Country report

The effects of digestate pyrolysis liquid on the thermophilic anaerobic digestion of sewage sludge — Perspective for a centralized biogas plant using thermal hydrolysis pretreatment

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ABSTRACT

The use of pyrolysis process to valorize digestate from anaerobic digestion (AD) of municipal sewage sludge for biochar production was piloted in a central biogas plant. The pyrolysis also generates pyrolysis liquid with high organics and nutrient contents that currently has no value and requires treatment, which could potentially be done in AD. As the pyrolysis liquid may contain inhibitory compounds, we investigated the effects of adding the pyrolysis liquid on AD of sewage sludge and thermal hydrolysis pretreated sewage sludge (THSS) simulating the full-scale centralized biogas plant conditions. In batch assays, the pyrolysis liquid as such did not produce any methane, and the 1% and 5% (v/w) shares suppressed the methane production from THSS by 14–19%, while a smaller decrease in methane production was observed with sewage sludge. However, in the semi-continuous reactor experiments, pyrolysis liquid at a 1% (v/w) share was added in sewage sludge or THSS feed without affecting the methane yields or digestate characteristics. The laboratory results indicated that pyrolysis liquid can be treated in AD, while extrapolating the results to the centralized biogas plant indicated minor increase in the overall methane production and an increased potential for ammonium recovery.

1. Introduction

For decades, anaerobic digestion (AD) has been a common technique used for sanitizing sewage sludge, and the importance of the produced biogas has also increased, along with targets to produce renewable energy. Recently, large-scale centralized biogas plants have been implemented to improve the economics of sludge management and, for example, to promote the economics of upgrading biogas so that it can be used in vehicles. At the same time, promoting sustainability for example through using of the sludge nutrients, has created the need for upgrading the digestate into a more economically transferable and safe product. The need for digestate upgrading is urgent because the use of digested sewage sludge as such in agriculture is limited, which stems from the concern regarding the potential presence of organic contaminants, pathogens, microplastics, and heavy metals (Alvarenga et al., 2015; Corradini et al., 2019). Thus, AD process of sewage sludge requires complementing technologies to ensure the efficient use of nutrients while enhancing the utilization of the energy potential of sewage sludge.

Different technologies have been integrated or studied in sewage sludge management systems that utilize AD, such as thermal hydrolysis pretreatment (THP) of the feed, which aims at destroying pathogens and improving biogas production through the solubilization of organics (Barber, 2016; Bougrier et al., 2008). THP is conducted at temperatures of 120–180 °C and is more effective than standard hygienization (1 h at 70℃) in the destabilization of flocs and cell lysis, which leads to increased biodegradability and decreased viscosity of the sludge (Bougrier et al., 2008; Carrere et al., 2016). Applied or studied downstream treatment technologies for digestates from sewage sludge AD plants include the pyrolysis, combustion, and hydrothermal carbonization of the dewatered digestate, as well as evaporation and stripping of the liquid digestate (Hämäläinen et al., 2021; Salman et al., 2017). Coupling of these processing technologies with AD targets both the reduction of digestate volume and contaminants, as well as the increase in the concentration of nutrients and carbon, aiming to generate valuable and safe nutrient products or carbon sinks and/or additional energy recovery.

Pyrolysis has been studied for various biomasses such as lignocellulosic biomasses (Yogalakshmi, 2022) and waste materials, such as the organic fraction of municipal solid waste (Yang et al., 2018) and sewage

sludge (Naqvi et al., 2021) as well as for digestates from AD plants treating these type of waste materials (Pecchi and Baratieri, 2019). The pyrolysis of organic matter is conducted in the absence of oxygen, and it yields three product fractions: solid biochar, liquid pyrolysis oil and pyrolysis gas (Torri and Fabbri, 2014), the amounts and compositions of which are affected by the biomass feed composition and moisture content as well as the pyrolysis conditions, including temperature, applied heat transfer rates, and residence times (Bridgwater, 2012).

Pyrolysis is normally considered for biomasses with a low moisture content (below 10%) (Fonts et al., 2009), which is justified with energy balances because the water content of the feed is directly proportional to pyrolysis energy consumption (Kim and Parker, 2008) and to the water content of the resulting pyrolysis oil (Shen and Zhang, 2005). For waste materials with high initial moisture content, for example sewage sludge, a low moisture content has been achieved in laboratory studies using drying at < 110 °C (Naqvi et al., 2021), while in full-scale sewage plant scale-up evaluations drying is assumed to be accomplished by using heat from burning of pyrolysis gas (Li and Feng, 2018). However, because the potential integration of pyrolysis with AD and other units in the biogas plant has many alternatives, the integrated system should consider—besides the energy balance of the pyrolysis—the overall energy balance of the plant and the different uses of the plant products, including the fate of nutrients, carbon, and contaminants (Barry et al., 2019; Li and Feng, 2018; Naqvi et al., 2021). These different targets and options of sewage management plants also motivate the study of pyrolysis with less-dried feeds. For example, the effect of the feed moisture content (12.7–45.8%) and pyrolysis temperature (450–850 °C) on the three pyrolysis products generated from organic fraction of municipal solid waste has recently been studied, and this research has reported that the effect of the feed moisture content on the energy distribution in pyrolysis products was relatively small (Yang et al., 2018). However, the feed moisture content affected the composition as well as the anaerobic toxicity of the pyrolysis liquid which decreased with the increasing feed moisture content (Yang et al., 2018). Furthermore, demonstration-scale trials concerning the implementation of pyrolysis in the centralized sewage biogas plant concept have shown that the preceding drying to > 90% total solids (TS) of digested sewage sludge may be costly, prompting to research on the pyrolysis for moist feed.

As a rule, lower pyrolysis temperatures (~290 °C) principally produce biochar, and higher temperatures (~750–900 °C) create pyrolysis gas, while moderate temperatures (~500 °C) mainly yield pyrolysis oil (Azuara et al., 2013; Bridgwater, 2012). Pyrolysis of slow heat transfer rates and long residence times (slow pyrolysis) generate mainly biochar, compared with fast heat transfer rates and short residence times that target for pyrolysis oil production, while intermediate conditions (intermediate pyrolysis) generate lower viscosity and tar content pyrolysis oils compared with fast pyrolysis (Hornung, 2012). The pyrolysis oil (yield 45–50 w%) from intermediate pyrolysis tends to be divided into two phases: a tarry organic phase (bio oil) (52–57% of the pyrolysis oil) and an aqueous phase (pyrolysis liquid 43–48%) (Bridgwater, 2012; Park et al., 2008; Torri and Fabbri, 2014). The pyrolysis oil from sewage sludge contains a variety of compounds including acids, alcohols, amines, and aldehydes originating from the sludge and the reactions taking place in the pyrolysis itself, but only 2–10 w% of water (Park et al., 2008), hence enabling its potential utilization in fuel applications or in the manufacture of chemicals (Bridgwater, 2012). The pyrolysis liquid is mostly comprised of water, the content of which depends on the pyrolysis temperature (Fonts et al., 2012), the biomass ash content and the number of OH-groups in the sewage sludge digestate (Fonts et al., 2009). The pyrolysis liquid originating from digested sewage sludge contains polar ketones and amines (Park et al., 2008) as well as volatile fatty acids (VFAs), ammonium-nitrogen and phenolics (Seyedi et al., 2019).

Although the bio oil fraction from pyrolysis is considered a useful product, the pyrolysis liquid from sewage sludge digestate often represents a waste management issue because of its low heating value and disposal regulations and thus, requires careful management (Torri and Fabbri, 2014). One option for managing the liquid from sewage sludge digestate pyrolysis is feeding it to the AD process. This approach could yield some additional methane (Hübner and Mumme, 2015) and could avoid supplementary wastewater treatment units or the need for increased capacity in the biogas plant. Furthermore, it could replace some dilution water used in centralized biogas plants to adjust the feed moisture prior to AD. However, feeding the pyrolysis liquid to AD may pose some risks to operating the AD process because those liquids from the pyrolysis of several biomasses have been found inhibitory in anaerobic batch tests (Hübner and Mumme, 2015; Yang et al., 2018), while only a couple of continuous flow anaerobic reactor studies enabling microbial adaptation are available (Seyedi et al., 2020; Torri and Fabbri, 2014). Thus, the effects of pyrolysis liquid on AD should be determined case by case.

The current study deals with a centralized biogas plant producing vehicle fuel from dewatered sewage sludge of several sewage plants. The biogas plant has several years of experience on the THP of the sewage sludge (referred here as THSS) and, for example, on ammonium recovery from the liquid fraction of the digestate. The plant has interest to screen different methods to develop digestate utilization, and thus, also pyrolysis for biochar production was piloted. As there was concern about the treatment of the produced pyrolysis liquid, its utilization and treatment in the existing AD of the biogas plant was studied in laboratory-scale simulating conditions of the full-scale plant.

The objective of the current study was to evaluate the effect of the pyrolysis liquid of digested sewage sludge on the performance of AD treating sewage sludge or THSS. The studied pyrolysis liquid originated from a pilot-scale pyrolysis, operated with relatively high moisture content digested sewage sludge (70–80% TS) from a full-scale centralized biogas plant applying THP and AD. The influence of the pyrolysis liquid on methane production was first studied in batch assays, after which the long-term operation was studied in continuously stirred tank reactors (CSTR). Subsequently, the feasibility of treating the pyrolysis liquid in AD was determined by using the laboratory results and the mass balances of the centralized biogas plant.

2. Materials and methods

2.1. Feeds, pyrolysis liquid, and anaerobic inoculum

In the current study, sewage sludge or THSS (thermal hydrolysis with Cambi®, 130–140 °C, 4 bar for 20 min) were used as the feeds for AD. The sewage sludge and THSS were collected every three to four months over the course of study from the reception and feed tank of thermophilic AD digester at the Topinoja centralized biogas plant (Turku, Finland), which annually treats 75,000 t (ca. 22% TS, 16,500 t-TS/a) of dewatered sewage sludge from six municipal wastewater treatment plants.

In the reception tank of the biogas plant from where the sewage sludge sample was taken, dewatered sludge obtained from various wastewater treatment plants is mixed as such and diluted with clean water to around 16% TS before being fed to the THP process semi-continuously, where the temperature is raised with steam injection (leading to a dilution to 12% TS content). The THP-treated sludge and condensate from the THP process led to the AD process. For the current study, a THSS sample was taken from the AD feeding line. Non-condensable gases from THP are directed to the AD process through a different route and, thus, are not present in the THSS sample used in the present study.

Pyrolysis liquid was obtained from an intermediate pyrolysis pilot treating mechanically dewatered digestate (TS 30%) at the Topinoja biogas plant. The pilot pyrolysis process comprised of a screw pre-dryer and vacuum dryer that in addition to removing water (TS content increased to 70–80%) also pre-heated the sludge for the following pyrolysis unit that had two screw-type reactors operating in parallel and at

normal pressure. The pilot had a capacity of 600–800 kg/h. The pyrolysis temperature was around 400 °C, and the residence time was around one hour. The approximate product mass rates from the pyrolysis were 150–200 kg/h sludge biochar, 50–70 kg/h pyrolysis gas, and 50–70 kg/h pyrolysis liquid, which contained both oil and aqueous liquid that were not further fractioned and used.

The inoculum used for the anaerobic batch and CSTR experiments (conducted at 55 °C) was digestate from the thermophilic digester at the Topinoja biogas plant. The sewage sludge, THSS, digestate, and pyrolysis liquid were stored at 4 °C for less than three months before being used in the experiments. Table 1 presents the characteristics of the feeds and inoculums used. The pyrolysis liquid sample used in this study was not analyzed for other parameters, but analyses of other samples from the same pilot has shown that in the pyrolysis liquid all halogens were below detection limit, except Cl (0.028 wt-%), all mineral oils (C10-C40) were below detection limit (<30–150 mg/kg), all metals were below 170 mg/kg, except S (2800 mg/kg), and all heavy metals (Cd, Co, Cr, Cu, Pb, Ni, Mo, V, Hg) were below 10 mg/kg. Table 1 also shows the computational THSS characteristics (as a reference to sewage sludge), illustrating the effects of THP on the sludge characteristics when the effect of dilution in the THP process with steam (from 16 to 10% TS) is extracted (calculations are shown in Section 2.4).

2.2. Biochemical methane potential assays

The biochemical methane potentials (BMP) of the sludge substrates alone and those amended with pyrolysis liquid—as well as pyrolysis liquid alone—were determined at thermophilic (55 °C) conditions. The BMP assays were conducted in triplicate in 120 mL serum bottles with a liquid volume of 60 mL. The inoculum volatile solids (VS) content in the batches was set to 7.7 g/L. A $VS_{substrate}/VS_{inoculum}$ ratio of 0.5 was used in all batches other than the one containing only pyrolysis liquid, in which the substrate concentration was set to 1.4 g of the soluble chemical oxygen demand (SCOD) per liter. The pyrolysis liquid was added in volumes of 1% or 5% of the wet weight of the substrate (v/w) in question (sewage sludge or THSS). Each batch also contained 5 g/L of buffer ($NaHCO_3$), and distilled water was added to reach volumes of 60 mL. The initial pH (>8) was adjusted to between 7 and 8 with 1 M HCl, after which the bottles were closed with gas-tight rubber stoppers. Anaerobic conditions were created inside each bottle by flushing it with nitrogen gas for three minutes. Assays containing only inoculum, buffer, and water functioned as a blank, and their methane production was subtracted from the methane production of the sample assays. The methane concentrations were measured one to three times a week, and prior to every measurement, the bottles were manually shaken to mix the contents. The methane concentration was analyzed with a Perkin Elmer Clarus 500 gas chromatograph flame ionization detector (GC-FID)

using He as the carrier gas, as described in Kokko et al. (2018), and the methane volume was calculated from the methane percentage in the serum bottle headspace as described in Angelidaki et al. (2009). The methane concentrations and volumes were reported as the averages of the triplicate assays.

2.3. Reactor experiments

Three parallel 6 L semi-continuously fed CSTRs (Kinnunen et al., 2015) (referred to as R1, R2, and R3) were operated for 221 d at 55 °C. The working liquid volume was 4 L, except for R3, in which it was decreased to 3.5 L on day 143 to manage sludge floating. Heating coils in an insulated frame with water recirculation provided a constant temperature for the reactors. The reactor contents were mixed with a mechanical mixer (11 rpm) operated for 30 min at 30-minute intervals until day 140, after which mixing was changed to a continuous mode. The reactors were fed 5 d per week, and prior to every feeding, a measured mass of digestate (reactor content) was removed to keep the reactor liquid surface level constant. The mixing was stopped while feeding. The biogas produced was collected in 10 L aluminum gas bags (Supelco) via gas-tight tubes (Masterflex Tygon).

The reactors were inoculated with 4 L of thermophilic inoculum, before which the inoculum was warmed in a closed container to the reactor temperature in a 55 °C water bath for 2 d. The feeding began the following day after inoculation, which is referred to as day 0. The reactors were manually fed every weekday according to the desired organic loading rate (OLR) by taking the mass of sewage sludge or THSS feed that had the precise amount of daily VS.

The operational parameters of the reactor setup are shown in Table 2. The initial OLR was 3 kg-VS/m³d and hydraulic retention time (HRT) 19.6 d, which were used to simulate the operation parameters used in the full-scale plant that the materials originated from.

For the first 44 d, all three reactors received THSS, after which the feed was changed in one reactor (R3) to sewage sludge diluted to the same VS content as THSS (from 11.8% to 7.8% TS) with tap water. From day 77 onwards, the feeds of all three reactors were adjusted by dilution (1.5 times (R1 and R2) or 2.25 times (R3)) with tap water to achieve the desired OLR and HRT. The reactors fed with THSS (R1) and sewage sludge (R3) were adjusted similarly to have OLR and HRT of 2.3 kg-VS/m³d and 13 d, respectively, whereas the other THSS-fed reactor (R2) was operated with higher OLR of 3 kg-VS/m³d and HRT of 12 d. At this point, the addition of pyrolysis liquid began (0.15% of the wet mass of the feed (v/w)) in the THSS (R2) and sewage sludge (R3) feeds, while the reactor fed with THSS only (R1) served as the control. Later, the share of pyrolysis liquid (in R2 and R3) was increased to 0.5% (v/w) on day 86 and further to 1% (v/w) on day 149. The pyrolysis liquid shares of 0.15%, 0.5% and 1 % (v/w) of the feed corresponded to 1.8–2.5%, 6.2–8.1%,

Table 1
Characteristics of sewage sludge, THSS, and pyrolysis liquid used in the batch and reactor experiments. THSS computational is calculated by considering the impact of dilution with steam during THP, while the measured THSS also includes the dilution factor from using steam. The thermophilic digestate was used as the inoculum.

	Sewage sludge	THSS computational	THSS measured	Pyrolysis liquid	Thermophilic digestate
pH	6.3	n.a.	6.1	9.1	7.9
TS (%)	15.6 ± 0.5	15.6	10.1 ± 1.0	0.12	8.6 ± 0.3
VS (%)	11.8 ± 0.5	11.8	7.7 ± 0.8	0.08	5.4 ± 0.4
VS/TS (%)	76 ± 0.3	76	76 ± 0.7	67 ± 2.6	62 ± 0.1
COD (g/L)	n.d.	143.5	93.4 ± 11.5	3.7 ± 0.1	69.9 ± 5.9
SCOD (g/L)	35.9 ± 0.5	49.5	32.2 ± 1.4	3.6	21.8 ± 1.5
TVFA (g-COD/L)	21.9 ± 1.7	10.0	6.5 ± 1.4	0.9 ± 0.1	2.0 ± 0.1
Total nitrogen (g/kg-TS)	n.d.	104	68 ± 0.3	n.d.	101
Total soluble nitrogen (mg/L)	7775	6989	4550	3600	6875
NH_4^+-N (mg/L)	932.8	1061	691	61.5	4885
PO_4^{2-} (mg/L)	2950	2309	1503	7.1	2302
BMP (L-CH_4/kg-VS)	332.8 ± 28.6	n.a.	342.1 ± 3.2	0	59.3 ± 4.0

THSS: thermally pretreated sewage sludge, TS: total solids, VS: volatile solids, COD: chemical oxygen demand, SCOD: soluble COD, TVFA: total volatile fatty acids, TKN: total Kjeldahl nitrogen, n.a. not applicable, n.d. not determined.

Table 2
Operational parameters and results from the reactor experiments. The results are the averages from the last HRT or the week of the period in question.

	Reactor													
	R1			R2					R3					
Feed	THSS	THSS	THSS	THSS	THSS	THSS	THSS	THSS	THSS	SS	SS	SS	SS	SS
Days	0–76	77–125	130–221	0–76	77–85	86–125	130–152	153–221	0–44	45–76	77–85	86–125	130–152	153–221
OLR (kg-VS/m^{3}d)	3	2.3[a]	1.2[a]	3	3[a]	3[a]	1.7[a]	1.2[a]	3	3	2.4[a]	2.4[a]	1.3[a]	1.3[a]
HRT (d)	19.6	13	26	19.6	12	13	26	26	19.6	19.6	13	13	26	26
Pyrolysis liquid (% (v/w))	0	0	0	0	0.15	0.5	0.5	1	0	0	0.15	0.5	0.5	1
Feed TS (%)	10.1	5.9	5.9	10.1	8.1	8.1	8.1	5.9	10.1	10.0	6.0	6.2	6.2	5.8
Feed VS (%)	7.7	4.4	4.4	7.7	6.1	5.9	5.9	4.4	7.7	7.8	4.3	4.5	4.5	4.1
Methane yield														
(L-CH$_4$ / kg-VS)	200 ± 41	406 ± 112	362 ± 32	245 ± 15	233[b]	349 ± 32	378 ± 32[c]	361 ± 54	121 ± 96	88 ± 12	106[b]	162 ± 5	456 ± 126[c]	376 ± 107
Methane concentration (%)	57 ± 5	62 ± 4	64 ± 6	59 ± 5	58 ± 4[b]	63 ± 5	63 ± 4	65 ± 7	57 ± 9	53 ± 4	56 ± 4[b]	60 ± 3	62 ± 5	63 ± 4
VS-removal (%)	23 ± 8	48 ± 7	67 ± 3	28 ± 2	n.d.	55 ± 4	60 ± 0.3	71 ± 1	28 ± 2	22 ± 6	n.d.	46 ± 3	53 ± 2	67 ± 2
Digestate characteristics														
TVFA (g-COD/L)	13 ± 2	7 ± 2	0.3 ± 0.3	14 ± 2	11 ± 1	4 ± 3	2 ± 0.5	0.3 ± 0.3	9 ± 2	16 ± 3	14 ± 4	7 ± 1	6 ± 1	0.6 ± 0.4
SCOD (g/L)	34 ± 4	20 ± 3	8 ± 2	36 ± 2	34 ± 3	13 ± 3	11 ± 1	7 ± 1	36 ± 4	36 ± 2	35 ± 1	23 ± 1	21 ± 1	8 ± 1
pH	7.6 ± 0.2	7.7 ± 0.2	7.8 ± 0.1	7.6 ± 0.2	7.7 ± 0.1	7.7 ± 0.2	7.9 ± 0.1	7.8 ± 0.1	7.6 ± 0.2	7.6 ± 0.2	7.4	7.6 ± 0.1	7.7 ± 0.1	7.8 ± 0.1

OLR: organic loading rate, HRT: hydraulic retention time, VS: volatile solids, TVFA: total volatile fatty acids, SCOD: soluble chemical oxygen demand, [a] diluted feed, [b] one week measurement only, [c] average of 0.77 HRT, n. d.: not determined.

and 17–17.4% of the fed amount of TS in feed, respectively, which simulated the potential share (15.5% of the AD feed TS content) at the full-scale biogas plant. On day 130, OLRs were reduced, and HRT was increased to 26 d in all reactors because of the high VFA and SCOD concentrations in the reactors (Table 2). On day 153, the OLR in R2 was further reduced to the same level as in R1 and R3. The feeding of the reactors paused between days 125 and 129 because of technical issues leading to a decrease in the temperature to room temperature.

2.4. Analyses and calculations

TS and VS were gravimetrically determined according to standard methods (APHA 2540). The pH of the samples was measured with a WTW pH 3210 m using a WTW SenTix® 41 electrode.

Total Kjeldahl nitrogen (TKN) was analyzed, as described in Kokko et al. (2018), and total soluble nitrogen, ammonium-nitrogen (NH_4^+-N), and phosphate phosphorous (PO_4^{2-}-P) were analyzed using Hach Lange kits (LCK303, LCK305, LCK338, LCK238, LCK349) according to the instructions provided by the supplier.

VFAs were determined with GC-FID, as described in Kokko et al. (2018). Total chemical oxygen demand (COD) and SCOD were analyzed according to Finnish standard methods (SFS 5504). The samples for SCOD and VFA analyses were centrifuged twice at 4000 rpm (15 min) before being filtered through 0.45 μm (Chromafil Xtra PET) and stored at 4 °C after conservation with 4 M H_2SO_4 and at −20 °C, respectively. For VFA analysis, a second equivalent filtration also preceded analysis. All analyses were conducted within a week of sample collection.

The volume of biogas produced in the CSTRs was measured three times a week (Monday, Wednesday, and Friday) using the water displacement method, and its content (CH_4 and CO_2) was analyzed, as described in Mönkäre et al. (2015). The specific methane yield was calculated for each week by summing the methane produced during a week (Monday to Monday) and the VS added during the week (Monday to Friday). The reactors were fed for 5 d a week, but the OLR in kg-VS/ m^3 d is expressed as the average daily amount of VS fed to the reactors over a one-week period. The reactor results (Table 2) cover the average of the results from the time of the latest HRT because it was assumed that the digestive conditions were stable enough after a reasonable adaptation period to reliably describe the applied conditions, rather than the adaptation to the conditions.

To differentiate the effects of THP treatment from dilution by steam in the THP process on sewage sludge characteristics, a computational THSS was calculated (Eq (1)) that eliminates the effects from dilution with steam, as follows:

$$THSS \ computational = THSS_{measured} \bullet \frac{TS_{THSSmeasured}(\%)}{TS_{sewagesludge}(\%)} \tag{1}$$

3. Results and discussion

3.1. Feeds, pyrolysis liquid, and inoculum characterization

The TS content of sewage sludge and THSS were 10.1% and 15.6%, respectively, here with a VS/TS ratio of 76. The difference in the TS of sewage sludge and THSS is because of the addition of water in the THP process in the form of steam providing heat energy and solid solubilization caused by the treatment temperature (Bougrier et al., 2008). The aim of thermal pretreatment is to inactivate pathogens and/or increase the solubility of the substrate by degrading and subsequently solubilizing polymers, such as fats and proteins. The increased solubility of organics can be measured, for example, by SCOD and VFA concentrations (Astals et al., 2012; Xue et al., 2015). Hence, in the current study, by comparing sewage sludge with the computational THSS, the SCOD concentration increased after THP compared with sewage sludge (49.5 vs. 35.9 g/L), confirming enhanced solubility. However, as the total volatile fatty acid (TVFA) content simultaneously decreased from 21.9 g-

COD/L of sewage sludge to 10 g-COD/L in computational THSS, it is likely that VFAs evaporated during THP and ended up mostly in the non-condensable gases fed directly to the AD reactor. The total soluble nitrogen concentration in sewage sludge (7775 mg/L) was slightly higher than in computational THSS (6989 mg/L), but the ammonium-nitrogen to total soluble nitrogen ratio was higher (0.15) in computational THSS than in sewage sludge (0.12). The decrease in total soluble nitrogen can be a result of protein hydrolysis leading to ammonia formation and subsequent evaporation during THP.

The pilot-scale pyrolysis (400 °C, 1 h, 70% TS) of 1,000 kg of mechanically dewatered thermophilic digestate (30% TS) generated 200 L of pyrolysis liquid with a COD of 3.7 g/L, of which VFAs contributed 0.9 g-COD/L. In addition to VFAs, the COD in the pyrolysis liquid also comprise many other organics, found from other pyrolysis liquid samples generated at the same pilot-scale pyrolysis, including phenols (0.4 wt-%), nitrogen-containing compounds (0.7 wt-%), alcohols (0.2 wt-%), and aldehydes (0.1 wt-%). In addition to these substances, oxygenated hydrocarbons and methoxy-substituted aromatics originating from the digestate are formed by the pyrolysis reactions and which are possibly inhibitory to anaerobic microorganisms (Hübner and Mumme, 2015; Seyedi et al., 2020). The COD and the TVFA concentrations of the present pyrolysis liquid were much lower than those reported for the pyrolysis liquid (COD of ca. 200 g/L and TVFA of 26 g-COD/L) obtained from a pyrolysis at 800 °C of a commercially dried biosolid consisting of a mixture of digested primary sludge and raw waste activated sludge (Seyedi et al., 2019); this is likely because of the different origin, composition, and higher moisture content (20–30%) of the pyrolysis feed and much lower pyrolysis temperature (400 °C) used in the current study, as also reported by Yang et al. (2018). The VFAs in the present pyrolysis liquid comprised acetic acid (37% of the TVFA), butyric acid (24%), and valeric acid (39%), while in the pyrolysis liquid (800 °C) originating from the above-mentioned biosolids the dominant VFA (90%) was acetic acid (Seyedi et al., 2019).

The total soluble nitrogen content in the pyrolysis liquid was 3.6 g/L, of which 61 mg/L was ammonium-nitrogen, and the phosphate concentration was 7 mg/L. Nitrogen is more soluble in thermal treatments than phosphorus which tends to end up in the biochar fraction (Barry et al., 2019). The total nitrogen and ammonium-nitrogen concentrations in the present pyrolysis liquid were 7–10-fold lower than what has been reported for a pyrolysis liquid (25.6 g/L of total nitrogen) from dried sewage sludge (91% TS) produced at 350 °C (Yue et al., 2019) and for a pyrolysis liquid from commercial biosolids produced at 800 °C (63 g/L in ammonia–nitrogen) (Seyedi et al., 2019). The nitrogen compounds can be attributed to the alkalinity of the pyrolysis liquid (Azuara et al., 2013), which seems typical for pyrolysis liquids of a sewage sludge origin (Seyedi et al., 2019; Yue et al., 2019). In the studied pyrolysis liquid, the main cause for the alkaline pH of 9.1 may be the low TVFA concentration and presence of buffering compounds (Villamil et al., 2018).

3.2. BMP assays

The effect of pyrolysis liquid (1% or 5% (v/w) shares) on methane production both from sewage sludge and THSS was assessed in BMP assays, and as a reference, methane production from sewage sludge or THSS was assessed as such, as well as methane production from pyrolysis liquid alone (Fig. 1).

Methane production started in all batches with sludges with small deviations and most (>95%) of the methane was produced in around 30 d. The methane production from parallel runs of sewage sludge batches was more scattered than that of THSS, which could be because of the higher heterogeneity of sewage sludge compared with THSS. The BMPs of the sewage sludge and THSS were 333 ± 29 and 342 ± 3 L CH$_4$/kg-VS, respectively. The pyrolysis liquid alone did not produce any methane, indicating that the COD in the pyrolysis liquid was not readily biodegradable and/or that it contained some inhibitory compounds
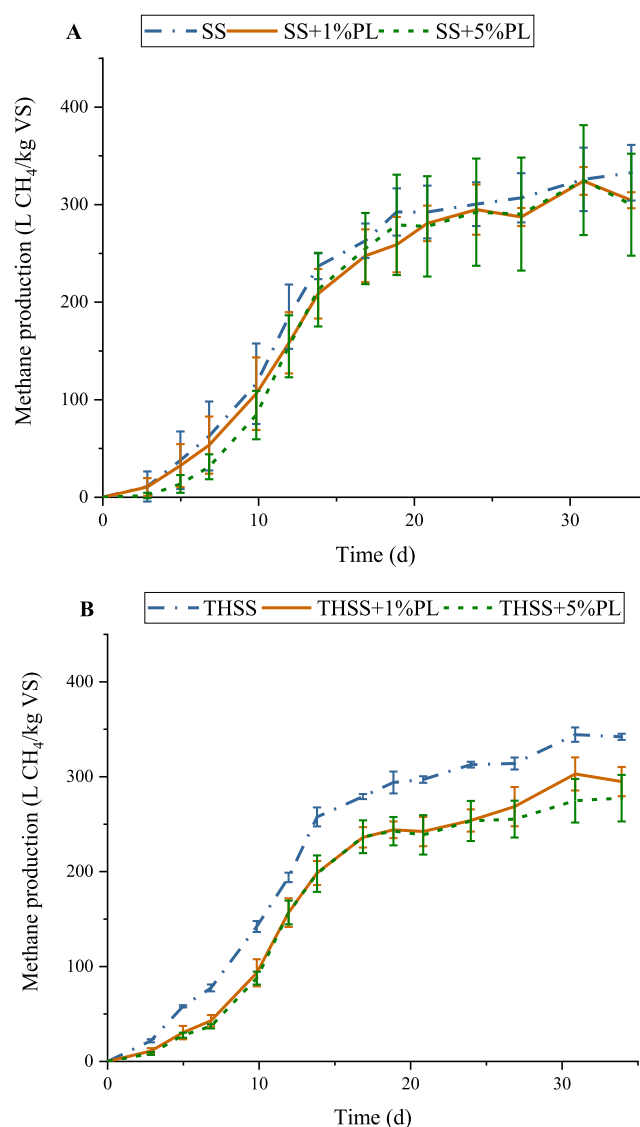
Fig. 1. Cumulative methane production in thermophilic (55 °C) BMP assays of sewage sludge (A) and THSS (B) with 0%, 1%, and 5% shares (v/w) of pyrolysis liquid. The inoculum methane production has been subtracted from the results. The intersecting vertical lines represent standard deviations for the averages of the methane productions from the triplicate batches. SS: sewage sludge, THSS: thermally hydrolyzed sewage sludge, PL: pyrolysis liquid.

preventing methane production (see Section 3.1). The addition of pyrolysis liquid decreased methane production from THSS: after 10 d of batch digestion, the methane production with 1% or 5% (v/w) shares of pyrolysis liquid was 66% and 62% of the methane production from THSS alone, respectively. After 20 d, 82% and 80% of the methane were produced, respectively. THSS with 1% and 5% (v/w) additions of pyrolysis liquid eventually resulted in 14% and 19% lower BMPs, that is, 295 ± 15 L CH$_4$/kg-VS and 277 ± 25 L CH$_4$/kg-VS, respectively, than THSS (342 L CH$_4$/kg-VS). In contrast, methane production from sewage sludge seemed nearly unaffected by the addition of pyrolysis liquid. Only the batches with 5% (v/w) of pyrolysis liquid started to produce methane with a 3-d delay, and after 12 d, the difference in methane production was around 12%, and the final BMP value difference was 10% (305 ± 8 L CH$_4$/kg-VS for 1% (v/w) of pyrolysis liquid and 300 ± 52 L CH$_4$/kg-VS for 5% (v/w)). The fact that THSS was more inhibited than sewage sludge could be because of the different VFA contents of these substrates because this sewage sludge contained more VFAs than THSS. Because of the higher VFA content, the starting of methane

production could be faster from sewage sludge, which could diminish the inhibitory impacts of pyrolysis liquid (Torri and Fabbri, 2014).

Pyrolysis liquid seemed to have inhibitory effects on methane production, with THSS already at a 1% (v/w) share. Previously, pyrolysis liquid from sewage sludge at a 6% (v/w) share has been reported to delay and decrease the methane production in batch assays from cow dung by doubling the time before the peak production of methane was reached relative to the production without pyrolysis liquid addition (Yue et al., 2019). Thus, the treatment or disposal of pyrolysis liquid alone through AD was considered unattractive (Yue et al., 2019). It is also noteworthy that the different proportions (1% vs. 5 % (v/w)) of the present pyrolysis liquid added to THSS resulted in similar BMPs. This would indicate that the present pyrolysis liquid contained at least some of the above-mentioned inhibitory compounds, i.e., nitrogen-containing compounds, phenols, and/or their derivatives, concentrations of which were already sufficient at the lower pyrolysis liquid share to hinder the microorganism activity.

The BMP results suggested that the pyrolysis liquid had a negative effect on methane production and slowed down the start of methane production from sewage sludge and THSS, which was further studied in the CSTR studies. Because of the decrease of 14–19% in methane production in BMP assays from THSS upon the addition of 5% (v/w) pyrolysis liquid, a lower share in the CSTR studies was used (Section 3.3.).

3.3. Reactor experiments

The AD of sewage sludge and THSS with and without pyrolysis liquid were studied in three laboratory CSTRs at 55 °C (Fig. 2, Table 2). For the first 44 d of operation, all three reactors received THSS at an OLR of 3 kg-VS/m³d and HRT of 19.6 d, which were the operation parameters of the full-scale plant the materials originated from. On day 45, one of the reactor feeds (R3) was changed to sewage sludge while keeping the OLR and HRT the same.

In the beginning of the runs (days 1–44), the methane yields in all three reactors increased up to 143–174 L/kg-VS and SCOD concentrations to 34–37 g/L (Fig. 2). As a result of the change of the feed to sewage sludge (R3), the methane yield decreased to 88 ± 12 L/kg-VS, while in the reactors fed with THSS, the methane yields increased to above 200 L/kg-VS. The SCOD concentrations in all three reactors remained at 34–36 g/L, and the TVFA concentrations steadily increased from 4 to 8 g-COD/L to 11–14 g-COD/L, here with propionate and isovalerate as the main VFAs. The instabilities and incomplete feed degradation during days 0–76 were likely because of the high OLRs (3 kg-VS/m³d) that resulted in overloading the reactors and accumulation of TVFAs, though similar or even higher (up to 6 kg-VS/m³d) OLRs were used at the full-scale plant. The reason for the accumulation of VFAs in the laboratory runs could not be traced, but it could also be because of the different feeding regimes because in the laboratory, the feeding was once a day for 5 d a week, while the full-scale plant applied a more continuous feeding regime.

Starting from day 79, 0.15% (v/w) pyrolysis liquid was mixed to the feeds of one THSS (R2) and sewage sludge-fed reactors (R3), and after 6 d, the share was raised to 0.5% (v/w). The OLRs were also decreased to 2.3–2.4 kg-VS/m³d (R1, R3) on day 77 by diluting the feeds, while in R2, the OLR was held at 3 kg-VS/m³d. These results indicate that the addition of pyrolysis liquid did not have a drastic (negative) effect on the process; rather, the dilutions and changes in OLRs resulted in an increase in the methane production of each reactor and decrease in VFA concentrations (Table 2). At the end of the period (days 77–125), the methane yield from THSS (R1) increased up to 406 ± 112 L/kg-VS, while those from THSS (R2) and sewage sludge (R3) amended with pyrolysis liquid had smaller increases up to 349 ± 32 L/kg-VS and 162 ± 5 L/kg-VS, respectively (Table 2). The significant increase in methane production had likely derived from the methanation of the VFAs that had accumulated before day 77 because the TVFA concentrations decreased from 13 to 14 g-COD/L to 7 ± 2 g-COD/L (R1), 4 ± 2 g-COD/L
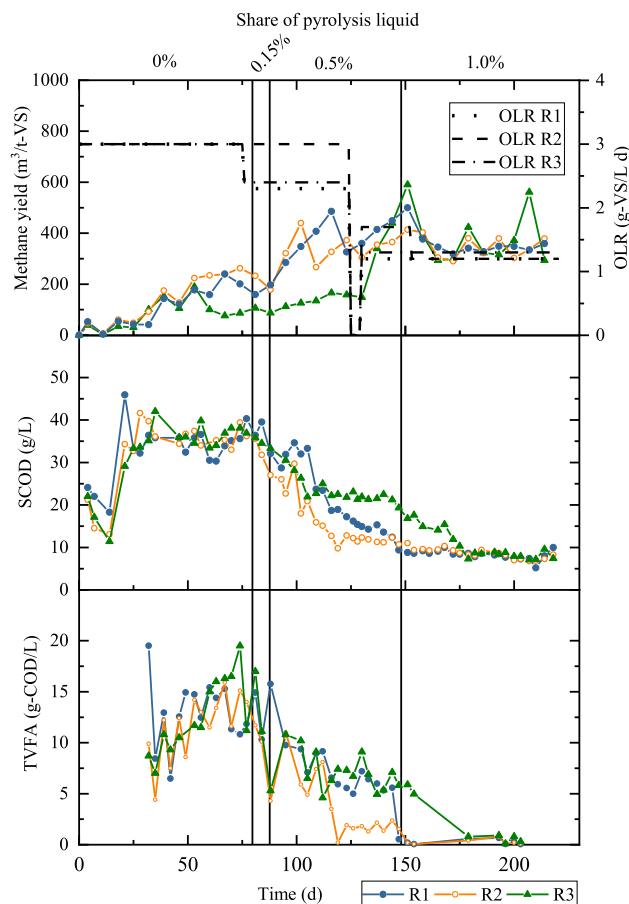
Fig. 2. The methane yields and OLRs used (A) in the reactor experiments with THSS (R1, R2, and R3) and sewage sludge (R3 from day 44 onwards), as well as the SCOD concentrations (B) and TVFA contents (C) of the reactor digestates. The pyrolysis liquid shares in the feeds of R2 and R3 as % (v/w) are marked above the graph. OLR: organic loading rate; SCOD: soluble chemical oxygen demand; TVFA: total volatile fatty acids. The feeding ended, and reactors were at room temperature during days 125–129; hence, the OLRs were reduced to zero.

(R2) and 7 ± 1 g-COD/L (R3). On day 77, the predominant VFAs were propionate (47–50%) and butyrate (26–27%) in the THSS-operated reactors (R1 and R2), but at the end of this period (day 125), the predominant VFA was propionate, accounting for 74–86% of the TVFAs. In contrast, the main VFAs on day 77 in the sewage sludge-operated reactor (R3) were propionate and acetate, comprising each about 35% of the TVFAs, and at the end of the period (day 125), the share of propionate increased to 54% while that of acetate declined to 14%. The SCOD concentrations also decreased from around 34–35 g/L to 20–23 g/L (R1, R3) and 13 g/L (R2).

Because of technical issues, the reactor temperatures declined to room temperature, so the reactor feeding ceased during days 125–129. On day 130, the TVFA concentrations were still rather high (4–7 g-COD/L) in R1 and R3; thus, OLRs were further decreased to 1.2 kg-VS/m³d (R1, R3) and 1.7 kg-VS/m³d (R2) for ensuring more complete organic degradation. The share of pyrolysis liquid was maintained at 0.5% (v/w). On days 130–152, the methane yields were around 380–450 L/kg-VS (R1 and R2) with THSS, while with sewage sludge, the methane yield increased from 162 L/kg-VS up to 456 L/kg-VS (R3). These methane yields were above the determined BMP values for THSS (342 L/kg-VS) and sewage sludge (333 L/kg-VS), indicating that accumulated SCOD and VFAs were still converted to methane. By day 152, the TVFA concentrations in R1 and R2 dropped to 0.2 g-COD/L, while in R3, TVFAs still comprised 5.9 g-COD/L.

On day 149, the pyrolysis liquid shares were raised to 1% (v/w) (R2, R3), and OLR in R2 decreased to 1.2 kg-VS/m³d (R2), while that in R3 was maintained at 1.3 kg-VS/m³d. The final period (from day 153 onwards) resulted in a similar methane yield in all three reactors, being 362 ± 32 L CH₄/kg-VS (R1), 361 ± 54 L CH₄/kg-VS (R2), and 376 ± 107 L CH₄/kg-VS (R3). Sewage sludge amended with pyrolysis liquid (R3) had, however, more fluctuation in the methane yields, implying that the operation with sewage sludge was more unstable than with THSS. However, R3 had a smaller working volume, which may also have accounted for the differences in the results. The final running period also enabled efficient organic degradation, hence resulting in final TVFA contents of 0.3 ± 0.3 g-COD/L (R1), 0.3 ± 0.3 g-COD/L (R2), and 0.6 ± 0.4 g-COD/L (R3), as well as SCOD concentrations below 10 g/L. The VS removals were also the highest (67–71%) in all the reactors during the final period (Table 2).

The results show that mixing of pyrolysis liquid at 1% (v/w) in THSS (R2) and sewage sludge (R3) did not inhibit methane production, as confirmed by the similar methane yields and digestate characteristics in all three reactors during the stable operational period (days 153–221) when the digestates' TVFA and SCOD contents were at their lowest. All reactor digestates had a pH in the range of 7.4 to 8.0 for the entire operation (Table 2). The nutrient composition of the digestate did not show any difference from adding pyrolysis liquid; this was analyzed only during the last 22 d of operation (Table 3); rather, differences between the main feeds (THSS and sewage sludge) were observed. The ammonium-nitrogen concentrations increased 5-fold in the THSS digestates (up to 2,300 mg/L) and 3-fold in the digestates of sewage sludge (up to 1,370 mg/L) compared with the feeds. In addition, the relative amount of NH₄⁺-N from total soluble nitrogen in the THSS digestates was higher (63% (R1), 64% (R2)) than in the sewage sludge digestates (39% in R3). These results suggest that the ammonification of organic nitrogen was more exhaustive in the THSS reactors.

The higher methane yields toward VS with THSS than with sewage sludge (obtained when the higher OLRs (2.3–3 kg-VS/m³ d) were used during days 0–125) may have been because of the THP promoting the hydrolysis step in AD. Thermal pretreatment usually enables increased loading rates and solid concentrations of the feed, thus increasing the methane yield (Higgins et al., 2017). Hence, it is likely that THSS had higher tolerance toward the higher OLRs and shorter HTRs than sewage sludge, which were used at the beginning of the reactor experiment (Table 2). However, when the OLRs and HRTs were decreased and prolonged, respectively, the sewage sludge-operated reactor (R3) started to produce methane superior to THSS reactors. A similar observation was obtained in one previous continuous reactor study: the reactor fed with THSS had higher OLRs than sewage sludge by having a 1.3-fold higher methane yield at an OLR of 3.8 kg COD/m³ d, while increasing the OLR to 4.4 kg COD/m³ d decreased the methane yield from sewage sludge by 5.4% but increased the methane yield from THSS by 6.2% (Choi et al., 2018). This may be because of the increased possibility of inhibition by ammonia and increased alkalinity and viscosity because the HRT is prolonged in THSS reactors, giving more time for protein degradation (generating ammonia) and for extracellular microbial by-

product formation, the reactions of which have been accelerated by THP (Barber, 2016).

The batch tests indicated that THSS was prone to inhibition by the pyrolysis liquid, whereas sewage sludge had less of a negative effect from the addition of pyrolysis liquid. One of the reasons for the difference in the susceptibility to inhibition of the two substrates, besides the differing VFA contents (see Section 3.2.), could be changes in C/N balance (review by Feng and Lin, 2017) which is possibly affected during THP. On the other hand, the semi-continuous reactor experiments showed no effect from the addition of pyrolysis liquid for either THSS or sewage sludge. The difference in the inhibitory effect by the pyrolysis liquid between the reactor experiment and the BMP assay could be accounted for the lower pyrolysis liquid shares and for the fact that the digestion process was already working when the pyrolysis liquid addition was started. It is possible that semi-continuous feeding is better suited for the addition of pyrolysis liquid than batch assays because it seems to allow the microorganisms to acclimate to the prevailing substrates and enable higher pyrolysis liquid loadings (Seyedi et al., 2020; Zhou et al., 2019). It has also been shown in anaerobic batch studies that the inhibitory effect stemming from pyrolysis liquid can be alleviated by the addition of either nutrients or biochar (or both together) that enhance the growth of the microbes or detoxify the inhibitory compounds, respectively (Wen et al., 2020). Seyedi et al. (2020) studied the co-digestion of synthetic primary sewage sludge with aqueous pyrolysis liquid from commercial biosolids in a long-term (523 d) semicontinuous reactor trial with stepwise increases in pyrolysis liquid load (from 0.05 (3% of fed sewage sludge COD) to 0.5 (25%) g-COD/L-d), demonstrating that the microorganisms were capable of acclimating to the addition of the pyrolysis liquid with no statistical difference in the methane productions between the control and pyrolysis liquid–supplied digesters at the end of the operation. Zhou et al. (2019) observed that pyrolysis liquid from corn stover, here as the only substrate in wastewater digestate inoculum, yielded methane at up to 3% (v/v) share of the inoculum, but at higher shares (5–10%), the methane yields decreased and ceased, whereas in continuous mode (HRT of 20 d), even a loading of 18% (v/v) of pyrolysis liquid generated biogas (yield 90 mL/mL-pyrolysis liquid, of which 50–65% is CH₄), though with a decreasing trend from a 6% pyrolysis liquid share (160 mL/mL-pyrolysis liquid). These aforementioned studies were conducted at a constant OLR and HRT of the feed (primary sludge or inoculum) (Seyedi et al., 2020; Zhou et al., 2019), while in the present study, OLR, and HRT were altered, along with the pyrolysis liquid share in the reactor experiment. Based on the above-mentioned results, pyrolysis liquid could be added to anaerobic digesters, but its origin and characteristics determine its applicable share of the main feed. In addition, it should be further examined whether greater OLR (>1.2 kg-VS/m³d) and shorter HRT (<26–30 d) than what has been used in the present study (during days 153–221) would be more sensitive to the presence of pyrolysis liquid because the studied conditions at 1% (v/w) pyrolysis liquid loading resulted in relatively robust reactor performance. Screening of optimum conditions, such as OLR, using laboratory reactor experiments is useful, as for example, even up to 50% higher methane yield per ton food waste with optimum OLR was achieved in a laboratory study (Megido et al., 2021).

4. Practical implication

The present results and information from the Topinoja biogas plant have enabled the assessment of the effects of adding the pyrolysis liquid to the AD feed (Fig. 3) in case pyrolysis will be implemented in digestate upgrading. An example of this assessment was conducted for the centralized Topinoja biogas plant using the amounts of sludge treated in the plant at the time of the experiments. Because the pyrolysis unit was operated at a pilot scale, its mass flows and product distributions were extrapolated to the Topinoja full-scale plant by mass-balance calculations.

The biogas plant treats approximately 75,000 t/a of sewage sludge
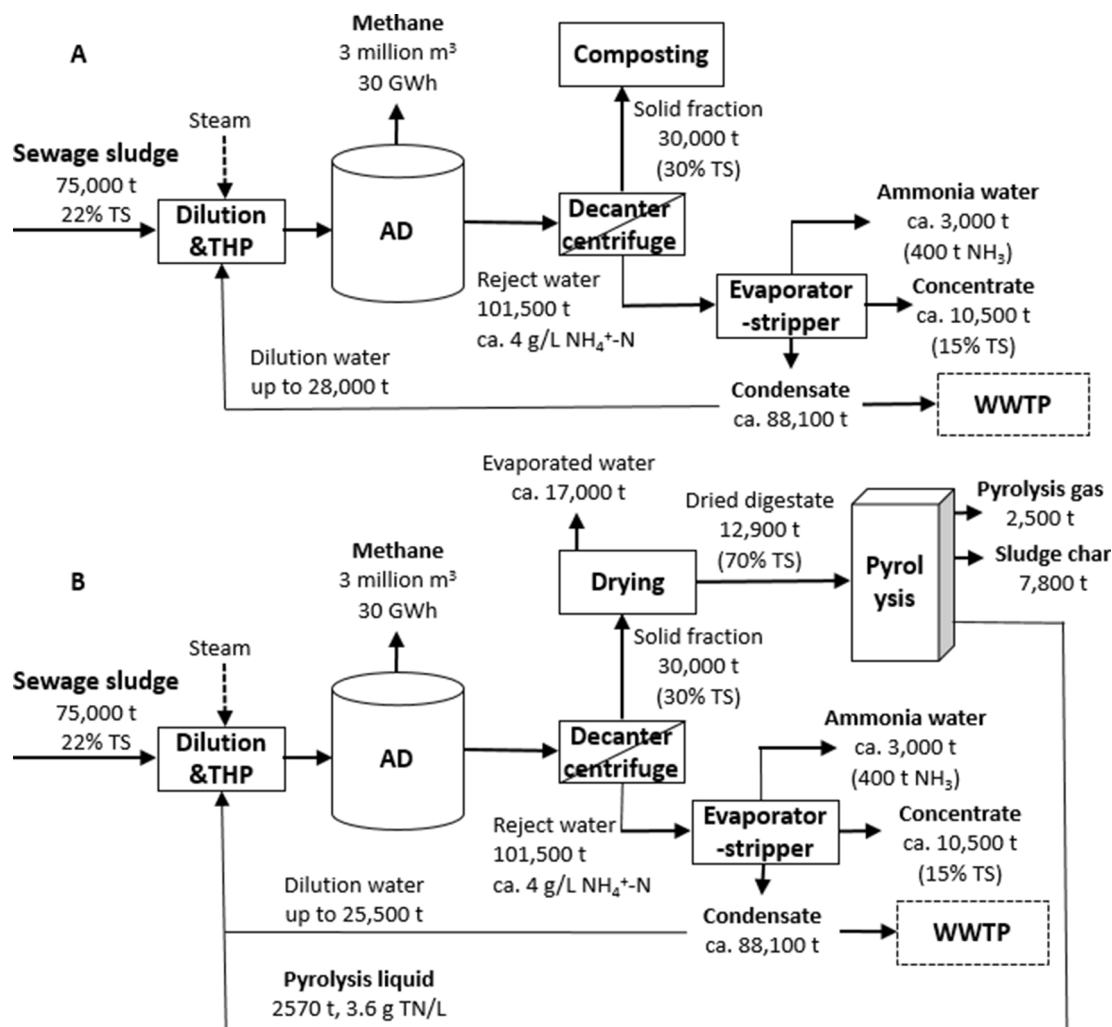
Table 3

Nitrogen and phosphorous concentrations in the digestates of the reactor experiment. The values are the averages of three samplings of two parallel samples of the last 22 days of the operation of reactors (days 200–221) fed with THSS (R1), THSS amended with 1% (v/w) pyrolysis liquid (R2), or sewage sludge amended with 1% (v/w) pyrolysis liquid (R3).

Nutrient	Reactor		
	R1	R2	R3
Total nitrogen (g/kg-VS)	153 ± 5	165 ± 3	155 ± 9
Total soluble nitrogen (mg/L)	3530 ± 100	3590 ± 60	3490 ± 210
NH₄⁺-N (mg/L)	2240 ± 57	2300 ± 142	1370 ± 107
PO₄²⁻ (mg/L)	1130 ± 100	1210 ± 130	1220 ± 90

Fig. 3. The process layout of the biogas plant at the time of the experiments (A) and the extrapolation on the integration of a pyrolysis process unit into the same plant (B). The pyrolysis liquid would replace 9% of the dilution water. TS: total solids, TN: total nitrogen, NH$_4$-N: ammonium-nitrogen. The structure for the layout has been .
adapted from Hämäläinen et al. (2021)

(dewatered to solid contents of ~ 22% TS before transporting to Top-inoja). The sewage sludge is a mix of primary and secondary sludge from several wastewater treatment plants using an activated sludge process (simultaneous chemical phosphorus removal). In the Topinoja plant, sewage sludge is diluted to ca. 16% TS and then thermally hydrolyzed in a THP unit that uses steam to raise the temperature (TS decreases to ca 12%), after which the feed (ca. 137,500 t/a) is fed to the AD process. The biogas plant generates ca. 30,000 t of dewatered digestate (TS 30%) annually, which is further composted and used for landscaping pur-poses. The reject water from the dewatering (ca. 101,500 t/a) is treated in an integrated evaporator-stripper process. The evaporator-stripper process produces around 3,000 t/a of ammonium water at 12–15 NH$_3$–% concentration, which is around 10,500 t/a of concentrate at 15% TS, while the rest is relatively pure condensate water that is used as process water to replace clean water in sludge dilution; the rest of the condensate water is discharged to the municipal wastewater treatment plant. Because the dewatered digestate currently has a low-value use, pyrolysis of dewatered digestate could produce a new product—sludge biochar—allowing carbon sequestration and phosphorus recovery, potentially with economic value. The gas fraction from pyrolysis could be combusted for energy that would supply the energy required for the thermal drying of the digestate before pyrolysis, while the pyrolysis liquid is considered a waste stream, with its use remaining open.

If the pyrolysis was to be applied in full scale as in the pilot, the dewatered digestate (30,000 t/a) would enter the thermal and vacuum drying unit prior to pyrolysis. The drying unit dries the digestate to ca. 70% TS content, removing ca. 17,000 t of moisture released as exhaust gas, after which the dried digestate is pyrolyzed at 400 °C for 1 h. The pyrolysis liquid produced annually (ca. 2,600 t) would be considered to be fed to the AD process and replace 9% of the process water used for dilution prior to THP. Based on the current study, the volume of py-rolysis liquid would not suppress methane production because its share of the total input volume and total input TS to the AD process would remain at 1.9% (v/w) and below 17%, respectively. Because of the apparently low biodegradability of the COD of the pyrolysis liquid (ca. 9.5 t COD/a), the pyrolysis liquid would not increase methane produc-tion. The total nitrogen content in the pyrolysis liquid (ca. 9.3 t/a) could potentially be ammonified in the AD process, thus enhancing the ni-trogen recovery in the evaporator-stripping unit.

Pyrolysis integration into biogas plants primarily aims to produce sludge digestate biochar that is potentially more valuable in further use than digested and composted sewage sludge as such (Sousa and Fig-ueiredo, 2016) and to increase the overall energy efficiency of the plant (Salman et al., 2017). The feeding of pyrolysis liquid to AD would pro-vide a means for its treatment. To show the economic and environmental feasibility of the process, pyrolysis integration into a centralized biogas

plant still requires energy, life cycle assessment (LCA), and economic evaluation for the investment costs of a full-scale pyrolysis process and pre-pyrolysis drying unit.

5. Conclusions

The effects of pyrolysis liquid addition on AD of sewage sludge and THSS were studied to evaluate whether pyrolysis liquid could be treated in centralized biogas plant thus avoiding external wastewater treatment. Pyrolysis liquid appears inhibitory towards methane production in batch from THSS, even at a 1% (v/w) share, while sewage sludge seems less liable. However, in semi-continuous CSTRs no inhibition is observed with the pyrolysis liquid addition at shares likely relevant to centralized biogas plant (1% (v/w)). The extrapolated results show that pyrolysis liquid addition to AD feed causes minor increase to the biogas yield but could positively impact the recovery of ammonium-nitrogen.

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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