



Hydrothermal carbonization of pulp and paper industry wastewater treatment sludges - characterization and potential use of hydrochars and filtrates

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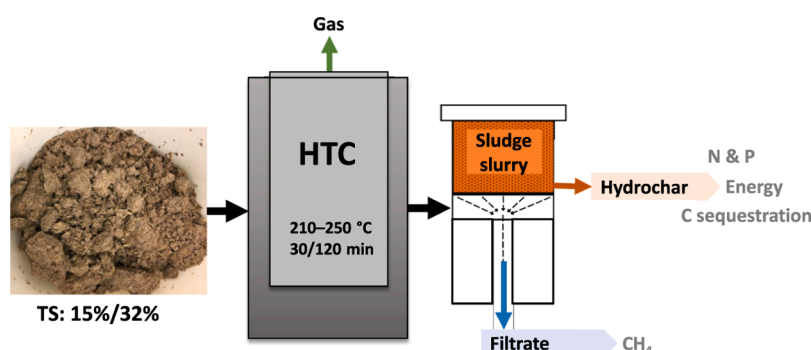
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HIGHLIGHTS

- Mixed sludge from pulp and paper mill wastewater treatment was treated with HTC.
- HTC enhanced energy recovery in hydrochars having 37% increased heating value.
- No significant sludge dewaterability improvement was observed after HTC.
- HTC increased filtrate organics content and volumetric methane production potential.
- Mixed sludge hydrochars are potential for carbon sequestration.

GRAPHICAL ABSTRACT



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ABSTRACT

The pulp and paper industry's mixed sludge represents waste streams with few other means of disposal than incineration. Hydrothermal carbonization (HTC) could be advantageous for the sludge refinement into value-added products, thus complementing the concept of pulp and paper mills as biorefineries. Laboratory HTC was performed on mixed sludge (at 32% and 15% total solids) at temperatures of 210–250 °C for 30 or 120 min, and the characteristics of the HTC products were evaluated for their potential for energy, carbon, and nutrient recovery. The energy content increased from 14.9 MJ/kg in the mixed sludge up to 20.5 MJ/kg in the hydrochars. The produced filtrates had 12–15-fold higher COD and 3–5-fold higher volumetric methane production than untreated sludge filtrates, even though the methane yield against g-COD was lower. The increased value of the hydrochars in terms of energy content and carbon sequestration potential promote HTC deployment in sludge treatment and upgrading.

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1. Introduction

Global pulp and paper manufacturing uses, in addition to various wood and other plant materials, plenty of water and chemicals in different production processes. Thus, the industry generates large volumes of wastewaters with different compositions and with relatively high biological and chemical oxygen demand (BOD and COD) concentrations (several g/L), wood debris, and soluble wood material, as well as chemical residues (Faubert et al., 2016). This wastewater is commonly treated through primary sedimentation and biological treatments in an activated sludge process at the mill, producing mixed sludge that consists of primary and secondary sludge. Primary sludge contains wood fibers, papermaking fillers, pitch, and by-products of lignin, whereas secondary sludge is mostly composed of microbial mass and non-biodegradable lignin (Faubert et al., 2016). Due to the high organic carbon content of the sludge (approximately 50 %TS), its presence in landfill may cause leaching and greenhouse gas production, and thus is not permitted by the European Union Waste Framework Directive (2008/98/EC), which has prompted sludge incineration for energy recovery. However, incineration of high-water-content sludges necessitates efficient mechanical and thermal dewatering, which can account for more than half of the wastewater treatment costs at pulp and paper mills because of the difficulty of dewatering the secondary sludge, which contains extra-cellular polymeric substances (Meyer et al., 2018). Thus, direct incineration is not considered economically feasible. The development of mixed sludge utilization is recommended for the current aim of introducing the concept of biorefinery into pulp and paper industry mills, including, for example, bioprocesses, such as anaerobic digestion (AD) and fermentation, and thermal processes, such as pyrolysis and hydrothermal carbonization (HTC), which represent solutions to produce energy from waste sludge (Gottumukkala et al., 2016).

HTC has attracted interest in several fields for its potential role in the refining of various raw biomasses (Pecchi and Baratieri, 2019) as well as in the management of the sludge (Ahmed et al., 2021; Lin et al., 2015) as it allows the use of moist biomass as feedstock, reducing the need for dewatering. HTC is conducted at moderate temperatures (200–300 °C), and pressure is autogenously generated (Fang et al., 2018), which enables the water contained in the sludge to function as a solvent, reactant, or even a catalyst during the treatment (Mäkelä et al., 2015). HTC generates three product components: (i) a solid hydrochar that can be further deployed in energy generation, in soil for nutrient recovery and carbon sequestration, in removal of heavy metals and pesticides from water, and in improving the outcome of composting and fermentation (Sun et al., 2020); (ii) a liquid product (referred to here as a filtrate) from which nutrients can be extracted for recovery; and (iii) a gas comprising mainly of CO₂ (Aragón-Briceño et al., 2021). Hence, by refining sludge into value-added products, HTC could potentially be incorporated into the concept of biorefinery in the pulp and paper industry. In practice, the deployment of HTC should be considered on a case-by-case basis, depending on the existing local infrastructures, such as power plants and their feedstocks, as well as on the logistics for hydrochar transportation. Also, any existing wastewater treatment facility at the mill or locally could be engaged in the filtrate treatment. The utilization alternatives for hydrochar and filtrate should be considered based on the local targets for renewable energy and carbon sequestration, taking into account also other political and environmental objectives.

Studies on the use of HTC for lignocellulosic biomass have mostly focused on virgin materials and agricultural or food waste (Fang et al., 2018; Pecchi and Baratieri, 2019), and little attention has been paid to lignocellulosic pulp and paper waste sludges. The few published studies on the HTC of pulp and paper industry sludges have only considered the energy content and fuel properties of hydrochar (Martinez et al., 2021; Saha et al., 2019; Wang et al., 2021). However, because of the increasing need of nutrient recycling, carbon sequestration and of the large volumes of mixed sludge generated, mixed sludge hydrochar's role as a nutrient and carbon source should also be examined simultaneously

with energy recovery. Furthermore, the value of the extracted filtrate should be further delineated, such as in AD for increasing methane recovery and subsequent nitrogen recovery by stripping, as previous studies have only considered the use of filtrate as diluent for HTC feed. (Areeprasert et al., 2014; Kabadayi Catalkopru et al., 2017; Mäkelä et al., 2018).

After HTC treatment, the treated sludge is separated into hydrochar and filtrate, usually by filtration, an essential part of the HTC process. However, the existing studies have not compared the effects of HTC to mere filtration of the sludge. The studies on HTC have been promising improving sludge dewaterability and the utilization of moist waste for energy recovery (Areeprasert et al., 2014; Mäkelä and Yoshikawa, 2016). However, as there are only few studies on HTC treatment of pulp and paper industry sludges, it would be necessary to study the matter more comprehensively to determine, whether the whole HTC process can bring additional value to sludge utilization. HTC deployment in pulp and paper could reduce sludge volume and improve its applicability as a hydrochar in carbon sequestration, energy recovery, or nutrient recovery, and as a filtrate in the generation of renewable energy.

The objective of this study was to evaluate the potential role of HTC in pulp and paper industry sludge management and the process of upgrading to value-added products. To test the capability of HTC in decreasing the volume of mixed sludge and simultaneously increasing its energy content and land applicability, HTC was performed at laboratory scale using a mechanically dewatered mixed sludge at two dilutions of 32% and 15% total solids (TS) at temperatures of 210–250 °C and residence times of 30 and 120 min. A pilot filtration process was applied to induce the HTC-treated sludge to produce hydrochar and filtrate, and as a reference, filtration alone was used to produce sludge cake and cake filtrate. The generated hydrochar and filtrate products were characterized, and their potential uses were assessed.

2. Materials and methods

2.1. Sludge and inoculum

The pulp and paper industry sludge for the HTC treatment experiments was a mixture of primary and secondary sludge (referred to as a mixed sludge) from the activated sludge process used in treating wastewater from pulp-and-paper mill integration (Finland), which uses wood as a raw material and both kraft and mechanical pulping processes. The sludge had been mechanically dewatered at the mill. For the biochemical methane potential (BMP) assays, granular sludge (7.4% TS, 6.8% VS) from a mesophilic upflow anaerobic sludge blanket (UASB) reactor treating industrial wastewater was used as an inoculum (Jokioinen, Finland; Singh et al., 2019). All sludges were stored at 4 °C for 1–2 months until used.

For the HTC treatments, the mixed sludge was used as received, with 32% TS and as diluted with tap water to 15% TS (referred to as diluted mixed sludge). Sludge dilution to 15% TS was conducted right before the HTC treatment by adding 530 ml of tap water to 470 g of mixed sludge (32% TS). Mixed sludge characteristics are shown in Tables 1 and 2.

2.2. HTC treatments

The HTC treatments were conducted in a two-liter Parr® 4500 pressure reactor with an external circulating water cooling system (see supplementary material), as previously described in detail (Hämäläinen et al., 2021). The wet weight of the input sludge for the experiments was 700 g for mixed sludge (32% TS) and 1 kg for diluted mixed sludge (15% TS); the weight difference between them was due to the difference in their density, as only 700 g of mixed sludge was enough to fill the working volume (1 L) of the reactor. The treatment temperatures were 210 °C, 230 °C, and 250 °C with residence times of 30 or 120 min. Each treatment had one replicate and the sludges were not mixed during the HTC treatments due to their fibrous texture.

Table 1

The CHNS-analysis results, computational oxygen contents and phosphorous concentrations in the mixed sludge cakes and in their respective hydrochars. The results are averages of 2 replicates.

Sample	C (% TS)	H (% TS)	N (% TS)	S (% TS)	O ^c (% TS)	P (% TS)
Mixed sludge	42.4 ± 0.1	5.8 ± 0.02	1.2 ± 0.04	0.4 ± 0.03	50.2 ± 0.2	0.4
Mixed sludge cake	42.6 ± 0.2	5.8 ± 0.00	1.3 ± 0.06	0.4 ± 0.04	49.9 ± 0.3	0.2
<i>Mixed sludge hydrochars</i>						
210 °C for 30 min	46.1 ± 0.7	5.7 ± 0.01	1.1 ± 0.1	0.4 ± 0.0	46.7 ± 0.8	0.5
210 °C for 120 min	48.7 ± 0.4	5.6 ± 0.01	1.6 ± 0.05	0.4 ± 0.02	43.6 ± 0.4	0.4
230 °C for 30 min	49.2 ± 0.5	5.7 ± 0.02	1.5 ± 0.05	0.4 ± 0.03	43.3 ± 0.6	0.3
230 °C for 120 min	52.4 ± 0.3	5.6 ± 0.02	1.6 ± 0.02	0.5 ± 0.01	39.9 ± 0.3	0.3
250 °C for 30 min	52.4 ± 0.7	5.4 ± 0.02	1.5 ± 0.07	0.5 ± 0.01	40.2 ± 0.8	0.5
250 °C for 120 min ^a	55.5 ± 1.0	5.1 ± 0.04	1.6 ± 0.06	0.5 ± 0.04	37.3 ± 1.0	0.6
Diluted mixed sludge ^b	42.4 ± 0.2	5.8 ± 0.03	1.2 ± 0.05	0.4 ± 0.04	50.2 ± 0.2	0.3
Diluted mixed sludge cake	42.6 ± 0.2	5.8 ± 0.01	1.7 ± 0.08	0.5 ± 0.04	49.4 ± 0.3	0.3
<i>Diluted mixed sludge hydrochars</i>						
210 °C for 30 min	46.1 ± 0.5	5.8 ± 0.06	0.9 ± 0.01	0.3 ± 0.02	47.0 ± 0.6	0.3
210 °C for 120 min	47.6 ± 0.1	5.7 ± 0.08	1.2 ± 0.05	0.3 ± 0.00	45.2 ± 0.8	0.4
230 °C for 30 min	47.5 ± 0.4	5.8 ± 0.07	1.1 ± 0.03	0.3 ± 0.01	45.4 ± 0.5	0.3
230 °C for 120 min	50.6 ± 0.1	5.6 ± 0.01	1.3 ± 0.02	0.3 ± 0.01	42.2 ± 0.1	0.4
250 °C for 30 min	53.0 ± 0.1	5.6 ± 0.01	1.5 ± 0.04	0.4 ± 0.01	39.6 ± 0.1	0.7
250 °C for 120 min	56.8 ± 0.3	5.2 ± 0.02	1.8 ± 0.01	0.4 ± 0.01	35.8 ± 0.3	0.7

TS: total solids

^a failed HTC-treatment and sample recovery

^b computational CHNS-analysis

^c calculated as difference between 100 and total sum of C, H, N and S on TS basis

The reactor vessel achieved the target temperatures within approximately 70–95 min. The temperature was manually adjusted using Parr® 4848 reactor controllers and held at the target temperature for the pre-set residence time. Above 100 °C, the vessel pressure increased from atmospheric pressure up to 20–40 bar, depending on the applied temperature. The realized temperatures fluctuated but remained within ± 8 °C from the target temperature. The 250 °C runs were started when the vessel temperature had reached 245 °C because of difficulties in attaining the targeted temperature within 90 min. Part of the generated gases was released at the end of the treatment to speed up cooling. Cooling the sludge to 50 ± 6 °C by water circulation took around 30–40 min, after which the HTC-treated sludges were recovered from the vessel, weighed, and stored at 4 °C prior to their filtration.

Filtrations of the HTC-treated sludges and of the original mixed and diluted mixed sludges as a reference were performed using a small-scale pressurized filtration unit at 60 °C (see supplementary material). The solid and liquid products are referred to as hydrochar and HTC filtrate, respectively, while the reference products of the original sludges are referred to as the cake and cake filtrate. The filtration procedure is described in detail in Hämäläinen et al. (2021). In mass balance calculations, both the weight of the hydrochar as well as the TS content of the

hydrochar are considered.

2.3. Biochemical methane potential assays

The BMPs of the HTC and cake filtrates were determined in mesophilic (35 °C), static, 30-day long batch assays in triplicate. The assays were assembled in 120 ml serum bottles with a liquid volume of 64 ml, containing 1.7 g of inoculum (1.75 g-VS/L), the filtrate sample in final concentration of 1.75 g of soluble chemical oxygen demand (SCOD) per liter, NaHCO₃ (4 g/L) as a buffer, and distilled water to reach the liquid volume. The initial pH was adjusted to between 7 and 8 with HCl (1 M), after which the bottles were closed with rubber stoppers and flushed with nitrogen gas for around 3 min. As control assays, bottles containing only inoculum, water, and buffer were prepared to subtract inoculum's methane production from the methane production of the sample assays. The methane concentrations in the BMP assays were measured with a GC-FID (Perkin Elmer Clarus) and calculated as described previously (Hämäläinen et al., 2021; Kinnunen et al., 2015).

2.4. Chemical analysis and calculations

The TS (referred to also as dry solids) and VS were gravimetrically determined according to the standard APHA 2540 method. The ash content measurements at 550 °C followed the same gravimetric principle. The pH was measured with a WTW pH 3210 m using a WTW Sentix® 41 electrode. Then, COD and SCOD were analyzed according to Finnish standard methods (SFS 5504). Volatile fatty acids (VFA) were determined with GC-FID, as described previously (Kokko et al., 2018). For the VFA and SCOD analyses, samples were filtered through a 0.45 µm filter (Chromafil Xtra PET). The total nitrogen and soluble ammonium-nitrogen in the filtrates were analyzed using Hach Lange kits (LCK 238, LCK 338, LCK 305, and LCK 303) according to the company instructions. The other cations in the filtrates were analyzed according to the ion chromatography standard SFS-EN ISO 10304-1 using an ion chromatograph (Dionex DX-120, USA) with an AS40 autosampler, Ion-Pac 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.

The total carbon, hydrogen, nitrogen, and sulphur concentrations of the mixed sludges, hydrochars, and cakes (Table 1) were determined by elemental analysis in a Thermo Scientific FlashSmart Elemental Analyzer (CHNS/O) with thermal conductivity detector (TCD), before which dried samples (dried overnight at 105 °C) were homogenized by grinding them with mortar into a fine powder. The sample size for CHNS analysis was 2–3 mg, weighed on a microgram balance (Mettler Toledo WXTS Microbalance) in tin cups. BBOT-standard (2,5-Bis[5-*tert*-butyl-2-benzo-oxazol-2-yl]) provided by Thermo Fisher Scientific was used for calibration. Helium was used as a carrier gas and oxygen to oxidize the sample. The other elements in the hydrochars, cakes, and filtrates were determined with inductively coupled plasma mass spectrometry (Hämäläinen et al., 2021). The higher heating values (HHV) of the hydrochars and cakes were determined in duplicate according to the ISO 1928 standard with a Parr® 6725 Semi-Micro Oxygen Bomb Calorimeter. For this analysis, the sample size (dried at 105 °C overnight) was 0.2–0.3 g. All the chemicals used in the analyses were of analytical grade.

The sludge mass converted to gas in the HTC treatment was computationally obtained from the difference in the masses of the input sludge and the obtained hydrochar and filtrate after HTC.

The parameters used for assessing the energy properties of mixed sludges, cakes, and hydrochars in Table 2 were calculated as presented in Equations (1)–(4). Solid yield (Eq. (1)) on a dry ash-free basis describes the recovered amount of solid fraction (cake or hydrochar) without ash from the mixed sludge without ash (Mäkelä et al., 2015). Similarly, energy yield (Eq. (2)) represents the amount of recovered energy from the original sludge. The energy densification (Eq. (3))

Table 2

Solid fuel properties of the mixed sludge (32% TS) and diluted mixed sludge (15% TS) and of their respective cakes and hydrochars.

Sample	TS (%)	VS (%)	VS/TS (%)	Ash 550 °C (%)	HHV (MJ/kg TS)	Solid yield (% daf)	Energy yield (%)	Energy densification (daf)	Carbon content (% daf)
Mixed sludge	32.1 ± 0.8	28.0 ± 0.6	87	12.7 ± 0.4	14.9 ± 0.02	n.a.	n.a.	n.a.	48.6 ± 0.1
Mixed sludge cake	49.7 ± 1.0	43.8 ± 0.8	88	11.9 ± 0.04	15.0 ± 0.01	95.2 ± 4.8	48.99 ± 2.6	1.00 ± 0.00	48.4 ± 0.2
<i>Mixed sludge hydrochars</i>									
210 °C for 30 min	46.64 ± 1.1	40.7 ± 1.0	87	12.7 ± 0.2	16.0 ± 0.4	93.0 ± 1.1	99.50 ± 1.3	1.08 ± 0.00	52.8 ± 0.7
210 °C for 120 min	50.24 ± 1.4	43.8 ± 1.2	87	12.8 ± 0.05	16.0 ± 0.1	88.1 ± 1.5	94.24 ± 1.9	1.08 ± 0.00	55.9 ± 0.5
230 °C for 30 min	47.39 ± 0.2	40.9 ± 0.2	86	13.8 ± 0.02	16.7 ± 0.2	87.4 ± 2.5	97.96 ± 3.1	1.14 ± 0.00	57.1 ± 0.6
230 °C for 120 min	52.16 ± 5.0	46.6 ± 0.7	89	15.3 ± 0.1	17.9 ± 0.8	79.7 ± 5.0	95.68 ± 6.3	1.24 ± 0.00	61.9 ± 0.4
250 °C for 30 min	54.34 ± 5.7	45.9 ± 5.0	84	15.5 ± 0.4	20.1 ± 0.1	73.5 ± 3.6	98.85 ± 5.1	1.40 ± 0.01	62.0 ± 0.6
250 °C for 120 min ^a	49.07 ± 7.5	36.1 ± 4.3	74	19.7 ± 2.0	20.4 ± 0.1	51.6 ± 3.4	70.52 ± 10.1	1.49 ± 0.04	69.1 ± 1.3
Diluted mixed sludge	15.5 ± 1.2	13.5 ± 1.0	87	12.8 ± 0.3	14.9 ± 0.02	n.a.	n.a.	n.a.	48.6 ± 0.2
Diluted mixed sludge cake	49.0 ± 1.5	43.0 ± 1.7	88	12.2 ± 0.7	15.0 ± 0.1	95.4 ± 0.8	67.05 ± 0.5	1.00 ± 0.00	48.6 ± 0.6
<i>Diluted mixed sludge hydrochars</i>									
210 °C for 30 min	48.21 ± 1.3	42.4 ± 1.1	88	12.0 ± 0.2	16.1 ± 0.02	93.2 ± 3.7	98.01 ± 4.2	1.08 ± 0.00	52.3 ± 0.6
210 °C for 120 min	47.63 ± 0.6	41.7 ± 0.6	88	12.5 ± 0.2	16.6 ± 0.2	85.0 ± 3.3	91.88 ± 4.0	1.11 ± 0.00	54.4 ± 0.2
230 °C for 30 min	48.08 ± 0.7	41.7 ± 0.6	87	13.2 ± 0.1	16.5 ± 0.03	86.3 ± 1.4	92.52 ± 1.7	1.11 ± 0.00	54.7 ± 0.4
230 °C for 120 min	46.81 ± 0.8	39.6 ± 0.7	85	15.5 ± 0.1	18.1 ± 0.01	64.0 ± 2.3	75.48 ± 2.6	1.26 ± 0.00	59.9 ± 0.2
250 °C for 30 min	47.84 ± 0.3	40.1 ± 0.3	84	16.1 ± 0.1	18.8 ± 0.1	66.9 ± 2.5	82.07 ± 3.0	1.32 ± 0.00	63.2 ± 0.2
250 °C for 120 min	45.38 ± 0.2	36.5 ± 0.1	80	19.6 ± 0.2	20.5 ± 0.1	48.4 ± 1.6	64.57 ± 2.1	1.49 ± 0.00	70.7 ± 0.2

TS: total solids, VS: volatile solids, HHV: higher heating value, daf: dry ash free

^a failed HTC-treatment and sample recovery, n.a.: not applicable

describes how energy is concentrated in the hydrochar and cake relative to the mixed sludge and is calculated by relating their HHVs.

$$\text{Solid yield}(\%, \text{daf}) = \frac{m_{\text{product}} / \left(1 - \frac{\text{ash}_{\text{product}}}{100}\right)}{m_{\text{sludge}} / \left(1 - \frac{\text{ash}_{\text{sludge}}}{100}\right)} \cdot 100\% \quad (1)$$

$$\text{Energy yield}(\%) = \frac{m_{\text{product}} \cdot \text{HHV}_{\text{product}}}{m_{\text{sludge}} \cdot \text{HHV}_{\text{sludge}}} \cdot 100\% \quad (2)$$

$$\text{Energy densification (daf)} = \frac{\text{HHV}_{\text{product}} / \left(1 - \frac{\text{ash}_{\text{product}}}{100}\right)}{\text{HHV}_{\text{sludge}} / \left(1 - \frac{\text{ash}_{\text{sludge}}}{100}\right)} \quad (3)$$

where *daf* signifies dry ash-free, *m* dry (overnight at 105 °C, equals TS) sample mass (kg), and *product* stands for either hydrochar or cake. The ash-free carbon content, and O/C and H/C -ratios were calculated as follows in Equations (4), 5 and 6:

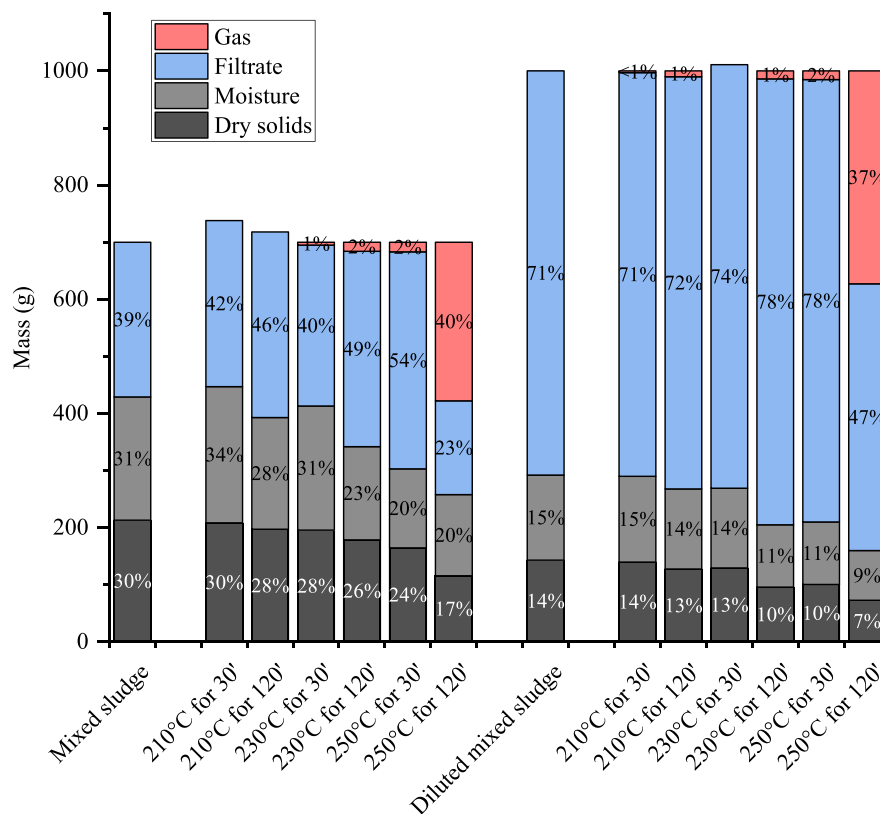


Fig. 1. The mass distribution of the mixed sludge and diluted mixed sludge after filtration (=cakes) as well as after the HTC treatment followed by filtration (hydrochars). The masses of the cakes and hydrochars are divided into dry solids (TS) and the remaining moisture content. The amount of mixed sludge fed to the HTC was 700 g and that of diluted mixed sludge 1000 g.

$$\text{Carbon content (\%, daf)} = \frac{C_{\text{sample}}}{1 - \frac{\text{ash}}{100}} \quad (4)$$

where C denotes sample total carbon content (%), respectively and sample denotes either mixed sludge, diluted mixed sludge, cake, or hydrochar.

When comparing the SCOD and TVFA concentrations of the mixed sludge and diluted mixed sludge filtrates, a computational factor was used to consider the addition of water used for dilution in diluted mixed sludge samples. Thus, the diluted mixed sludge filtrate SCOD and VFA concentrations were obtained with Eq. (5).

$$\text{Concentration as undiluted} = \frac{c \cdot V_{\text{HTC filtrate}}}{V_{\text{HTC filtrate}} + V_{\text{cake filtrate}} - V_{\text{water added}}} \quad (5)$$

where c denotes concentration (SCOD or VFA) and V volume.

3. Results and discussion

3.1. Mass distribution

The mass distribution of the mixed sludges after filtration or after HTC and filtration is shown in Fig. 1. HTC treatments had an effect on the mass distribution by altering hydrochar composition (dry solids and moisture) and HTC filtrate shares relative to filtration alone, except at the mildest HTC conditions (Fig. 1). The mass of the hydrochars decreased (from 61% to 37% and from 29% to 16%) and those of the filtrates increased (from 39% to 54% and from 71% to 78%) from the masses of cake and filtrate, and mixed and diluted mixed sludge, respectively, due to the HTC treatment (Fig. 1). Based on the mass distribution after the HTC treatments (Fig. 1), the amount of gas generated was small (less than 2%) in all HTC treatments for both sludges, except in

the most severe HTC conditions (37%–40% of the initial mass), indicating the dissolved solids were mainly recovered in the filtrate. Overall, the effects of HTC treatment on the relative mass distribution into the hydrochar and gas fractions seemed independent of the initial mixed sludge TS content (Fig. 1).

The cakes had ash-free solid yields of 95%, implying that filtration alone extracted only a small part of the dry ash-free (DAF) solids into the cake filtrate (Table 2). The hydrochars' ash-free solid yields were 51.6%–93.0% for mixed sludge and 48.4%–93.2% for diluted mixed sludge and decreased with increasing treatment severity (Table 2), which indicates that after both the HTC treatments and filtration, the amount of dissolved (and at 250 °C, evaporated) dry ash-free solids were up to 51.6% of the input solids. The TS content of the cakes was 49–50% and the VS content 43–44%, which was similar to or higher than in the mixed sludge and diluted mixed sludge hydrochar, in which the TS content was 46%–54% and 45%–48% and the VS content 36%–47% and 36%–42%, respectively (Table 2). The VS/TS ratios of the hydrochars and cakes (0.80–0.88) were similar to or slightly lower than in the mixed and diluted mixed sludges (0.88).

The hydrochar total masses (including both dry solids and moisture) were reduced only 1–1.8-fold after filtration relative to the cake total masses (Fig. 1), implying the dewaterability of the mixed and diluted mixed sludge with the applied filtration unit was only slightly improved after HTC. Only after the severest treatments (250 °C, 120 min), could major improvements in dewaterability be estimated (1.65–1.8-fold reductions). HTC has been reported to improve the dewaterability of sewage sludge by attaining a 5-fold decrease in the masses of sewage sludge hydrochars relative to the untreated filter-cakes of sewage sludge at HTC temperatures of 195 °C and 240 °C (Saveyn et al., 2009). The dewaterability improvement in sewage sludge was also observed as higher TS (50%) and lower VS/TS (30%–40%) content in the hydrochars after filtration (piston filter press, 400 kPa, 1000 s with cationic polymer

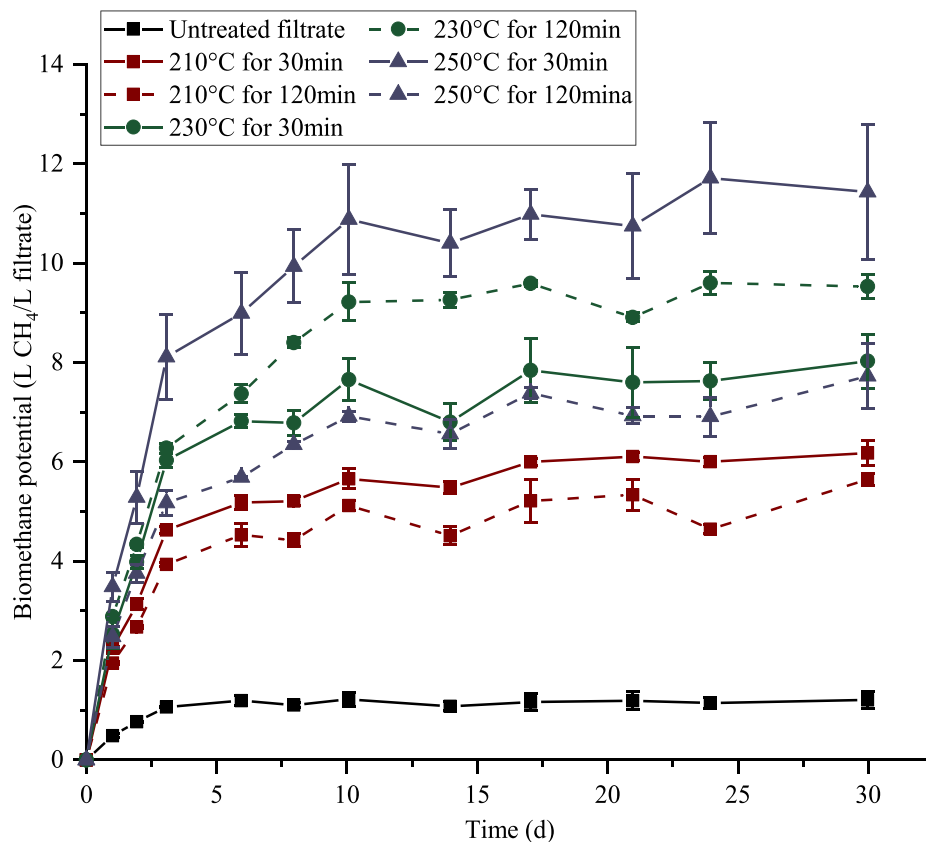


Fig. 2. Biomethane potentials of the mixed sludge cake filtrate (untreated filtrate) and HTC cake filtrates of mixed sludge (TS 32%) from different HTC conditions. The methane production of the inoculum has been subtracted from the results.

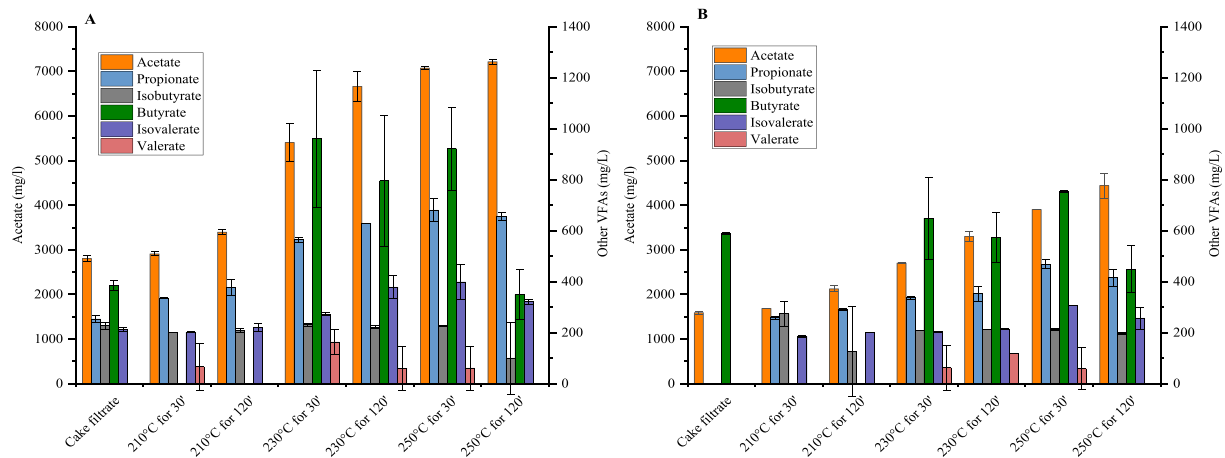


Fig. 3. The volatile fatty acid (VFA) profiles in the cake filtrates and HTC filtrates obtained from mixed sludge (A) or diluted mixed sludge (B).

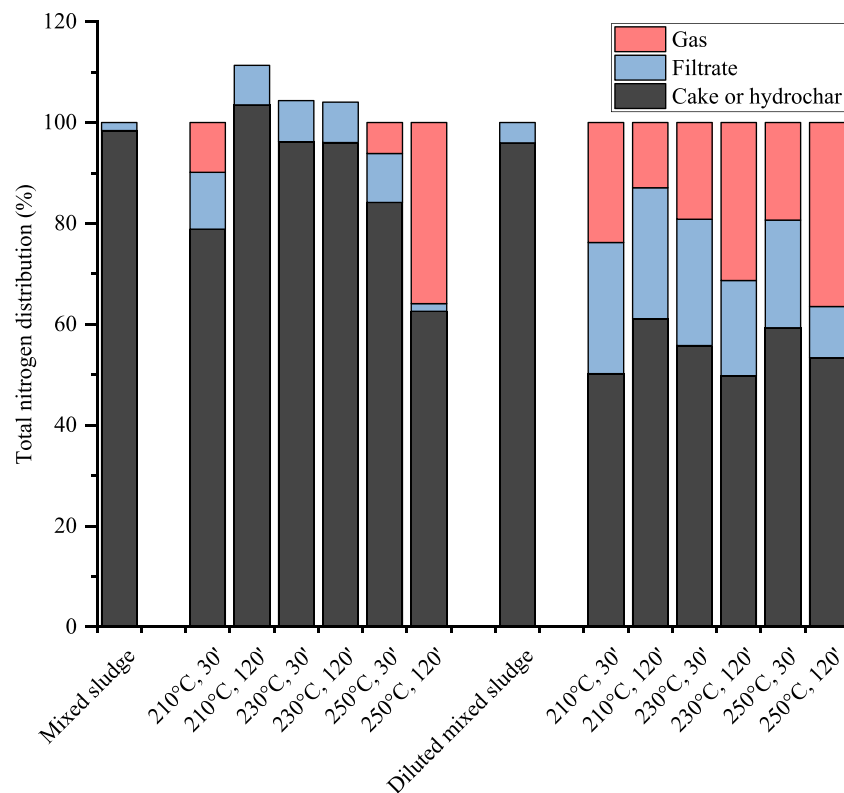


Fig. 4. Distribution of total nitrogen in mixed sludge and diluted mixed sludge (Diluted MS) after filtration (cake and filtrate) and HTC-treated mixed sludge and diluted mixed sludge after filtration (hydrochar, filtrate and gas).

added prior to filtering) compared to the untreated filter-cakes of sewage sludge (10%–20% TS, 60%–70% VS/TS) (Saveyn et al., 2009). In the present study, no such increases in TS or VS content were obtained in the hydrochar and sludge cakes, as the TS of the hydrochars were 93%–109% of the cake TS (Table 2). However, our earlier study on HTC of digested sewage sludge with the same operation parameters, HTC, and filtration equipment as used in the present study showed improvement in the dewaterability by increasing the TS content in hydrochar by 200% (from 30% of the sludge-cake up to 60% of the hydrochar) (Hämäläinen et al., 2021). It is likely that the type of pulp-and-paper mill sludge, specifically one containing plenty of fiber-like material rather than colloidal matter, which possesses a high water-holding capacity, affects the filtration performance positively (Meyer et al., 2018) even without HTC, and thus the impact of HTC is lower. Furthermore, the used

filtration equipment deserves further consideration as it increased the cake TS up to even 50% from the 32% TS achieved with the mill site's full-scale equipment.

3.2. Energy recovery from hydrochar

The effects of HTC treatment on energy recovery from pulp and paper mill mixed sludge were assessed based on the HHVs and energy yields, while the NO_x and SO_x emission potential and the possibility for slagging and fouling during incineration of hydrochar were addressed by determining the sulfur and nitrogen contents and by the ash content and the changes in alkali metal compositions, respectively.

The HHVs of the hydrochars steadily increased with increasing treatment temperature and residence time for both mixed sludges

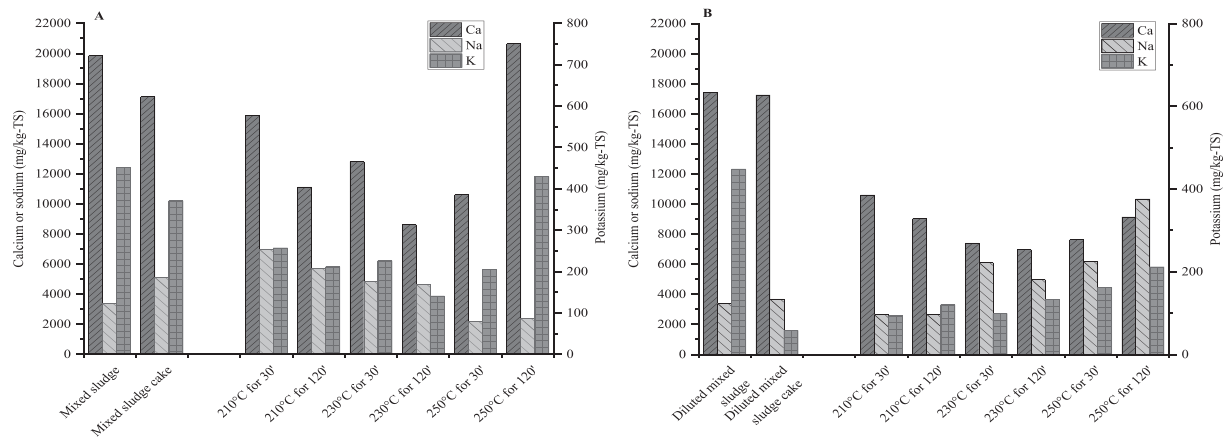


Fig. 5. Calcium, sodium, and potassium concentrations in the mixed sludge and in its cake and hydrochars (A), and in the diluted mixed sludge and in its cake and hydrochars (B).

(Table 2). The HHVs of the mixed sludges were 14.9 MJ/kg-TS, 15 MJ/kg-TS in the cake, and in the hydrochars the HHVs increased to 16.0–20.4 MJ/kg-TS and 16.1–20.5 MJ/kg-TS from the mixed and diluted mixed sludge, respectively. The increasing HHVs resulted in energy densifications of 1.08–1.49 for both mixed and diluted mixed-sludge hydrochars (Table 4). The energy yields of the mixed and diluted mixed-sludge hydrochars were between 70.5% and 99.5% and between 64.6% and 98.0%, respectively (Table 2). In the mixed-sludge hydrochars, a clear decrease in the energy yields was observed only after the severest treatment (at 250 °C for 120 min), whereas in the diluted mixed-sludge hydrochars, there was a decreasing trend with the

increasing treatment temperature and residence time.

The ash content (Table 2) increased from that of the mixed sludges and their cakes (12%) up to 19.7% in the hydrochars, upon which the prolonging of the residence time (from 30 to 120 min) had an increasing effect at 230 °C and 250 °C treatment temperatures, which is undesirable because ash only adds to the hydrochar volume and causes fouling and slagging during incineration (Jenkins et al., 1998). The hydrochar ash content was independent in the initial TS content of the mixed sludge (Table 2). Although the percentage of ash content increased, the ash yields decreased according to the treatment severity from 93% to 80% in mixed sludge hydrochars and from 85% to 72% in diluted mixed-

Table 3

The characteristics and nutrient contents of the mixed sludge and diluted mixed sludge cake filtrates and of their respective HTC filtrates.

Sample	pH	COD	SCOD	TVFA	NON-VFA-COD	BMP	Total phosphorous	PO ₄ ²⁻	Total nitrogen	NH ₄ -N	NH ₄ -N/N _{tot}
	(-)	(g/L)	(g/L)	(g-COD/L)	(g/L)	(L CH ₄ /kg-SCOD)	(mg/L)	(mg/L)	(g/L)	(g/L)	(%)
Mixed sludge cake filtrate	6.15	4.3 ± 0.02	3.8 ± 0.02	4.9 ± 0.02	−1.1	318.5 ± 45	1.02	0.00	0.18	0.10	56
<i>Mixed sludge HTC filtrates</i>											
210 °C for 30 min	5.17	33.5 ± 0.2	30.5 ± 0.05	4.5 ± 0.2	26.0	190.6 ± 8	0.49	15.81	1.17	0.13	11
210 °C for 120 min	5.16	23.6 ± 0.03	23.3 ± 0.01	5.0 ± 0.1	18.3	251.0 ± 5	0.46	20.46	0.73	0.10	13
230 °C for 30 min	4.90	35.5 ± 0.03	36.3 ± 0.01	9.7 ± 0.8	26.6	221.1 ± 15	0.53	28.71	0.87	0.05	6
230 °C for 120 min	4.65	44.4 ± 0.02	44.5 ± 0.03	10.8 ± 0.7	33.7	215.8 ± 5	0.96	43.82	0.71	0.01	2
250 °C for 30 min	4.51	50.6 ± 0.04	51.8 ± 0.02	11.6 ± 0.2	40.2	229.7 ± 22	0.56	60.78	0.77	0.01	1
250 °C for 120 min ^a	4.54	28.2 ± 0.03	28.2 ± 0.01	10.2 ± 0.5	18.0	266.5 ± 23	0.99	33.09	0.28	0.02	6
Diluted mixed sludge cake filtrate	6.30	2.7 ± 0.02	2.6 ± 0.01	2.8 ± 0.04	−0.2	n.d.	1.36	0.00	0.14	0.07	48
<i>Diluted mixed sludge HTC filtrates</i>											
210 °C for 30 min	5.10	23.1 ± 0.01	23.3 ± 0.01	3.1 ± 0.07	20.2	n.d.	0.66	28.24	0.92	0.15	17
210 °C for 120 min	5.15	25 ± 0.03	24.4 ± 0.02	3.3 ± 0.4	21.1	n.d.	0.74	31.34	0.90	0.13	14
230 °C for 30 min	4.89	28.7 ± 0.01	28.9 ± 0.03	5.5 ± 0.1	23.4	n.d.	0.95	34.79	0.85	0.09	10
230 °C for 120 min	4.62	31.6 ± 0.04	31.7 ± 0.02	6.2 ± 0.2	25.5	n.d.	1.22	35.49	0.61	0.02	3
250 °C for 30 min	4.35	41.4 ± 0.03	41.0 ± 0.00	7.4 ± 0.2	33.6	n.d.	0.69	51.69	0.69	0.01	2
250 °C for 120 min	4.33	40.6 ± 0.02	39.3 ± 0.01	7.1 ± 0.00	32.2	n.d.	1.13	65.11	0.55	0.01	2

COD: chemical oxygen demand, SCOD: soluble COD, TVFA: total volatile fatty acids, BMP: biomethane potential

^a failed HTC-treatment and sample recovery, n.d. not determined

Table 4

Metal contents of the mixed sludge (32% TS) and diluted mixed sludge (15% TS) and of their respective cakes and hydrochars. Note that Al and Fe are given in a different unit (g/kg-TS) than the other metals (mg/kg-TS).

Sample	Al	Fe	Cr	Ni	Cu	Zn	As	Cd	Au	Pb	Hg
	(g/kg-TS)	(g/kg-TS)	(mg/kg-TS)	(mg/kg-TS)	(mg/kg-TS)	(mg/kg-TS)	(mg/kg-TS)	(mg/kg-TS)	(mg/kg-TS)	(mg/kg-TS)	(mg/kg-TS)
Mixed sludge	56.0	1.83	27.95	8.46	21.0	115.77	1.41	1.29	0.07	10.59	0.17
Mixed sludge cake	40.4	3.47	18.76	5.14	17.2	85.13	1.10	0.95	0.07	8.06	0.21
<i>Hydrochars from mixed sludge</i>											
210 °C for 30 min	45.0	1.59	21.77	5.22	50.9	90.52	1.54	1.02	0.31	10.44	0.10
210 °C for 120 min	38.0	1.44	18.12	4.43	15.4	77.56	0.76	0.80	0.21	6.69	0.09
230 °C for 30 min	42.7	1.56	20.98	5.70	18.5	88.55	0.90	1.04	0.09	8.71	0.09
230 °C for 120 min	43.4	1.29	20.32	6.43	16.2	68.42	0.80	0.89	0.08	7.25	0.09
250 °C for 30 min	48.4	1.54	28.04	7.90	18.2	77.46	1.13	0.97	0.08	8.84	0.10
250 °C for 120 min ^a	66.0	2.69	33.77	8.52	26.9	123.85	1.30	1.60	0.10	13.14	0.14
Diluted mixed sludge	38.6	1.37	19.46	4.36	14.4	80.22	0.87	0.83	0.08	6.98	0.07
Diluted mixed sludge cake	40.3	1.41	19.72	4.74	15.1	77.06	0.72	0.89	0.06	8.00	0.08
<i>Hydrochars from diluted mixed sludge</i>											
210 °C for 30 min	41.3	1.37	19.47	5.13	15.6	88.97	0.75	0.93	0.18	7.42	0.09
210 °C for 120 min	46.7	1.48	22.05	6.01	19.9	91.05	0.97	1.01	0.19	8.43	0.14
230 °C for 30 min	44.9	1.44	22.90	6.77	17.5	89.61	0.65	1.04	0.17	8.47	0.09
230 °C for 120 min	51.6	1.58	24.43	8.40	98.4	126.41	0.89	1.22	0.11	15.26	0.10
250 °C for 30 min	63.8	1.89	33.97	10.50	25.3	108.66	1.16	1.37	0.10	11.91	0.18
250 °C for 120 min	75.0	2.77	36.94	12.92	28.9	113.92	1.18	1.40	0.11	13.37	0.16

TS: total solids

^a failed HTC-treatment and sample recovery

sludge hydrochars, indicating that part of the ash inorganics were increasingly dissolved when HTC temperature and residence time were increased.

The fates of the elements in HTC were evaluated based on their contents in the hydrochars and cakes (Table 1, Fig. 5) and the mass balance results (Fig. 1). The ash-free carbon content increased from 48.6% in the mixed sludges and cakes to 52.8%–69.1% and to 52.3%–70.7% in the hydrochars (Table 2), and the oxygen content decreased to about 35.8%–47.0% in all hydrochars from an oxygen content of 50.2% in the mixed sludges (Table 1). In contrast, the hydrogen content was nearly unaffected by the HTC-treatment (Table 1) as the hydrogen content decreased only during the severest treatments at 250 °C.

Biomass generally has lower sulfur content than coal (on average $1.4 \pm 1.7\%$ DAF) and thus has the capability to reduce SO_x emissions if replacing coal (Netherlands Energy Research Centre [ECN]; Williams et al., 2012). In the present study, sulfur content was higher in mixed sludge hydrochars than in the original mixed sludge or in its cake, but the hydrochars from diluted mixed sludge possessed a lower sulfur content than the original diluted mixed sludge or its cake (Table 1). Diluted mixed-sludge hydrochars had on average 25% lower sulfur content than mixed sludge hydrochars, indicating that the diluted mixed sludge was more prone to release sulfur in the liquid and gas phases during HTC treatment than mixed sludge. The sulfur yields were 78%–100% and 52%–73% in hydrochars from mixed and diluted mixed sludge, respectively, showing that sulfur was reduced in both mixed sludges by HTC. Nitrogen content that contributes to NO_x emissions in the present mixed sludges and in their hydrochars was in the range of that in coal (on average $1.5 \pm 0.4\%$ DAF) (Netherlands Energy Research Centre [ECN]) (Table 1). Like sulfur, nitrogen dissolved and/or evaporated more from diluted mixed sludge than mixed sludge during HTC (Fig. 4), as the nitrogen yields in diluted mixed sludge hydrochars were of 53%–61% and those of mixed sludge hydrochars ranged from 63% (at 250 °C, 120 min) to above 100%.

The presence of low melting temperature alkali metals in biomass derived solid fuels differentiates them from coal, which leads to concerns about their deposition on furnace walls (Chen et al., 2021). Therefore, their reduction from biomasses intended for energy recovery would be favorable to diminishing the formation of slag. The greatest

dissolution of potassium and calcium occurred at 230 °C for both mixed sludges, and overall, the diluted mixed-sludge hydrochars resulted in lower yields of potassium and calcium (18%–23% and 25%–55%, respectively) than mixed-sludge hydrochars (33%–53% and 34%–74%, respectively). Sodium dissolved to a lesser extent than potassium or calcium, as its yields increased with treatment severity from 65% to 100% in the diluted mixed-sludge hydrochars but decreased with treatment severity from 100% to 36% in mixed-sludge hydrochars. Based on the mass balance, mere filtration of the mixed sludges only affected the dissolution of potassium and calcium, resulting in yields of 56% and 91% in diluted mixed-sludge cakes, and of 78% and 82% in mixed-sludge cakes, respectively, whereas sodium was not dissolved by filtration alone (with yields of 100% in both cakes).

The results show that HTC improved the fuel properties of the mixed sludges by generating hydrochars with higher HHV and ash-free carbon content and lower oxygen content compared to the respective cakes, and the improvement was independent of the initial TS content of the mixed sludge. The hydrochars' HHV, energy densification, and carbon and ash content all increased with treatment severity, whereas the energy yields decreased because of the decrease in hydrochar masses. The increases in HHV and energy densification via increases in treatment severity derived mainly from the increased carbon and decreased oxygen content, likely resulting from the decarboxylation reactions that took place during HTC (Lin et al., 2015). The other reactions causing changes in the elemental composition of sludge, i.e., demethylation and dehydration, seemed less prominent as the hydrogen content was nearly unaltered (Lin et al., 2015; Martinez et al., 2021). In earlier studies, HTC was argued to improve the solid fuel properties of pulp-and-paper industry sludges more the higher the temperatures used, which could be observed as increased HHVs and energy densifications and decreased oxygen content (Martinez et al., 2021; Saha et al., 2019). However, as also observed in the present study, the ash content in hydrochars tends to increase along with treatment severity (Martinez et al., 2021), but ash yields decrease with increasing HTC temperature (Mäkelä et al., 2016).

The fact that the dissolution of sulfur and nitrogen was more favorable in the HTC treatments of diluted mixed sludge than mixed sludge indicate energy recovery from mixed-sludge hydrochar by incineration could possibly result in higher NO_x and SO_x formations (Lin et al., 2015)

relative to the incineration of diluted mixed-sludge hydrochars or even the cakes or mixed sludge. On the contrary, potassium and calcium concentrations in both mixed sludge hydrochars were reduced by dissolution during HTC, which would diminish the fouling or slagging in furnaces caused by the alkali metals in hydrochar ash if incinerated (Smith et al., 2016). As the lowest yields of potassium and calcium were obtained in hydrochars at 230 °C and 120 min, some absorption in hydrochar after their dissolution could have occurred after the temperature was further increased to 250 °C (Reza et al., 2013). However, the studied pulp-mill sludge had initially low potassium content compared to other lignocellulosic biomasses, such as corn stover and switch grass, as potassium in virgin wood is associated with hemicellulose and extractives that have already been removed in the preceding pulping process (Reza et al., 2013). The calcium content in the hydrochars were, in contrast, high compared to other biomasses (Smith et al., 2016), which likely resulted from the use of calcium carbonate as an agent for paper coating in paper making (Nurmesniemi et al., 2007).

Overall, the HTC treatment of the present mixed sludges of different TS contents (32% and 15%) resulted in quite similar solid fuel properties in their hydrochars, whereas differences in their ash yields and dissolutions of sulfur, nitrogen, and ash components were observed, supporting the conclusion that HTC of mixed sludge for energy recovery could be more feasible for lower TS content mixed sludge. Mäkelä and Yoshikawa (2016) found that increasing sludge TS content in the HTC feed increases the obtained energy yield and carbon recovery in hydrochars, suggesting that sludge with high TS content could react more favorably to HTC treatment than low TS sludge. However, they also found that feed TS content inversely correlates with the hydrochar ash content (Mäkelä and Yoshikawa, 2016). The differences in the fuel properties of hydrochars between different studies probably originates, aside from the operation conditions, from the feedstock composition differences, which can be highly case specific (Saha et al., 2019; Wang et al., 2021). It is also noteworthy that the methods for separating the obtained HTC-treated sludge into hydrochar and filtrate differ (Martinez et al., 2021; Saha et al., 2019), probably impeding their comparison; for example, the large range in reported solid yields (41%–87% DAF) can be partly explained by the separation method used, whether it be laboratory scale vacuum filtration through 1.6 or 20 µm filter paper, or pressure filtration. The filtration technique may also affect the amount of organic material (COD) in the resulting filtrates, which then directly influences the filtrate properties.

3.3. Filtrate

The HTC filtrates were more acidic (4.3–5.2) than the cake filtrates (6.2–6.3), and the pH of the HTC filtrates decreased from 5.1 to 4.3–4.5 with an increase in treatment temperature from 210 °C to 250 °C (Table 3). The COD concentrations in the HTC filtrates were several folds higher compared to the cake filtrates, at 8-fold (4.3 vs. 23.6–50.6 g/L) and 12-fold (2.7 vs. 23.1–41.4 g/L) higher for mixed and diluted mixed sludge, respectively (Table 3). The SCODs in the HTC filtrates covered 91%–100% of the respective CODs, while the SCOD in the cake filtrates covered 88% (mixed sludge) and 96% (diluted mixed sludge) of the COD (Table 3). The diluted mixed sludge HTC filtrates had a lower SCOD (23–41 g/L) than that of mixed sludge (23–52 g/L), but when taking into account the dilution of the mixed sludge (32% TS diluted to 15% TS) (Eq. (5)), the SCOD in the diluted mixed-sludge HTC filtrates were on average 1.3-fold higher than in those of mixed sludge. The VFAs accounted for 15%–36% and 13%–20% of the HTC filtrates' SCOD from mixed and diluted mixed sludge, respectively, while the SCOD of the original mixed sludges and cake filtrates was completely made of VFAs. Most of the HTC filtrates (except after the treatment at 210 °C for 30 min) had higher TVFA concentration than the cake filtrates (Fig. 3; Table 3), increasing 2.3-fold with a temperature increase from 210 °C to 250 °C. The VFA concentrations in the diluted mixed-sludge HTC filtrates were 3.1–7.1 g-COD/L, which was on average 64% of those

concentrations in the mixed-sludge HTC filtrates (4.5–10.2 g-COD/L), but when taking into account the dilution of the mixed sludge (Eq. (5)), they were on average 94% of the mixed-sludge HTC filtrates' VFA concentrations. The non-VFA content of the SCOD in the HTC filtrates also increased with the treatment temperature, as at 210 °C the non-VFA accounted for 18.3 g-COD/L and at 250 °C the non-VFA content was up to 40 g-COD/L. The dominant VFA was acetic acid, the concentration of which increased with treatment severity from 2900 to 7210 mg/L (mixed-sludge HTC filtrates) and from 1680 to 4440 mg/L (diluted mixed-sludge HTC filtrates). Butyric acid was generated at 230 °C and 250 °C, reaching concentrations of 350–960 mg/L and 450–750 mg/L, respectively.

The BMPs were determined for the HTC and cake filtrates from mixed sludge. The specific BMPs of the HTC filtrates were lower (190–266 L-CH₄/kg SCOD) than that of the cake filtrate, which was 318 ± 45 L-CH₄/kg SCOD (Table 3). However, as the concentration of SCOD was much higher in the HTC filtrates (23–44 g/L) than in the cake filtrate (4 g/L), the volumetric BMPs were 5–6-fold higher in the HTC filtrates than in the cake filtrate (1.2 L-CH₄/L) (Fig. 2). The volumetric BMPs in the HTC filtrates increased along with increases in temperature and residence time from 6.2 to 11.4 L-CH₄/L (Fig. 2), except for the severest treatment at 250 °C for 120 min (7.7 L-CH₄/L).

In the present study, the HTC treatment clearly increased the COD, SCOD, and TVFA concentrations relative to the cake filtrates, and the increasing effect was notable at higher treatment temperatures and residence times. Most of the increased COD comprised of non-VFAs (Table 3), and was apparently not readily degradable as indicated by the lower specific BMP compared to the cake filtrate. The non-VFA COD could possibly encompass other acids and lignocellulose degradation products, such as glycolic acid, levulinic acid, phenols, furfural, and hydroxymethyl furfural, of which at least furfurals are inhibitory for microorganisms in AD (Aragón-Briceño et al., 2021; Kim and Karthikeyan, 2021). The fact that the diluted mixed sludge yielded on average 35% and 3% higher COD and non-VFA COD concentrations than mixed sludge, when the dilution factor was considered (Eq. (5)), respectively, could result from enhanced carbon dissolution obtained by lowering the sludge TS content (Mäkelä et al., 2018). The COD increase with temperature increase can be assumed to derive from the increased dissolution of VS from the sludge during HTC, as the amount of dissolved VS increased from 9% at 210 °C to 50%–53% at 250 °C in hydrochars from both mixed sludges. However, the COD concentration increases were also derived from the hydrolysis of organic matter during the HTC treatments (Merzari et al., 2019) as indicated by the fact that although the amount of VS dissolved by filtration alone was nearly the same as after HTC at 210 °C and filtration (6%–7%), the COD in cake filtrates was 11%–12% of the COD in the HTC filtrates at 210 °C. Thus, the COD concentrations in the HTC filtrates are affected by the filtration method and the feedstock sludge type; for example, much lower CODs (using vacuum filtration with a 1.6 µm pore size filter) have been reported for both primary and biosludge HTC filtrates from a pulp and paper mill (126–331 mg/L and 24–81 mg/L, respectively, at temperatures of 180 °C–240 °C) than in the present study (Martinez et al., 2021).

As the HTC filtrate characteristics indicate, the filtrates contain plenty of soluble organic matter and nutrients (see Section 3.4) and cannot be disposed of without further treatment. The alternatives to the use or treatment of the HTC filtrates include recycling the filtrates back into the HTC reactor when additional water is needed for the feedstock dilution (Kabadayi Catalkopru et al., 2017), feeding it to a wastewater treatment plant (Mäkelä et al., 2018) or producing methane through AD (Hämäläinen et al., 2021). The effect of filtrate recirculation on the HTC products, with the aim of adjusting the feed moisture content prior to HTC treatment, has been evaluated by several authors (Mäkelä et al., 2018; Tasca et al., 2019; Wang et al., 2019) and filtrate recirculation has been demonstrated to enhance dewaterability and the mass and energy yields of hydrochar compared to hydrochar where no filtrate circulation was used. There is an improvement because the circulated filtrate

contains organic acids generated in HTC that promote polymer deposition and dehydration reactions in HTC (Tasca et al., 2019). The circulation of the filtrate to HTC has also been reported to result in hydrochars with increased carbon stability in soil compared to hydrochars where no filtrate circulation was used, which is due to a decrease in hydrochar volatile matter with lower amount of decomposed carbon (Schulze et al. 2016). The filtrate could be fed to the wastewater treatment plant in a mill, where it could supply part of the nutrient additions needed in the pulp and paper mill wastewater treatment (Hynninen, 1998). On the other hand, filtrate treatment may require an increase in wastewater treatment capacity. As shown in the present study, HTC filtrates are rich with COD and VFAs. Thus, methane production, for example, in an existing high-rate anaerobic reactor, together with other concentrated wastewater streams at the mill site could be considered if the filtrate volumes, potential inhibitory compounds, and low pH could be managed.

3.4. Nutrients, carbon, and heavy metals

Hydrochar utilization was evaluated from the perspective of using the nutrients and carbon recovered in the hydrochar for application in soil, in which the nutrient concentrations are regarded as more useful than their yields that were discussed above (see Section 3.2). The filtrates' potential for nutrient recovery was also addressed based on the nutrient concentrations.

The hydrochars and cakes contained nearly all the phosphorous (>99%) present in the mixed and diluted mixed sludges, while up to one third of total nitrogen was in the HTC filtrates and 2%–4% was in the cake filtrates (Fig. 4). According to the mass distribution, all the HTC filtrates contained less than 0.18% of the total phosphorous (Table 3). However, phosphate was found in the HTC filtrates in concentrations of 15.8–65.1 mg/L, while phosphate was not present at all in the cake filtrates. The nitrogen content in the hydrochars was in the range of 9–18.4 g/kg-TS, increasing with treatment temperature, whereas the cake nitrogen content was 13–17 g/kg-TS, which was slightly higher than the initial mixed-sludge concentration (12.4 g/kg-TS) (Table 1). Nitrogen in the diluted mixed sludge was more prone to dissolve into the HTC filtrate ($27 \pm 6\%$ of the total nitrogen) than nitrogen in the mixed sludge ($7 \pm 3\%$ of the total nitrogen), as shown by the nitrogen mass balance (Fig. 2). The HTC filtrate nitrogen concentrations (0.28–1.17 g/L) decreased with increasing treatment severity with both mixed sludges and were higher than in the cake filtrates (0.14–0.18 g/L) (Table 4). The ammonium nitrogen concentration in the HTC filtrates also decreased from 0.13 to 0.15 g/L to 0.01–0.02 g/L with increasing severity (Table 4). The amount of nitrogen in the gas phase appeared to be greater in the treatments of diluted mixed sludge, increasing by the treatment severity (13%–36% of total nitrogen), than in those of the mixed sludge (0–10%), except at 250 °C for 120 min (36%) (Fig. 4).

The contents of other nutrients (potassium, calcium, and sodium) in hydrochars, cakes, and in mixed sludges are presented in Fig. 5. Of these nutrients, the calcium and potassium content was lower in hydrochars than in the mixed sludges and cakes, while the sodium content was in some cases higher than in the mixed sludges. The calcium content was 11–21 g/kg-TS and 7–11 g/kg-TS in mixed and diluted mixed sludge hydrochars, respectively, while the initial sludge concentrations were 20 g/kg-TS and 17 g/kg-TS, respectively. Sodium concentrations increased from 3.6 g/kg-TS in the mixed sludge up to 7.0 g/kg-TS (at 210 °C) but decreased with treatment severity to 2.4 g/kg-TS, whereas in the diluted mixed-sludge hydrochars the concentrations increased up to 10 g/kg-TS with an increase in temperature to 250 °C. The mixed sludge hydrochar potassium content (141–430 mg/kg-TS) was on average 1.8-fold higher than that of the diluted mixed sludge (93–211 mg/kg-TS). The contents of heavy metals (Cr, Fe, Ni, Cu, Zn, As, Cd and Pb) present in the mixed sludges remained nearly the same in the hydrochars and cakes, and their yields were 100%. However, Fe and Zn were also found in the HTC filtrates in concentrations of 0.01–0.51 mg/L

and 0.01 mg/L, respectively, as was aluminum in concentrations of 0.05–0.2 mg/L (Table 4). Of the metals in the hydrochars, aluminum was found in the highest content (38–75 g/kg-TS), as it was in the original mixed sludges (39–56 g/kg-TS) (Table 4).

It appears that HTC only slightly promoted the dissolution of the phosphorus and partially that of nitrogen in the filtrates (as compared to filtration alone) from the studied pulp and paper mill sludges. Additionally, the sludge TS content seemed to determine whether nitrogen was dissolved in the filtrate and to what extent, rather than the different HTC conditions (Fig. 4), the lower TS content sludge releasing more nitrogen to the liquid and gas phases than higher TS content sludge. The HTC filtrates' decreasing total nitrogen concentrations by treatment severity indicated that organic nitrogen was released to the liquid phase during HTC but was then converted to ammonia and ammonium nitrogen, which are easily evaporated at higher temperatures, leading to decreased total nitrogen and ammonium nitrogen concentrations in the HTC filtrates (Idowu et al., 2017).

Phosphate was present only in the HTC filtrates, and its concentration increased with treatment severity. Alkali phosphates have high solubility, but phosphate remains in the hydrochar when the original feed contains aluminum and iron, which interact with it (Alhndi et al., 2020). The present mixed sludge contained aluminum at a content of 56 mg/kg-TS, which was a more probable reason for the decreasing phosphorus solubility than the iron with concentrations of 1.8 mg/kg-TS in the original mixed sludge. Adding metals, e.g., in sludge pretreatment prior to HTC, to adjust the initial metal content in the sludge, could enable the recovery of phosphorus in the hydrochar (Alhndi et al., 2020). The bioavailability of phosphorous in the hydrochar should be determined, if fertilizer use is being considered, as it could be bound to the added metals and mineral compounds (Huang and Tang, 2015). Hence, the origin and type of the sludge treated in HTC evidently affects the resulting nutrient contents of the hydrochar and filtrate. For example, the nitrogen content of hydrochars (at 260 °C) produced from two mixed pulp and paper mill sludges from different mills either decreased from the original 2.3% to 2.1% or increased from the original 0.7% to 1.6% (Saha et al., 2019).

Similar to nitrogen, the contents and yields of phosphorous, potassium, calcium, and sodium were all higher in the mixed sludge hydrochars than in the diluted mixed-sludge hydrochars, but the changes in these concentrations were small between the hydrochars and filtrates from the different HTC conditions. Hence, the use of HTC in the optimization for nutrient recovery from pulp and paper mixed sludge could focus instead on the pretreatment of the sludge to increase or decrease its metal and TS contents, and on the minimization of nutrient evaporation to the gas phase. For example, the filtrates could be treated in a stripping process if the nitrogen concentrations would be at feasible levels. The hydrochar nutrients and carbon could be recovered by its application in soils where it would increase the soil nitrogen and carbon supply (Bargmann et al., 2014) and reduce soil acidity (Dai et al., 2017), which could increase tree growth, and thus, forest productivity and returns from forests to the pulp and paper industry (Mohammadi et al., 2019). However, as the nutrient contents were comparatively low in the original mixed sludges relative to other waste biomasses (Aragón-Briceño et al., 2021), the hydrochars in this study would not fulfill, for example, the criteria for forest fertilizers set by the Finnish authorities because the P + K content was on average $0.47 \pm 0.16\%$ -TS and the calcium contents were between 0.9 and 1.3%-TS, covering only a fourth and sixth of the minimum required content, respectively (Decree of Ministry of Agriculture and Forestry of Finland, 2011).

The fact that the HTC-treatments increased the ash-free carbon content of the mixed sludges (from 48.5% to above 52%) (See Section 3.2) (Table 2), encourages the examination of the role of HTC treatment of pulp and paper industry sludges in carbon sequestration. HTC temperature has been found to influence the stability of carbon in straw digestate hydrochars; hydrochar at 250 °C emitted 28% less carbon (3.2% of total carbon) when applied in soil than at 230 °C (4.4% of total

carbon), and hydrochar at 230 °C emitted 60% less carbon than hydrochar at 210 °C (11.9% of total carbon), which could be explained by the protonation of OH-groups, aromatization and decreasing O/C and H/C ratios (Schulze et al., 2016). The carbon stability of hydrochar can be evaluated via the dissolved organic carbon content, which directly correlates with the carbon release induced by hydrochar in soil (Bargmann et al., 2014) and by the hydrochar volatile matter that inversely affects it (Schulze et al., 2016). According to a life-cycle assessment (LCA), the HTC-treatment of pulp and paper sludge and with its subsequent soil application could possibly obtain net reductions of 1.13 tons of CO₂-equivalent to one ton of dried sludge (Mohammadi et al., 2019). In addition to the HTC temperature, the duration of hydrochar soil application influences the amount of emitted carbon, as a short-term soil application (3 months) appears to increase the soil's carbon emission through decomposition and leaching, but during a long-term application (1 year), two thirds of the carbon in hydrochar is still in the soil, independent of whether the soil is sandy or coarse (Malghani et al., 2013).

4. Conclusions

HTC treatment of pulp and paper mill sludges produced hydrochars with increased HHVs (from original 15 up to 20.5 MJ/kg) and energy densification (up to 1.49) improving energy recovery, while sludge dewaterability was little affected. HTC produced filtrates with high COD, increasing with treatment severity up to 51 g/L, which could supplement methane production though 65–79% was non-VFA-COD. Hydrochar characteristics were unaffected by the sludge solids content, while lower sludge solids content generated filtrates with less COD and nutrients. Hydrochars' carbon and nutrient contents increased with treatment severity, but for their low nutrient content, carbon sequestration could be prioritized.

CRedit authorship contribution statement

Anna Hämäläinen: Investigation, Visualization, Writing – original draft. **Marika Kokko:** Supervision, Writing – review & editing. **Viljami Kinnunen:** Resources, Methodology. **Tuomo Hilli:** Supervision, Methodology. **Jukka Rintala:** Project administration, Writing – review & editing.

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.

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