Operation of an anaerobic filter compared with an anaerobic moving bed bioreactor for the treatment of waste water from hydrothermal carbonisation of fine mulch

J. F. Meier, U. Austermann-Haun, J. Fettig, H. Liebe and M. Wichern

ABSTRACT

This experimental study investigates the anaerobic digestion of waste water from hydrothermal carbonisation of fine mulch (wood chips) in combination with a co-substrate for the first time. Two anaerobic reactors, an anaerobic filter (AF) and an anaerobic moving bed bioreactor (AnMBBR), were operated over a period of 131 days at mesophilic conditions. The organic loading rate was increased to a maximum of 8.5 g L^{-1} d^{-1} in the AF and the AnMBBR. Both reactors achieved similarly efficient chemical oxygen demand removal rates of 80% approximately (approx.) and high methane production rates of approx. 2.7 L L^{-1} d^{-1}. Nevertheless, signs of an inhibition were observed during the experiments.

Key words | anaerobic digestion, biogas, hydrothermal carbonisation, inhibition, waste water treatment

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INTRODUCTION

The process of hydrothermal carbonisation (HTC) is an artificial coalification process whereby biomass is converted into a lignite coal-like product. The whole process takes place in water inside a high pressure reactor at or above saturation pressure and might be slightly exothermic (Ramke *et al.* 2010; Funke & Ziegler 2011). Process temperatures range from 180 to 250 °C, typical reaction times are 1 to 14 hours, and water vapour pressure is between 10 and 15 bars (Ramke *et al.* 2009a, 2010; Funke & Ziegler 2010; Wirth *et al.* 2012).

The final products of the process are classified as a solid phase (so-called biochar), a liquid phase and a gaseous phase. The solid phase contains 50 to 80 weight% of the organic remains (Libra *et al.* 2011). It is regarded as a potential soil conditioner, a raw material for activated carbon adsorbents, a carbon sink, a catalyst, or a lignite-like fuel (Ramke *et al.* 2009b; Libra *et al.* 2011). The gaseous phase mainly consists of carbon dioxide (90% approximately) and represents only 2–5 weight% of the organic remains.

Therefore it constitutes a minor loss of organic carbon during the HTC process. The liquid phase, however, can contain 5 to 20 weight% of the organic remains in the form of dissolved organic compounds (Ramke *et al.* 2009a; Libra *et al.* 2011). As a result, the liquid phase is considered to be the major contribution to the energy loss of the HTC process. It is important to point out that during the dewatering process of the HTC biochar, 0.8 to 3.5 kg waste water kg^{-1} dry solids is produced; in addition, 1.2 to 1.9 kg waste water kg^{-1} dry solids of condensate is generated (Erlach 2014).

The HTC waste water has a low pH value (<pH 5 mainly) and is highly polluted with dissolved organic compounds, which results in a high specific chemical oxygen demand (COD). Depending on input substrate and process conditions, the COD varies between 30 and 85 g L^{-1} (Fettig *et al.* 2013). Predominant compounds of the dissolved organic content are high amounts of volatile organic acids (VOAs), such as formic acid and acetic acid, which are the

two most commonly found acids. Other substances include alkenes, amino acids, aromatics, catechols, cresols, cyclopentenones, esters, furans, furfurals (5-HMF, 2-furfural), indoles, ketones, lignins, phenols, piperazines, polycyclic aromatic hydrocarbons (PAHs), pyrazines, pyridines, and sugars (arabinose, galactose, glucose, xylose, levoglucosan) (Funke & Ziegler 2010, 2011; Gerhardt *et al.* 2010; Weiner *et al.* 2012). The waste water requires further treatment before disposal. A study by Ramke *et al.* (2010) demonstrated the feasibility of an aerobic treatment of HTC waste water, in which organic compounds were aerobically degraded with COD degradation rates of 50 to 62%. However, the aerobic waste water treatment consumes vast quantities of energy for aeration, and organic compounds are irreversibly oxidized to carbon dioxide.

The anaerobic waste water treatment is considered to be a more cost-effective solution because of the high content of volatile organic substances in the HTC waste water. Various studies on the anaerobic treatment of HTC waste water are showing promising results (Ramke *et al.* 2010; Wirth *et al.* 2012, 2015; Blöhse 2013; Fettig *et al.* 2013; Oliveira *et al.* 2013; Wirth & Mumme 2013). Nevertheless, problems such as the inhibition of the anaerobic biocenosis and the continuous production of biochar that results from polymerisation of HTC waste water compounds have been observed (Fettig *et al.* 2013; Wirth & Mumme 2013). Due to the fact that the research on this subject is still limited, more work is needed to enhance the understanding in this field.

The aim of this study is to investigate the long-term stability of the degradation process of HTC waste water from fine mulch (wood chips) in continuously operated reactors. A co-substrate (CS) is added in order to provide a readily available and biodegradable carbon source to supply all necessary nutrients and trace elements. This research focuses on process performance and on optimal mixing ratio of HTC liquor and CS. Two different reactor types have been set up in order to compare produced biogas volume and quality, specific gas rate, COD removal rates, as well as the ratio of VOAs to carbonate buffer capacity total alkaline carbonate (TAC).

MATERIAL AND METHODS

Feedstock

HTC waste water was produced from fine mulch (green waste, mostly wood chips). The carbonisation occurred in a laboratory-scale HTC batch reactor with 25 L operating volume. Twelve separate batches were processed with a residence time of 4.5 hours at temperatures exceeding 180 °C and a peak of 220–230 °C. All batches were blended and stored in 10 L plastic canisters at room temperature. Beer from a local brewery was dosed as a CS. The composition of CS, HTC liquor and the resulting mixed feedstock are listed in Table 1. The mixed feedstock shows a well-balanced C:N:P ratio for the anaerobic digestion (Kroiss & Svardal 2015). No separate source of nitrogen or phosphorus was added. Most concentrations of the mixed feedstock example tend to be in between the two initial feedstocks. In the case of total solids (TS), total volatile solids (TVS), total suspended solids (TSS), and volatile suspended solids (VSS), the final concentrations were either higher or lower than both initial ones. This can be explained by flocculation and precipitation processes, especially with the forming of HTC biochar and biomass growth inside the receiving tank. The biochar tends to sediment on the bottom as well as the walls of the receiving tank.

Experimental setup

The experiments involved two anaerobic reactor systems, namely one anaerobic filter (AF) and one anaerobic moving bed bioreactor (AnMBBR). Both were made of transparent PVC-U tubing ($d_{AF} = 8$ cm, $d_{AnMBBR} = 12$ cm) with a total volume of 3.74 L each and operated in upward-flow. Biofilm carriers made of PE (ENVIMAC Engineering GmbH, Oberhausen, Germany, type: Pall-Rings, 1.5×1.5 cm) with a specific surface area of 350 m^2 m^{-3} were used. The AF was filled with 2.7 L (ca. 72% degree of filling) and the AnMBBR with 2.1 L (ca. 56% degree of filling) of biofilm carriers. That equals a bio carrier surface of 0.60 m^2 in the AF and 0.47 m^2 in the AnMBBR. Therefore, the hydraulic working volume was 3.53 L of the AF and 3.57 L of the AnMBBR. The smaller amount of biofilm carriers in the AnMBBR was applied to ensure a smooth process and to prevent clogging. The AnMBBR had a loose filling of biomass carriers, while the AF in contrast had a fixed bed with a total height of 500 mm and a diameter of 80 mm. A set of sieves was installed inside the AF between the bottom end and the top end of the bed at regular intervals of 100 mm to keep the carriers immersed throughout the entire trials.

Both reactors were wrapped with insulating material and heated to their operating temperature (38 °C) by means of separately controlled hot water jackets. The hot water was provided in a laboratory heating bath (Julabo Labortechnik GmbH, Seelbach, Germany, type: Variomag, model: E). The fresh waste water was stored in a

Table 1 | Composition of the CS and the HTC waste water used in this study

Parameter	Unit	CS	HTC liquor	Example of mixed feedstock[a]
Homogenised chemical oxygen demand (COD$_{total}$)	[mg L^{-1}]	123,000	33,200	38,200
Soluble chemical oxygen demand (COD$_{soluble}$)	[mg L^{-1}]	119,500	31,900	37,300
Ammonia nitrogen (NH$_4$-N)	[mg L^{-1}]	17.8	22.0	12.7
Nitrate nitrogen (NO$_3$-N)	[mg L^{-1}]	36.8	122.0	70.4
Nitrite nitrogen (NO$_2$-N)	[mg L^{-1}]	0.11	0.59	0.51
Total nitrogen (TN$_b$)	[mg L^{-1}]	605	303	238.0
Total phosphorus (P$_{total}$)	[mg L^{-1}]	223	33	57.8
C:N:P-ratio	[–]	800:3.9:1.5	800:7.3:0.8	800:5:1.2
Total solids (TS)	[mg L^{-1}]	–	389.2	664.4
Total volatile solids (TVS)	[mg L^{-1}]	–	160.0	439.6
Total suspended solids (TSS)	[mg L^{-1}]	13,800	25,600	19,488
Volatile suspended solids (VSS)	[mg L^{-1}]	12,000	17,700	15,513

[a]Sampling from receiving tank, mixing ratio was 200 mL CS + 500 mL HTC liquor + 300 mL tap water.

continuously stirred receiving tank (not insulated) and fed continuously into the two reactors using separate peristaltic pumps (Watson-Marlow, Rommerskirchen, Germany, type: 101 U/R). In order to recirculate the reactor contents, each reactor had a recirculation system consisting of a peristaltic pump (Heidolph Instruments GmbH & Co. KG, Kelheim, Germany, type: PD 5001), a gas-tight overflow on top of the reactor and a separate buffer tank (2.5 L, insulated). The recirculation stream was pumped from the buffer tank into the lower end of the reactor. The flow rate of the recirculation was 120 L d^{-1} in the AF and 270 L d^{-1} in the AnMBBR, while the inflow was 1 L d^{-1} each. The upstream velocity in each reactor, as a result of supply and recirculation, was 1 m h^{-1}. Separate outflow systems were utilised to continuously direct the output of the reactors to plastic tanks (not insulated) where the outflow was kept separate. The biogas output of the anaerobic reactors was captured in the reactor heads and directed through a gas counter for quantification (Dr.-Ing. Ritter Apparatebau GmbH, Bochum, Germany, type: Milligascounter). The biogas was collected in gas collecting bags for further analysis of its composition. The receiving tank, buffer tanks and outflow tanks (plastic tanks) were not connected to the gas systems, nor were they gas tight.

Analytical methods

The determination of TS, TVS, TSS and VSS was performed according to standard methods (DIN 38409-2 1987; DIN EN 12879 2001; DIN EM 12880 2001). COD, NH$_4$-N, NO$_3$-N, NO$_2$-N, TN$_b$ and P$_{total}$ of the liquid samples were measured with test cuvettes according to the manufacturer's methods (Hach Lange GmbH, Berlin, Germany). For the COD$_{soluble}$, water samples were filtrated with 0.45 μm cellulose acetate filters (Sartorius Stedim Biotech GmbH, Goettingen, Germany, type: Minisart, No. 16555). For pre-treatment of some of the test cuvettes, a LT100 digester (Dr. Lange GmbH, Dusseldorf, Germany) was used. Test results were analysed spectrophotometrically using the photometer DR 3900 (Hach Lange GmbH, Berlin, Germany). The ratio of VOAs to TAC was determined with a TitrolLine 6000 (SI Analytics GmbH, Mainz, Germany). For the analysis, sulfuric acid 0.05 mol L^{-1} (0.1 N) volumetric solution was used (AppliChem GmbH, Darmstadt, Germany). pH-value and temperature were measured with the Multi 340i Set (WTW GmbH, Weilheim, Germany). Resulting gas volumes were converted to standard conditions (standard pressure p$_0$ = 1.01325 bar and standard temperature T$_0$ = 273.15 K) according to VDI 4630 (2006). Gas chromatographic analysis was carried out regularly with a GC-2014 (Shimadzu Deutschland GmbH, Duisburg, Germany), which measures CH$_4$, CO$_2$, N$_2$ and H$_2$S using a thermal conductivity detector. Column Porapak N 80/100 (length 3 m, inner diameter 2 mm) was used with helium as carrier gas (20 mL/min). Analysis time was 23 minutes with detector temperature 125 °C, injector temperature 90 °C and oven temperature 65 °C.

Experimental procedure

The reactors were inoculated with active granular sludge from an expanded granular sludge blanket reactor of a fruit juice company, which treats waste water from production

and cleaning processes at mesophilic temperatures. The sludge had a TSS content of $40 \, \text{g L}^{-1}$ and a VSS content of $32.8 \, \text{g L}^{-1}$ (82%). Each reactor was filled with 1.2 L of sludge. The residual volumes, including the buffer tanks, were filled up with tap water. After inoculation, the reactors were heated to their set temperature of 38 °C.

During the start-up (Phase 1 (CS I), 17 d), both reactors were fed with 200 mL of CS and 800 mL of tap water to yield an operating mixture of 1,000 mL. The organic loading rate (OLR) was increased to $5 \, \text{g L}^{-1} \, \text{d}^{-1}$. Afterwards, the main phase (Phase 2 (CS + HTC), 93 d) started, where the volumetric fraction of tap water was gradually replaced with HTC waste water, as shown in Figure 1. The hydraulic retention time (HRT) was initially set to 3.4 d by holding the inflow constant at $1 \, \text{L d}^{-1}$. The HRT varied from 3.8 to 4.1 d in AF and from 3.7 to 4.5 d in AnMBBR during the experiments. After two HRT intervals, the amount of HTC waste water to be given to the mixture was increased moderately, while the amount of CS was kept constant at 200 mL per litre.

The decreasing OLR in the AF at days 61 and 86 was due to a clogging of the inflow tubing. From day 85, the OLR was lowered by reducing the inflow in order to limit an upcoming inhibition. Between days 105 and 110, the feed of both systems was stopped because of unstable conditions in both reactors (discussed in the following sections). During the experiments, no excess sludge was discharged.

Monitoring of the systems was performed for the liquid and gaseous phases. Measurement data of the gas counter, pH-value, temperature and amount of the effluent were noted each working day. For analysing the liquid phase, samples were collected from the receiving tank (inflow samples) and the outflow tanks (outflow samples) three times a week. The pH-value and temperature were measured inside the buffer tanks. For the gaseous phase, full gas bags were collected and analysed twice a month.

RESULTS AND DISCUSSION

Performance of the two anaerobic reactors

Table 2 shows the resulting average OLR with and without the CS (OLR_{HTC}) during the different test phases. Test phase 2 (CS + HTC) was subdivided into separate periods in accordance with the different average OLRs. The percentage of HTC waste water on the total OLR in this phase began at 10% (d = 18–30) and rose to 47% in both systems in the end (d = 85–92). Maximum OLR_{HTC} was 3.5 gCOD $\text{L}^{-1} \, \text{d}^{-1}$ in both systems. The corresponding maximum sludge loading was 0.77 gCOD gVSS^{-1} and 0.79 gCOD gVSS^{-1}, respectively. The maximum observed OLR correlated with the maximum OLR in Fettig *et al.* (2013). They reported maximum OLRs of 3.4, 3.5 and 4.2 gCOD L^{-1} d^{-1} at stable reactor performance in a mesophilic AF by treating HTC liquor from spent grains, sugar beet chips and food remains, respectively. They used no CS in their experiments, but diluted their HTC waste water with tap water.

Average COD in the influent (COD_{fed}) and effluent, as well as the COD removal efficiencies (η) in both reactor systems, are illustrated in Table 3. During the second phase (CS + HTC), the CS constantly made up for 20 g COD L^{-1} in the inflow. Up to 17.1 g L^{-1} COD was provided by HTC
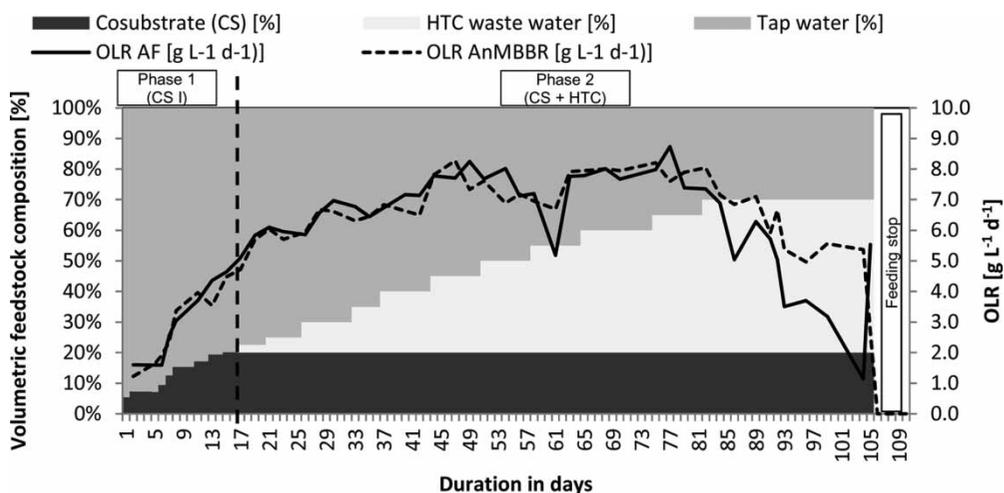

Figure 1 | Mixing ratio of HTC waste water, co-substrate (CS) and tap water, and OLR of the AF and the AnMBBR.

Table 2 | Average OLR and OLR of HTC waste water (OLR_{HTC}) during different test phases in the AF and AnMBBR; standard deviations are given in parentheses

Phase	Duration [d]	AF OLR [g L⁻¹ d⁻¹]		AF OLR$_{HTC}^a$ [g L⁻¹ d⁻¹]		AnMBBR OLR [g L⁻¹ d⁻¹]		AnMBBR OLR$_{HTC}^a$ [g L⁻¹ d⁻¹]	
1 (CS I)	1–17	3.3	(±1.94)	–	(−)	3.2	(±1.83)	–	(−)
	18–30	6.6	(±3.30)	0.6	(±0.38)	6.4	(±3.21)	0.6	(±0.37)
2 (CS + HTC)	31–42	7.3	(±3.63)	1.6	(±0.84)	6.8	(±3.42)	1.5	(±0.79)
	43–63	7.8	(±3.95)	2.6	(±1.29)	7.7	(±3.87)	2.5	(±1.27)
	64–84	8.2	(±4.02)	3.5	(±1.72)	8.2	(±4.03)	3.5	(±1.73)
	85–92	5.8	(±2.92)	2.8	(±1.40)	6.9	(±3.45)	3.3	(±1.62)
	93–105	3.6	(±1.98)	1.5	(±0.85)	5.6	(±2.57)	2.3	(±1.12)

^{a}Calculated with the percentage of the COD of the HTC waste water on the total COD.

waste water, corresponding to 46% of total COD. Adding the HTC waste water, the COD continuously increased in the outflow of both reactors, reaching 7 g L⁻¹ in the AF and 8.3 g L⁻¹ in the AnMBBR. Meanwhile COD removal decreased from 96% to 81% in the AF, and from 97% to 78% in the AnMBBR, showing only slight differences between the reactors.

Biogas production and quality

Figure 2 illustrates the pH-values and the gas rates (in L biogas per L reactor volume and day) as a function of operating time. Figure 3 shows the methane rates (in L methane per L reactor volume and day) and the methane concentrations (y_{CH4}) of the AF and the AnMBBR during the two operational phases, while Figure 4 contains the methane yields as L CH_4 per g COD_{fed}.

Both systems were inoculated with active granular sludge and fed with CS during the first 17 days. During this period no clear start-up was observed as described in Michaud et al. (2005). On the contrary, the first phase (CS I) was characterised by high gas and methane rates as well as high methane concentrations and high methane yields in both systems due to the use of the active biomass.

During the second phase (CS + HTC) the gas rate (in L biogas per L reactor volume a day) rose constantly in both systems to a maximum average of 4.4 to 4.6 L L⁻¹ d⁻¹ until day 80. Withdrawing the OLR leads to decreasing of the gas rates. The AnMBBR showed slightly higher results throughout this period. Fettig et al. (2013) reached 0.06 L L⁻¹ d⁻¹ gas rate by treating HTC liquor from spent grains and 0.88 and 1.3 L L⁻¹ d⁻¹ by treating HTC liquor made of both sugar beet chips and food remains at mesophilic conditions. They diluted their HTC waste water with tap water. Wirth et al. (2015) operated a mesophilic and a thermophilic AF with undiluted HTC liquor made from municipal sewage sludge. At an OLR of 5 g L⁻¹ d⁻¹, they attained maximum gas rates of 0.678 and 1.162 L L⁻¹ d⁻¹, respectively. Blöhse

Table 3 | Average COD in the influent and the effluent, and COD removal efficiency (η_{COD}) in the AF and AnMBBR in different test phases

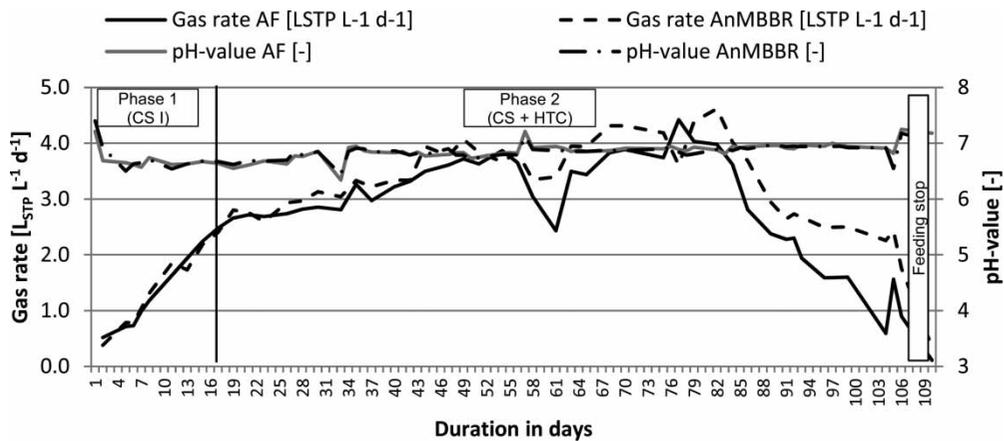| Phase	Duration [d]	Influent COD$_{fed}$ [mg L⁻¹]	Effluent AF COD$_{total}$ [mg L⁻¹]	Effluent AF ηCOD [%]	Effluent AnMBBR COD$_{total}$ [mg L⁻¹]	Effluent AnMBBR ηCOD [%]
1 (CS I)	1–17	12,321	435	96	311	97
	18–30	23,099	1,853	92	717	97
2 (CS + HTC)	31–42	24,383	2,580	90	1,837	93
	43–63	28,328	4,017	86	3,929	86
	64–84	32,025	6,198	81	6,151	81
	85–92	33,071	7,226	78	7,695	77
	93–105	37,100	7,015	81	8,322	78

Figure 2 │ Gas rates (in L biogas per L reactor volume and day) and pH-value of both AF and AnMBBR during the different operating phases.
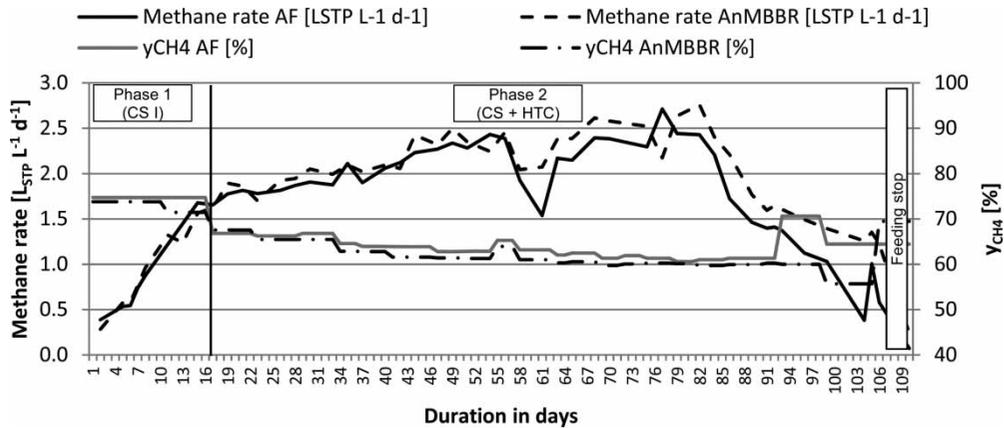

Figure 3 │ Methane rates (in L methane per L reactor volume and day) and methane concentrations (y$_{CH4}$) of both AF and AnMBBR during the different operating phases.
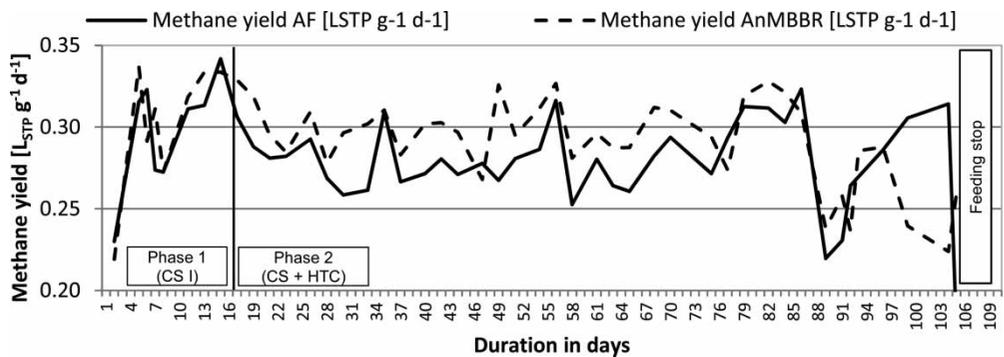

Figure 4 │ Methane yield (in L$_{STP}$ per g COD$_{fed}$ and day) of both AF and AnMBBR during the different operating phases. L$_{STP}$, liters at standard temperature and pressure.

(2013) treated HTC liquor from spent grains and used primary sewage sludge as a CS in a continuously stirred anaerobic digester with a volume of 100 L under mesophilic conditions. At a HRT of 40 d, a maximum gas rate of 0.6 L L^{-1} d^{-1} was achieved. With digested sewage sludge (HRT: 30 d) as a buffer, a maximum gas production of only 0.35 L L^{-1} d^{-1} was reached.

In accordance with the gas rate, the methane rate (in L CH$_4$ per L reactor volume and day) rose constantly to a maximum of 2.7 L L^{-1} d^{-1} in both systems during the

second phase. At this stage the OLR reached its maximum of nearly $8.5 \, \text{g L}^{-1} \, \text{d}^{-1}$ in each reactor. A methane rate of $0.05 \, \text{L L}^{-1} \, \text{d}^{-1}$ was reported by treating HTC liquor from spent grains, $0.61 \, \text{L L}^{-1} \, \text{d}^{-1}$ from sugar beet chips and $0.88 \, \text{L L}^{-1} \, \text{d}^{-1}$ from food remains, all diluted with tap water (Fettig *et al.* 2013). Wirth *et al.* (2015) obtained $0.513 \, \text{L L}^{-1} \, \text{d}^{-1}$ in a mesophilic AF and $0.809 \, \text{L L}^{-1} \, \text{d}^{-1}$ in a thermophilic AF at an OLR of $5 \, \text{g L}^{-1} \, \text{d}^{-1}$ while treating undiluted HTC liquor. Wirth & Mumme (2013) claimed methane rates of up to 0.45 and $0.25 \, \text{L L}^{-1} \, \text{d}^{-1}$ for a continuously stirred tank reactor (CSTR) and an AF. They treated undiluted HTC liquor from corn silage during a 42 d test period.

During the period of adding HTC waste water to the inflow, the methane yield (in L_{STP} (liters at standard temperature and pressure) per g COD_{fed} and day) ranged between 0.172 to $0.323 \, \text{L g}^{-1} \, \text{d}^{-1}$ in AF and 0.224 to $0.328 \, \text{L g}^{-1} \, \text{d}^{-1}$ in AnMBBR. The average methane yields were $0.278 \, \text{L g}^{-1} \, \text{d}^{-1}$ and $0.291 \, \text{L g}^{-1} \, \text{d}^{-1}$, respectively. Wirth & Mumme (2013) stated 0.163 to $0.236 \, \text{L g}^{-1} \, \text{d}^{-1}$ with their CSTR and 0.178 to $0.219 \, \text{L g}^{-1} \, \text{d}^{-1}$ in their AF. At the highest OLR, Wirth *et al.* (2015) gained $0.103 \, \text{L g}^{-1} \, \text{d}^{-1}$ in their mesophilic and $0.162 \, \text{L g}^{-1} \, \text{d}^{-1}$ in their thermophilic AF with a range of 0.103 to $0.178 \, \text{L g}^{-1} \, \text{d}^{-1}$ and 0.147 to $0.170 \, \text{L g}^{-1} \, \text{d}^{-1}$, respectively. Fettig *et al.* (2013) attained methane yields of 0.016, 0.177 and 0.241 while treating HTC liquor (diluted with tap water) from spent grains, sugar beet chips and food remains. In contrast, the methane yields as well as the gas and methane rates in this study were significantly higher and indicated a high biomass activity. This result was referred to the effect of the CS. According to our knowledge, there are no other laboratories that have done similar experiments with CSs. Therefore, it is not possible to compare our findings regarding the effectiveness of CS usage with other studies. As shown in Table 3, 96–97% of the CS was removed in the first 17 d. However, it is not certain whether the CS was further degraded with the same efficiency in the presence of the HTC waste water. The efficiency for degradation of the HTC waste water might be correspondingly lower. It should be emphasised that the benefits of a CS usage were not featured in the better degradation efficiency of the HTC liquor, but in the improved process stability and the higher methane yields.

Adding the HTC waste water in test phase 2 (CS + HTC) led to a constant drop of the methane concentrations in both systems (Figure 3). At day 18, y_{CH4} was at 74%vol in the AF and 73%vol in the AnMBBR. However, it dropped to 60% vol approximately (approx.) in both systems on day 92, which means a 17% reduction compared with phase 1 (CS I). Nonetheless, the quality of the produced biogas was

nearly equal in both reactors throughout this test phase. From day 85 the OLR was reduced in order to prevent inhibition (Figure 1). The biogas quality of the AnMBBR decreased further to a minimum of 58%vol of methane at the end of this phase, while in the AF, the methane content increased during the last days (d = 93–105) from a minimum of 61%vol to 67%vol. The observed biogas qualities corresponded to the values for methane concentrations from the digestion of excess sludge from municipal waste water treatment plants (60–70%vol CH_4) and the anaerobic treatment of organic highly polluted waste waters (50–85%vol CH_4) (DWA-M 363 2010). By treating HTC waste water from spent grains, sugar beet chips or food remains, methane yields of 76%vol, 70%vol and 67%vol were reported (Fettig *et al.* 2013). Wirth *et al.* (2015) stated a very stable methane concentration in both reactors throughout the experiments. The mesophilic reactor had 75%vol CH_4 approx., the thermophilic reactor 70%vol CH_4 approx. Wirth & Mumme (2013) obtained a range of 60–65%vol CH_4 by digesting HTC liquor from corn silage. Ramke *et al.* (2010) achieved a range from 47–57%vol CH_4 by treating sewage sludge HTC waste water in mesophilic batch tests. Therefore, this experiment showed an average biogas quality despite the slight decrease of the methane production.

The study confirmed an almost complete recovery rate of the eliminated carbon in the produced biogas for the first time. Apparently, neither a considerable loss of produced biogas in the receiver, recirculation and storage tanks nor a formation of solid carbon inside the reactor occurred, because the carbon mass balance was met by accounting for COD removed and methane produced. Fettig *et al.* (2013) attained only a 50% transformation efficiency of the carbon supplied to the reactors to the produced biogas by feeding HTC waste water made from spent grains, while 30–50% was attained when using sugar beet chips and 20–80% when using food remains. The use of the CS may be the key factor for this difference.

Process stability

Figures 5 and 6 illustrate the concentrations of TAC and VOAs and the Ripley ratio (VOA/TAC ratio), of the AF and the AnMBBR.

Phase 1 (CS I) was characterized by a slow increase of alkalinity and moderate levels of organic acids compared with the findings of Mulder (2003). The average Ripley ratio reached 0.1 in both systems.

During phase 2 (CS + HTC), the portion of HTC liquor in the inflow was increased. During this time, alkalinity
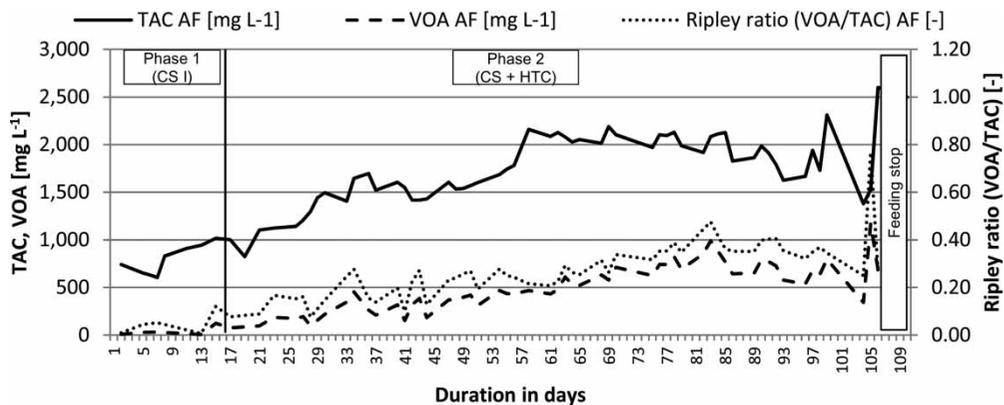
Figure 5 │ Concentration of total alkaline carbonate (TAC), volatile organic acids (VOAs) and the Ripley ratio (VOA/TAC ratio) in the AF.

varied between 2,000 and 2,500 mg L^{-1} in both systems. This concentration is more than double that in phase 1 (CS I), thus providing the evidence that the alkaline carbonate primarily originated from the HTC liquor. It is suspected that the mineral components of the HTC input substrate (wood chips) were the main source of the alkalinity.

Between days 43 and 84 of the experiment, the OLR was kept at a constant level in both systems, whilst the portion of the HTC liquor in the inflow was changed (Figure 1). This caused a continuous increase of VOA in both systems (Figures 5 and 6). During this period, the VOA in the AF grew from 400 to 730 mg L^{-1} and in the AnMBBR from 440 to 700 mg L^{-1}. At day 85 it reached its peak of 1,000 mg L^{-1} approx. in the AF and 700 mg L^{-1} in the AnMBBR. Although USEPA (2002) claimed that VOA should be less than 250 mg L^{-1} in an anaerobic waste water treatment reactor, Thormeyer (2009) affirmed that, at an acid concentration of >300 mg L^{-1}, increased attention has to be paid. Due to the high alkalinity level, the resulting Ripley ratio was 0.45 in the AF, and 0.35 in the AnMBBR,

which was relatively lower than expected. A Ripley ratio of 0.4 to 0.5 indicates a heavily loaded system, while a ratio of 0.3 to 0.4 indicates a system at full capacity (Lossie & Puetz 2008). Continuing the experiment with the maximum OLR may have led to a disruption of the biocenosis of both systems. The same conclusion was reached by treating HTC liquor resulting from spent grain and food remains (Fettig *et al.* 2013). They claimed a maximum concentration of VOA of 1,000 mg L^{-1} approx. at a maximum OLR of 7 g L^{-1} d^{-1} and found that, by lowering the OLR, the VOA increased further and eventually decreased slightly after a period of 4 weeks.

Constantly reducing the OLR from day 85 led to a slow decrease of the VOA in the AF, while in the AnMBBR, an increase to 1,000 mg L^{-1} was observed until day 104. On day 105 the VOA rose dramatically to 1,170 mg L^{-1} in the AF and 2,250 mg L^{-1} in the AnMBBR. During this time, the OLR was lowered to 3.6 g L^{-1} d^{-1} in the AF and 5.6 g L^{-1} d^{-1} in the AnMBBR. This leads to the presumption that an inhibition caused by organic acids had occurred.
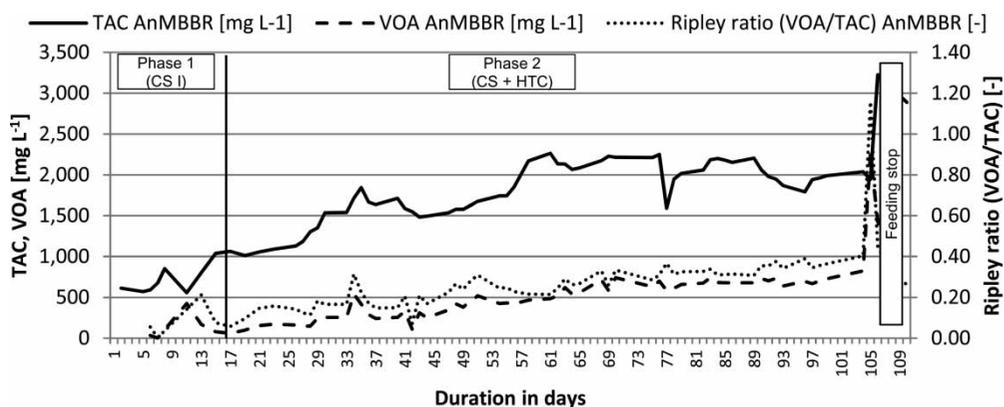

Figure 6 │ Concentrations of total alkaline carbonate (TAC), volatile organic acids (VOAs) and the Ripley ratio (VOA/TAC ratio) in the AnMBBR.

According to Deublein & Steinhauser (2008) and Chen *et al.* (2007), the inhibition caused by acetic acid starts at 1,000 mg L^{-1} and a pH-value of 7, by iso-butyric and iso-valeric acid at 50 mg L^{-1} at pH < 7, and by propionic acid at 700 mg L^{-1} at pH = 7 and 5 mg L^{-1} at pH < 7. Furthermore, the accumulation of VOA generally results in a drop of the pH-value, intensifying the inhibition (Deublein & Steinhauser 2008; Hinken *et al.* 2015). However, a drop of the pH-value was not observed at any time during phase 2 (CS + HTC). The increase of VOA concentration was possibly the result of this inhibition. The inhibition might have affected the acetogenic phase, which prevented a complete degradation of the substrate towards methane. An inhibition of the methanogenic bacteria has also to be considered. Nevertheless, after reducing the OLR from day 85, the AF reached a better recovery than the AnMBBR, as suggested by the better recovery of the η_{COD} (compare Table 3) and biogas quality (compare Figure 3). An inhibition caused by ammonia can be excluded because of the low nitrogen content and a neutral pH-value of the raw water (Table 1). Oliveira *et al.* (2013) detected high loads of phenolic compounds and furfural derivatives in the HTC liquor made of forest wood chips, which was the main component of the input substrates for the HTC liquor used in this study. Reza *et al.* (2014) assumed that these organic compounds inhibited the anaerobic processes.

Technical reactor performance problems

While feeding HTC waste water to the systems, a constant black fallout was monitored in the receiving tanks as well as in the tubing of both systems. Funke & Ziegler (2010) reported an ongoing condensation, polymerisation and precipitation of solid particles in the HTC liquor. The fallout resulted in clogging of tubing and pumps in both reactor systems. Samples of the fallout were collected and analysed for VSS. Almost 75% of the residues were inorganic matter. This leads to the conclusion that the fallout may consist of biochar which is formed from the HTC waste water. With regard to a full-scale waste water treatment plant, it is necessary to ensure cleaning installations in pipelines and other facilities in order to prevent operational problems.

CONCLUSIONS

This study proves the feasibility of the treatment of HTC liquor in combination with a CS. A better and more stable reactor performance than a treatment using mono-substrates only can be achieved. Furthermore, no significant differences between the performance of an AF and an AnMBBR were observed. The reason for the accumulation of VOA might be the presence of phenolic compounds and furfural derivatives, which are a product of the HTC of wood chips. An appropriate pre-treatment of the HTC waste water should be considered in order to obtain a more stable process. Therefore, further research should be focused on the use of a CS to stabilise and improve the anaerobic digestion of HTC process waters.

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