies (Table 5) is dictated by the digestate phosphorus concentration and may also be affected by the phosphorous removal method at WWTP. Phosphorous is often precipitated at WWTPs with aluminium or iron salts. In the present study, sewage sludge originated from WWTP using iron salts for phosphorous precipitation, resulting in iron concentrations of 180–230 mg/g-TS in the digested sewage sludge. The Al and Fe concentrations in the digestated sewage sludge were 41.9 mg/g-TS and 15.8 mg/g-TS in (Marin-Batista et al., 2020), whereas in (Merzari et al., 2020) the Al concentration in the digested sewage sludge, it was around 2–5 mg/g-TS. However, in these two studies, the unit processes of wastewater treatment, for example, phosphorous removal technologies were not defined, making it difficult to interpret some nutrient results.

Phosphorous only exists either in a solid or liquid state; hence, the phosphorous balance was created by summing the elemental phosphorous analysed in the filtrate and hydrochar. The total phosphorous mass balance in Fig. 4B exceeded the input mass of phosphorous in nearly all treatments, which was due to heterogeneity of the analysed material and a small sample amount in the ICP-MS analysis. However, it can be concluded that the majority (>90%) of the phosphorus was recovered in the hydrochar (Fig. 4A and 4B), to which the different HTC conditions gave little variety. The dissolved phosphorous in the filtrates were slightly higher for the HTC-treated diluted digestate (4–13%) than for digestate (2–5%). It has been reported that lower solids loading (studied TS ranged from 2.5 to 30%) of sewage sludge digestate promotes phosphorous solubility which can be attributed to the decreased precipitation of phosphorous with metal ions that are present in lesser amounts with lower solids input (Aragón-Briceño et al., 2020). The dissolution of phosphorous from the digestate was enhanced with the longer treatment times, except for HTC-treated digestate at 250 °C. Thus, to enable the utilisation of phosphorous, it should be either leached from the hydrochar (Becker et al., 2019), or the hydrochar should be amenable as a fertiliser (Bargmann et al., 2014).

The total nitrogen concentration in the hydrochars were 21.4–25.8 g-TN/kg-TS and reduced by 23–39% and 17–31% relative to the digestate and diluted digestate, respectively (Table 3). The total nitrogen concentrations in the filtrates varied in the range of 4.9–6.1 g/L for the digestate and 4.3–4.8 g/L for the diluted digestate, while the ammonium-nitrogen concentrations presented only slight variations between treatments (2.5–3.3 g/L). There was a significant increase in the total nitrogen and ammonium-nitrogen concentrations when compared with their concentrations in the liquid fraction of the digestate (0.32 g-TN/L, <2 mg-NH$_4$–N/L). However, in the reject water used to dilute the digestate, the total nitrogen and ammonium-nitrogen concentrations were 3.7 g/L and 2.9 g/L, respectively.

The present study has shown that HTC converts nitrogen from the solid phase of the dewatered digestate into the liquid phase. Similarly, a decrease in hydrochar nitrogen content compared with the dewatered digestate has been reported in other studies from 51 to 41–42 g-TN/kg-TS at HTC temperatures of 180–240 °C (Marin-Batista et al., 2020), from 40 to 19–28 g-TN/kg-TS at 250 °C (Aragón-Briceño et al., 2020), and from 58.1 to 31.2–42.7 g-TN/kg-TS at HTC temperature of 190–250 °C (Merzari et al., 2020). With a digestate without dewatering, a decrease in hydrochar nitrogen

Table 5
Comparison of different hydrochars from various HTC treatments obtained from literature with the hydrochars of the present study. The values are expressed against total solids.

Hydrochar origin	HTC conditions	HHV (MJ/kg)		Ash (%)		C (%)		N (%)		S (%)		P (g/kg)		Reference
		30 min	60 min	30 min	60 min	30 min	60 min	30 min	60 min	30 min	60 min	30 min	60 min	
Digested sewage sludge 1[a]	210 °C, 15% TS	11.35	11.38	51.80	52.20	30.41	30.01	2.58	2.38	1.91	2.00	49.53	37.38	present study
	230 °C, 15% TS	11.82	11.48	52.60	53.70	29.72	29.59	2.42	2.14	2.10	2.18	50.71	49.40	
	250 °C, 15% TS	11.86	12.19	54.00	57.00	30.41	30.38	2.31	2.30	2.23	2.19	46.50	50.18	
Digested sewage sludge 1[a]	210 °C, 25% TS	11.33	11.38	49.60	51.80	31.07	31.00	2.54	2.57	1.83	1.80	53.27	51.15	present study
	230 °C, 25% TS	11.63	11.89	51.60	53.70	31.40	30.30	2.70	2.40	1.93	1.77	46.54	47.29	
	250 °C, 25% TS	11.85	12.12	55.50	56.70	30.03	30.30	2.26	2.15	2.16	2.17	49.39	56.65	
Digested sewage sludge 2	180 °C, 16.5% TS	n.a.	14.70	n.a.	42.90	n.a.	30.80	n.a.	4.20	n.a.	1.00	n.a.	52.80	Marin-Batista et al., 2020
	210 °C, 16.5% TS	n.a.	14.90	n.a.	43.90	n.a.	31.80	n.a.	4.10	n.a.	1.00	n.a.	53.20	
	240 °C, 16.5% TS	n.a.	15.10	n.a.	48.10	n.a.	32.60	n.a.	4.10	n.a.	1.10	n.a.	63.00	
Digested sewage sludge 3	160 °C, 4.5% TS	16.97	n.a.	38.63	n.a.	35.53	n.a.	5.11	n.a.	1.07	n.a.	n.a.	n.a.	Aragón-Briceño et al., 2017
	220 °C, 4.5% TS	14.33	n.a.	45.11	n.a.	33.21	n.a.	2.01	n.a.	1.09	n.a.	n.a.	n.a.	
	250 °C, 4.5% TS	17.80	n.a.	36.88	n.a.	38.03	n.a.	4.23	n.a.	1.19	n.a.	n.a.	n.a.	
Digested sewage sludge 4	190 °C, 3% TS	9.27	7.97	57.21	67.1	19.22	14.16	1.58	1.07	n.a.	n.a.	7.2	7.4	Merzari et al. 2019
	220 °C, 3% TS	8.96	7.86	72.57	67.88	11.7	10.21	0.8	0.66	n.a.	n.a.	7.5	7.5	
	250 °C, 3% TS	8.59	9.37	73.42	76.97	12.51	12.02	0.7	0.69	n.a.	n.a.	7.4	6.7	
Digested sewage sludge 4	190 °C, 17% TS	16.3	15.96	35.66	37.05	36.61	35.07	4.27	3.95	n.a.	n.a.	9.20	9.40	Merzari et al. 2019
	220 °C, 17% TS	15.7	15.47	40.48	41.1	35.19	35.75	3.48	3.45	n.a.	n.a.	10.50	10.60	
	250 °C, 17% TS	15.98	15.33	43.36	43.14	35.3	35.57	3.16	3.12	n.a.	n.a.	10.80	10.90	
Raw sewage sludge 1	190 °C, 3% TS	19.45	20.71	24.91	24.40	44.56	46.11	2.23	2.10	n.a.	n.a.	6.20	6.80	Merzari et al., 2020
	220 °C, 3% TS	20.06	18.72	28.58	31.20	44.86	43.15	1.87	1.86	n.a.	n.a.	7.80	9.40	
	250 °C, 3% TS	18.06	19.17	34.63	37.18	41.68	41.21	1.89	1.99	n.a.	n.a.	9.90	10.2	
Digested sewage sludge 5	150 °C, 20% TS	n.a.	15.00[b]	n.a.	43.80	n.a.	33.40	n.a.	3.20	n.a.	0.30	n.a.	n.a.	Parmar K. and Ross A. 2019
	200 °C, 20% TS	n.a.	15.10[b]	n.a.	44.40	n.a.	34.00	n.a.	2.40	n.a.	0.90	n.a.	n.a.	
	250 °C, 20% TS	n.a.	15.30[b]	n.a.	47.50	n.a.	34.70	n.a.	2.40	n.a.	0.70	n.a.	n.a.	

n.a. not applicable.
[a] 120 min instead of 60 min.
[b] theoretical.

Table 6
Comparison of different filtrates from various HTC treatments obtained from literature with the filtrates of the present study.

Filtrate origin	HTC conditions	BMP (ml CH$_4$/g SCOD)		Soluble COD (g/l)		pH		Total Nitrogen (g/l)		NH$_4$–N (g/l)		Total Phosphorous (mg/l)		PO$_4^{2-}$ (mg/l)		Reference
		30 min	60 min	30 min	60 min	30 min	60 min	30 min	60 min	30 min	60 min	30 min	60 min	30 min	60 min	
Digested sewage sludge 1[a]	210 °C, 15% TS	n.a.	n.a.	30.00	31.90	9.34	9.37	4.6	4.8	2.33	2.59	725.20	772.28	128.80	96.92	present study
	230 °C, 15% TS	n.a.	n.a.	28.00	28.60	9.58	9.70	4.3	4.6	2.50	2.83	330.57	n.a.	86.51	87.92	
	250 °C, 15% TS	n.a.	n.a.	28.80	28.00	9.70	9.50	4.3	4.3	2.83	2.76	545.71	688.12	119.34	176.16	
Digested sewage sludge 1[a]	210 °C, 25% TS	183.1	182.6	38.90	44.40	8.42	8.69	5.4	6.1	2.62	3.23	701.30	810.95	39.94	48.50	present study
	230 °C, 25% TS	190.5	194.8	36.80	40.30	8.95	8.95	5.3	5.6	2.85	3.35	592.42	803.00	48.39	99.11	
	250 °C, 25% TS	206.5	185.3	38.50	38.80	8.90	8.91	4.9	5.0	2.71	2.93	892.50	509.53	67.45	67.54	
Digested sewage sludge 2	180 °C, 16.5% TS	n.a.	325[b]	n.a.	56.20	n.a.	7.40	n.a.	8.10[c]	n.a.	4.90	n.a.	11.1[d]	n.a.	n.a.	Marin-Batista et al., 2020
	210 °C, 16.5% TS	n.a.	279[b]	n.a.	61.50	n.a.	7.90	n.a.	9.00[c]	n.a.	5.20	n.a.	19.2[d]	n.a.	n.a.	
	240 °C, 16.5% TS	n.a.	<20[b]	n.a.	53.90	n.a.	8.90	n.a.	9.70c	n.a.	6.30	n.a.	25.3[d]	n.a.	n.a.	
Digested sewage sludge 3	160 °C, 4.5% TS	260	n.a.	12.60	n.a.	9.15	n.a.	11.11	n.a.	1.26[e]	n.a.	n.a.	n.a.	94.03[f]	n.a.	Aragón-Briceño et al., 2017
	220 °C, 4.5% TS	277	n.a.	13.00	n.a.	7.14	n.a.	12.31	n.a.	1.70[e]	n.a.	n.a.	n.a.	72.60[f]	n.a.	
	250 °C, 4.5% TS	226	n.a.	12.20	n.a.	8.08	n.a.	6.56	n.a.	1.70[e]	n.a.	n.a.	n.a.	103.83[f]	n.a.	
Digested sewage sludge 4	190 °C, 3% TS	n.a.	n.a.	6.40	6.70	7.10	6.80	1.30[c]	1.20[c]	0.70	0.70	19.60	22.70	n.a.	n.a.	Merzari et al. 2019
	220 °C, 3% TS	n.a.	n.a.	6.70	6.70	6.80	6.20	1.40[c]	0.90[c]	0.80	1.00	19.80	17.80	n.a.	n.a.	
	250 °C, 3% TS	n.a.	n.a.	8.30	5.70	7.30	6.90	1.30[c]	1.50[c]	0.80	0.80	19.30	12.20	n.a.	n.a.	
Digested sewage sludge 4	190 °C, 17% TS	n.a.	n.a.	49.80	55.10	6.00	6.00	4.50[c]	4.10[c]	2.70	3.80	0.30	0.40	n.a.	n.a.	Merzari et al. 2019
	220 °C, 17% TS	n.a.	n.a.	44.80	45.70	6.00	5.90	2.40[c]	1.50[c]	4.40	4.60	0.20	0.20	n.a.	n.a.	
	250 °C, 17% TS	n.a.	n.a.	57.50	46.80	6.00	5.50	1.70[c]	1.40[c]	6.90	6.50	0.20	0.20	n.a.	n.a.	
Raw sewage sludge 1	190 °C, 3% TS	n.a.	n.a.	10.50	13.40	6.00	5.30	0.10[c]	0.10[c]	0.40	0.60	32.50	38.40	n.a.	n.a.	Merzari et al., 2020
	220 °C, 3% TS	n.a.	n.a.	11.90	13.50	6.00	6.10	0.10[c]	0.10[c]	0.40	0.50	20.20	16.40	n.a.	n.a.	
	250 °C, 3% TS	n.a.	n.a.	15.30	13.70	5.80	6.00	0.10[c]	0.10[c]	0.60	0.60	16.10	11.10	n.a.	n.a.	
Digested sewage sludge 5	150 °C, 20% TS	n.a.	100.2	n.a.	31.00[g]	n.a.	5.60	n.a.	2.40	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	Parmar K. and Ross A. 2019
	200 °C, 20% TS	n.a.	181.7	n.a.	38.90[g]	n.a.	6.20	n.a.	4.50	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	
	250 °C, 20% TS	n.a.	151.9	n.a.	43.60[g]	n.a.	7.60	n.a.	4.70	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	

n.a. not applicable, COD: chemical oxygen demand.
[a] 120 min instead of 60 min.
[b] mL CH$_4$/g-VS.
[c] Total Kjeldahl nitrogen.
[d] % of total phosphorous in digestate.
[e] mg-N/L.
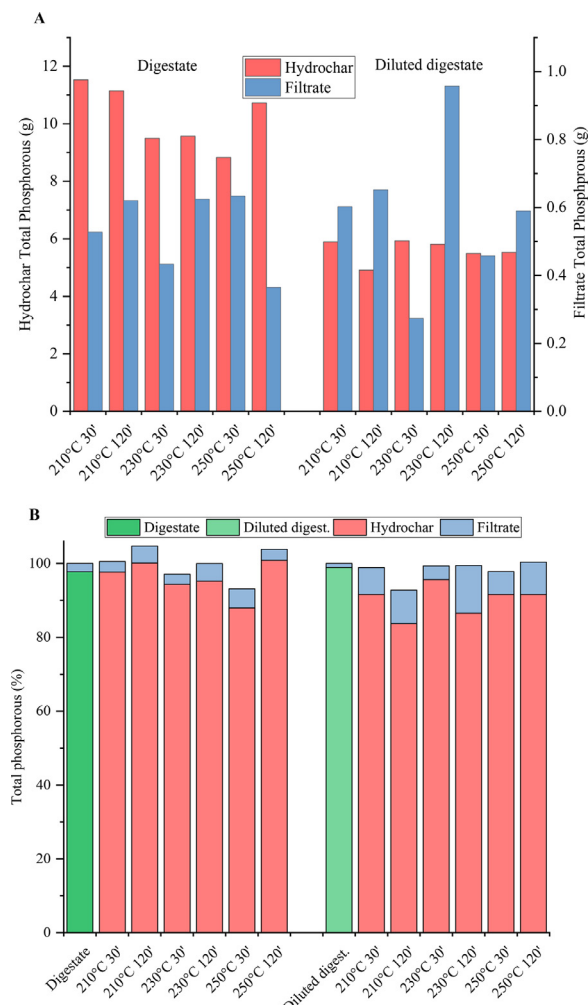[f] mg-P/L.
[g] total COD.

Fig. 4. The phosphorous mass distribution in grams (A) and in percentages of the input total phosphorous (B) into hydrochar and filtrate after the HTC treatment of digestate and diluted digestate at different temperatures (210–250 °C) and residence times (30 or 120 min). Digestates and hydrochars are presented as their total mass after filtration including their moisture. The input phosphorous mass seemed to be exceeded in a few treatments, which due to the heterogeneity of the analysed material and a small sample amount in the ICP-MS analysis, causing some error.

Fig. 5. The mass distribution of total nitrogen of unfiltered digestate and diluted digestate into hydrochar, filtrate and gas phases after the HTC treatments at temperatures of 210–250 °C and residence times of 30 or 120 min. Hydrochar and digestates are presented in total mass including their moisture content. The recovered total nitrogen in the product fractions compared to the total nitrogen in the input digestate is marked in percentages on the columns.

content from 50.4 to 20.1–42.3 g-TN/kg-TS was observed at HTC temperatures of 220 °C and 250 °C, while at an HTC temperature of 160 °C, the nitrogen content increased from 50.4 to 51.1 g-TN/kg-TS (Aragón-Briceño et al., 2017). An increase in the HTC temperature decreased the nitrogen content in the solid fraction (Aragón-Briceño et al., 2017; Merzari et al., 2020), which was also found to be the case in the current study. The observed increase of nitrogen percentage in the hydrochar fraction at a higher TS content of the hydrochar, was also reported by Aragón-Briceño et al. (2020), who tested HTC treatment with digested sewage sludge TS contents from 2.5 to 30%.

During HTC treatment, a decline in nitrogen content in hydrochars has been reported to occur because of the decomposition of labile and organic nitrogen compounds, while the volatile nitrogen compounds are already devolatilised below temperatures of 220 °C to the liquid and gas phases (Zhuang et al., 2018). The increase in ammonium-nitrogen concentration in the filtrate at increased HTC temperatures has been connected to the hydrolysis of proteins through peptides and amino acids to fatty acids and ammonia (Marin-Batista et al., 2020). The volatilisation of nitrogen compounds was observed in the current study (Fig. 5), both in the

filtrates and hydrochars upon increasing the HTC temperature and time.

The original nitrogen content and its distribution to the HTC products are presented in Fig. 5. The total nitrogen lost in the gas phase varied between 3% and 20%, which, however, was calculated by difference, therefore giving some room for error. The nitrogen recovery into the product fractions depended on the digestate TS because the digestate hydrochars retained 46–64% and the diluted digestate hydrochars 36–46% of the total nitrogen. The filtrates from the digestate and diluted digestate contained 26–40% and 41–48% of the total nitrogen, respectively. High volumes of filtrate and high concentrations of nitrogen in the filtrate present an interesting option for nitrogen recovery. If the filtrate was fed back to the biogas digestor, the ammonium-nitrogen could be recovered from the filtrate, in addition to that in the reject water from the mechanical dewatering of digestate, for example, with ammonium stripping. But then again, the unionised form of ammonium, ammonia (NH_3), at too high concentrations can inhibit methanogens in AD (Jiang et al., 2019), which could be avoided by treating the filtrate directly in ammonium stripping. However, the hydrochar also contained a large portion (21.4–27.0 g/kg-TS) of the total nitrogen.

The carbon contents of the hydrochars ranged from 29 to 31% (Table 3), which is typical for hydrochars from digested sewage sludge (Table 5). The carbon recoveries were on average 82±7% and 83±5% in the hydrochars from the digestate and diluted digestate, respectively, decreasing with treatment severity.

3.4. Trace elements, heavy metals and pharmaceuticals

The trace elements (Cu, Zn, Al and Ni) and heavy metals (Au, As, Cd, Cr, Hg and Pb) of the hydrochars and filtrates were analysed (Tables S1 and S2). All the concentrations were below the permitted limit values dictated by the EU (86/278/EEC) and Finnish authorities (Ylivainio and Turtola, 2016), except the limit concentration of mercury for fertilisers used in Finland (0.001 mg-Hg/g TS) was already exceeded in the digestates (0.02 mg-Hg/g-TS) and its concentration increased in HTC to 0.02–0.03 mg-Hg/g-TS in the hydrochars. Overall, the heavy metal and trace element concentra-

tions (per TS) were slightly increased in all hydrochars from those of the digestates, which could be attributed to the mass decrease of the solid phase during HTC and/or to the precipitation of these metal ions as salts in the hydrochar (Zhang et al., 2014).

Pharmaceuticals are known to be present in sewage sludge and digestates (Radjenović et al., 2009). The present results showed two hormones and 23 pharmaceuticals in the digestate, for example, 0.15 mg/kg-TS estrone, 2.4 mg/kg-TS tetracycline, 0.24 mg/kg-TS diclofenac and 0.93 mg/kg-TS doxycycline in the solid fraction and 8 µg/L tetracycline and 5.4 µg/L diclofenac in the liquid fraction of the digestate (Table S3). After HTC treatment, no hormones or pharmaceuticals analyszed were detected in the hydrochar fraction (below the detection limit). In the filtrate, only two pharmaceuticals were detected: 330 µg/L benzotriazole and 230 µg/L ibuprofen, while the concentrations of the other pharmaceuticals were below the detection limit. The detection limits for most of the hormones and pharmaceuticals in the hydrochar and filtrate were under 0.5 mg/kg-TS and1.0 µg/L, respectively, while the detection limits after HTC were higher for ciprofloxacin (<50 µg/L), tetracycline (<10 µg/L), and mirtazapine, sertraline, norsertraline and cetirizine (<5 µg/L) in the filtrate. Thus, the presence of ciprofloxacin and tetracycline in the filtrate cannot be excluded. Benzotriazole is widely used in cosmetics and in corrosion prevention, thus ending up in municipal wastewater (Zhang et al., 2011). Although in the current study HTC treatment removed most of the pharmaceuticals, not all possible hormones and pharmaceuticals, nor their degradation products, were analysed. Other studies have also concluded that HTC has potential to degrade organic pollutants while emphasising its limitedness in complete removal or detoxification of chlorinated aromatics and, for example, phenazone (vom Eyser et al., 2015; Weiner et al., 2013).

4. Practical implications

The present results and previous information on HTC treatment of digestate can be used to assess the potential of HTC for individual cases and, for example, to calculate a techno-economic analysis. In each case, the utilisation of biogas, hydrochars and filtrates, as well as the energy and nutrient contents in these streams, depend on many local factors, which further affect the technological system, its economics and sustainability. An example extrapolation calculation for integrating HTC into a biogas process was done for a centralised Topinoja biogas plant, from where the dewatered sewage sludge digestate for the current study was obtained and compared with the process at the time of the experiments (Fig. 6). The biogas plant annually treats 75,000 t of sewage sludge (22% TS) and produces 30,000 t of dewatered digestate (30% TS). The HTC assessment was done by averaging the results from three HTC runs with the digestate (210 °C for 120 min and 230 °C for 30 min or 120 min) considered relevant for practical application. It was assumed that ca. 40% of the digestate volume (36,000 t; 25% TS) ends up in hydrochar and the rest to filtrate (minimal losses of mass to the gas phase). In such a case, ca. 14,400 t of hydrochar would be produced, which has a TS content of 50% and an energy content of ca. 11.5 MJ/kg-TS. The hydrochar could currently be considered for different end use applications, for example, used in agriculture, where it would promote carbon and nutrient utilisation, thus benefitting circular economy, or for co-combustion, with an annual energy production from the hydrochar of ca. 82,800 GJ (Fig. 6). The economic benefit from the hydrochar production for energy recovery has been reported to even exceed the profits from biogas production per tonne of sewage sludge (Aragón-Briceño et al., 2021).

If the filtrate, ca. 18,000 t/a, was fed to the biogas process, it would enhance the annual methane production with ca. 140,000 m^3 (1.4 GWh), that is, 4.5%, from the current annual methane production of ca. 3 million m^3 (30 GWh). Furthermore, the feeding

of the filtrate to the biogas process would enable the recovery of the ammonium-nitrogen present in the filtrate (ca. 3.1 g-NH_4−N/L) from the reject water of the digestate after dewatering. In the Topinoja plant, ammonium is recovered from the dewatering reject water via ammonia stripping (ca. 4000 t of ammonium water; 12% NH_4−N) and directing filtrate to the biogas process could increase the volume of ammonium water up to 5000 t (Fig. 6).

It has been reported that the integration of HTC with AD has potential to increase the profits for WWTP (Aragón-Briceño et al., 2021), which however is case-dependant as the required capital costs for the investment to an existing WWTP vary and may not be covered by the revenues from hydrochar utilisation (Medina-Martos et al., 2020). Nevertheless, the utilisation of hydrochar may have more potential in respect to digestate due to its higher phosphorous and lower pharmaceutical contents as well as decreased end product volume, which decreases the transportation needs and costs. Furthermore, directing the hydrochar to agriculture could also promote carbon storage and carbon neutral agriculture, which should be further evaluated. Returning the filtrate with readily biodegradable organic and high ammonium-nitrogen contents to the biogas process requires optimisation of its downstream processes, e.g., the energy balance considerations and use of polymers in digestate dewatering.

5. Conclusions

The current study evaluated HTC treatment (at 210–250 °C, for 30 or 60 min) and subsequent filtration of mechanically dewatered digestate (TS 25%) from a full-scale centralised biogas plant treating mechanically dewatered sewage sludge. The volume of different hydrochars was 30–55% of the dewatered digestate's volume, and the TS content of the hydrochars was 53–64%. The hydrochars contained over 90% of the phosphorous in the digestate (up to 56 g/kg-TS), ca. 30% carbon per TS, pharmaceuticals were below detection limits, and heavy metals were under legislative limits (apart from mercury). The high phosphorous content of hydrochars could favour its use in agriculture as fertiliser. The hydrochars could also be, for example, co-combusted, since the hydrochars' HHV (11.3–12.2 MJ/kg-TS) was similar to that of the digestate, although the high ash content (50–57%) may reduce its attractiveness. As all the HTC conditions applied in this study generated hydrochars of little variations in properties, it could be recommended to use the lowest temperature (210 °C) and shortest residence time (30 min) for hydrochar production from digestate. Another HTC end product is filtrate, which had a high SCOD content of 39–44 g/L, of which 10–33% was VFAs, methane potential of ca. 190 L-CH_4/kg-SCOD and high nitrogen content of 4.9–6.1 g/L. Feeding the filtrate to the biogas digester would enable increased methane production and enhanced nitrogen recovery from the reject water of the anaerobic digestor. The temperature of 230 °C could be regarded as the optimum temperature for generating filtrates with the highest methane production potential and ammonium content enabling ammonium recovery. Extrapolating the results to a centralised biogas plant, indicated that the integration of HTC to a biogas plant could enhance the annual biogas production by 5% and ammonium recovery by 25%, while the produced hydrochar could be used to produce 83 GJ or to direct 350 t phosphorous to agriculture annually.

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.
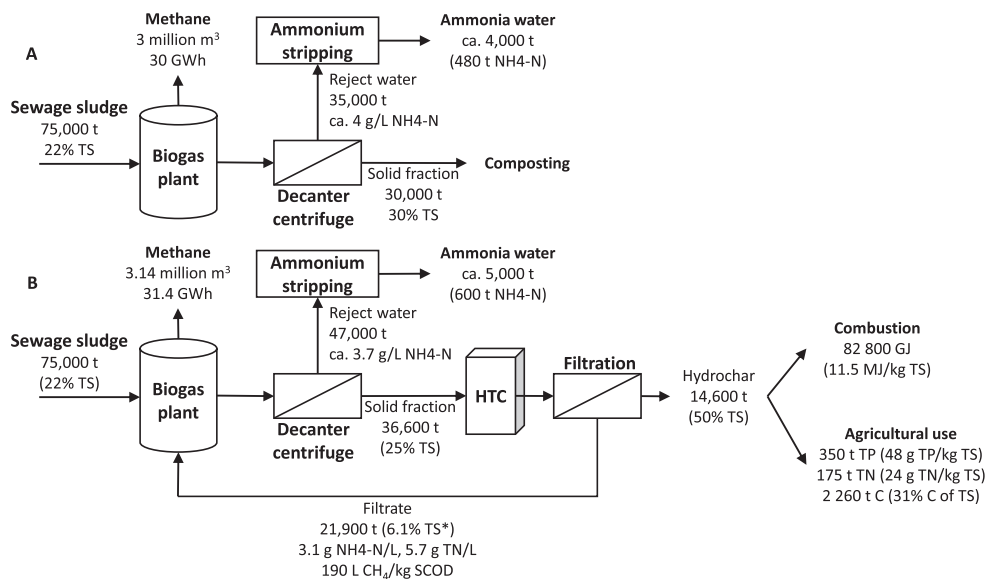
Fig. 6. The process layout of the biogas plant at the time of the present experiments (A) and extrapolation on how the integration of hydrothermal carbonisation (HTC) to the biogas plant would affect the overall scheme. For the hydrochar and filtrate characteristics, average values are taken from the following runs with digestate: 210 °C for 120 min and 230 °C for 30 min or 120 min. TS: total solids, TP: total phosphorous, TN: total nitrogen, NH_4–N: ammonium-nitrogen.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.watres.2021.117284.

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