Research Article

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Anaerobic digestion of wastewater from the production of bleached chemical thermo-mechanical pulp – higher methane production for hardwood than softwood

Madeleine Larsson,[a] Xu-Bin Truong,[b] Annika Björn,[a*] Jörgen Ejlertsson,[a,b] Bo H Svensson,[a] David Bastviken[a] and Anna Karlsson[b]

ABSTRACT

BACKGROUND: Chemical thermo-mechanical pulp (CTMP) mills holds a large biomethane potential in their wastewater. Their broadened market has involved increased bleaching and utilization of different raw materials. Therefore, the main aim of this study was to obtain and maintain a well-functioning anaerobic digestion (AD) process, with a high methane yield and total organic carbon (TOC) reduction, when digesting CTMP wastewater, from different production protocols including shifts in raw material and bleaching. A lab-scale upflow anaerobic sludge bed (UASB) reactor was used for the tests.

RESULTS: The variations in raw material (spruce, birch and aspen) and consequently in TOC-loading (3.6–6.6 kg TOC m^{-3} and day^{-1}) did not affect the UASB process negatively. Methane production values from 360 to 500 NmL g^{-1} TOC were obtained, with the highest yield for wastewater from the production of birch- followed by aspen- and spruce pulp. The acetic acid and filtered-TOC (fTOC) reduction ranged from 90 to 95% and 61 to 73%, respectively.

CONCLUSIONS: A well-functioning process maintained during shifts in raw material for pulp production which shows that AD is feasible for CTMP mills with a diversified product portfolio. Furthermore, the increased use of hardwood and bleaching will most likely increase their potential as a biomethane producer.

Supporting information may be found in the online version of this article.

Keywords: biogas; wastewater treatment; UASB; CTMP; softwood; hardwood

INTRODUCTION

The pulp and paper industry is an important industrial sector in Sweden, contributing 25% of the paper pulp consumption in Europe,[1] and it generates large amounts of wastewater rich in organic material that in many cases can be used for methane production via anaerobic digestion (AD).[2–4] Wastewaters of interest are methanol-rich condensate and alkaline bleaching effluents from kraft mills together with bleaching and composite streams from thermo-mechanical pulp- (TMP) and chemical thermo-mechanical pulp (CTMP) mills.[3] In contrast to mills only producing pulp for printing paper, the production of CTMP is increasing worldwide due to its use in hygiene products, liquid packaging, magazine paper, etc.[5] This increasing market has led to a more diversified CTMP-production including the use of different wood raw materials as well as different levels of bleaching. During 2013 approx. 900 000 tonnes of CTMP were produced in Sweden and further capacity expansions are planned for several of the mills during the coming years. Sivard and Ericsson estimated the potential biogas production from a typical CTMP mill, producing bleached spruce pulp, at 0.13 MWh per tonne produced pulp, which corresponds to a yearly potential of 115 GWh from Swedish CTMP production.[6] The implementation of an AD process as a complement to the present aerobic wastewater treatment at a mill would not only generate methane, but also reduce the mill's energy demand for aeration and sludge destruction due to lower production of waste activated sludge as well as a decrease in the need for nutrient additions.[3,7] According to information from pulp and paper producers taking part in the current study the wastewater treatment capacity in several Swedish pulp and paper mills limits the possibility to increase or change the production due to environmental constraints and space. The introduction of AD would partly solve these problems.

* *Correspondence to: A Björn, Dept of Thematic Studies, Environmental Change, Linköping University, 581 83 Linköping, Sweden. Email: annika.bjorn@liu.se*

a *Dept of Thematic Studies, Environmental Change, Linköping University, 581 83, Linköping, Sweden*

b *Scandinavian Biogas Fuels AB, Holländargatan 21A, 111 60 Stockholm, Sweden*

Table 1. Earlier studies on high-rate, continuous anaerobic digestion of CTMP wastewater. Note that the units presented for OLR, COD reduction and gas production may differ between studies as indicated by footnotes

Type of wastewater	Pulp production	Type of reactor	HRT (h)	OLR (kg COD m^{-3} day^{-1})	COD reduction (%)	Methane production (NmL g COD_{red}^{-1})	Reference
CTMP effluent	Bleached spruce	Lab-scale methanogenic upflow hybrid reactor	16–24	10–15	40/~50[a]	~300	Welander[9]
CTMP effluent	Bleached aspen	Pilot-scale anaerobic fixed film reactor	12–16	20	60	~300	Pichon *et al.*[11]
″	Bleached spruce	″	48–72	3	60	~200	
CTMP effluent	Bleached spruce	Pilot-scale upflow blanket filter reactor	2 days	4.7	45	~100	Pichon *et al.*[12]
CTMP effluent (Lielahti)	n.a.	Pilot-scale UASB	13	~14	41/57[a]	180[b]	Habets and de Vegt[10]
Shifts between CTMP- and TMP effluent (Quensel)	n.a.	″	n.a.	9 (TMP) – 18.5 (CTMP)	45	n.a.	
CTMP 'normal conditions'	unbleached		5.1	43/22[c]	38/38[a]	84/160[d]	Richardson *et al.*[13]
TMP	unbleached			23/14[c]	29/41[a]	160/210[d]	
CTMP 'high dissolution of fines'	unbleached			64/32[c]	23/34[a]	48/77[d]	

[a] Total COD reduction/soluble COD reduction
[b] Biogas production
[c] Total COD/soluble COD
[d] Methane production per total COD_{IN}/methane production per soluble COD_{IN}. Recalculated from data given by Richardson *et al.*[11]

Earlier research on continuous high-rate AD of CTMP wastewaters was mainly performed in the late 1980s/early 1990s (Table 1), when softwood (SW) was the dominating raw material (>90%).[8] Thus, when no specification of the raw material used for CTMP production is given in studies from this time period, which are reviewed below, the use of SW can be assumed. One of the main challenges identified at that time was the residual hydrogen peroxide (H_2O_2) present in the wastewaters when producing bleached CTMP.[9,10] In addition, the presence of complexing agents (e.g. DTPA), resin acids and high sulphur concentration were identified as possible challenges, when implementing AD at CTMP mills.[9,10] Welander developed a lab-scale anaerobic/aerobic wastewater treatment concept for a composite wastewater of a Swedish CTMP mill producing bleached spruce pulp.[9] The anaerobic part of the lab-scale wastewater treatment system included a peroxide removal step (biocatalytic decomposition), an acidogenic step including the addition of $AlCl_3$, $FeCl_2$ and $CaCl_2$ for detoxification (presumably precipitating resin acids and long chain fatty acids, LCFA) followed by a settler and finally a methanogenic upflow hybrid reactor. The setup resulted in a total COD (chemical oxygen demand) reduction of around 40% (~50% reduction of soluble COD; for details see Table 1). Pichon *et al.* reported COD reductions of 60% for both bleached aspen and bleached spruce CTMP wastewaters in a pilot-scale anaerobic fixed film reactor.[11] For aspen an organic loading rate (OLR) of 20 kg COD m^{-3} day^{-1} (hydraulic retention time (HRT)=12–16 h) was applied successfully, while only 3 kg COD m^{-3} day^{-1} (HRT=48–72 h) was manageable for spruce. The methane production was also lower for spruce than aspen (Table 1). The reason for the lower maximum OLR for spruce was according to the authors the higher sulphur content in this wastewater from the initial impregnation of the wood chips, which was not performed for aspen. It is stated that problems arose when the sulphur content was above 400 mg L^{-1}, however, the authors do not mention if sulphur was present in the aspen wastewater. Pichon *et al.* further investigated the impact of sulphur on AD.[12] In this case, a wastewater from a bleached SW CTMP process was applied at an OLR ~3 kg COD m^{-3} day^{-1} and HRT of 3 days in two pilot-scale anaerobic filter reactors. The experiment showed that the COD reduction dropped when COD $sulphur^{-1}$ was below 15 mg mg^{-1}. Further studies on the same wastewater, but with a fixed COD $sulphur^{-1}$ at 12 mg mg^{-1}, in an upflow blanket filter reactor, showed a COD reduction of 45%, which is comparable with Welander[9] (Table 1) but with a considerably lower methane production (Table 1).

Habets and de Vegt presented results from pilot-scale UASB (upflow anaerobic sludge bed) studies, which led to full-scale implementations at CTMP mills.[10] In the first case (Lielahti) a stable process performance with a total COD reduction of 41% (soluble COD reduction of 57%) and a specific biogas production of 0.18 m^3 kg COD^{-1} were obtained at an average OLR of 14 kg COD m^{-3} day^{-1} and HRT of 13 h (Table 1). Attempts to increase the OLR resulted in lowered COD reduction, which was suggested to be a result of inhibition by wood extractives. In the second case (Quensel) shifts between TMP and CTMP production were addressed, which meant changes in both wastewater composition and COD concentration. The pilot-scale UASB successfully maintained a COD reduction of 45% at OLRs between 9 and 18.5 kg COD m^{-3} day^{-1} provided that a flotation was performed prior to AD, removing fines rich in resin acids. In both studies the residual H_2O_2 was removed in a pre-acidification tank and the COD to sulphur ratio was

above the levels which according to Pichon *et al.*[12] had a negative impact on the AD process (see above). Richardson *et al.* also studied the effects of shifts in wastewater from CTMP ('normal conditions') to TMP and back to CTMP ('high dissolution of fines'), in a lab-scale reactor and with wastewater from the production of unbleached pulp.[13] With a HRT of 5.1 h the shifts resulted in OLRs of 43, 23 and 64 kg COD m^{-3} day^{-1}, respectively (Table 1). The authors conclude that the AD process handled the shifts in wastewater characteristics and OLR well, however, with a lower COD reduction as well as methane production when the CTMP wastewater included a higher concentration of fines (for details see Table 1). The total COD reduction was 38, 29 and 23% (soluble COD reduction of 38, 41 and 34%) which is the lowest COD reduction reported among the studies referred to above and the only study on wastewater from the production of unbleached CTMP (Table 1). However, the OLR is higher and the HRT lower than the other studies (Table 1).

The above studies report soluble COD reductions of 30–60% (Table 1). This broad span is probably related to factors such as the wood raw material used, presence and amounts of different process chemicals, OLR, HRT, sub-optimal AD due to lack of nutrients, etc. It should be noted that the main focus of the above studies was to obtain an optimal wastewater treatment, while the potential for production of methane as an energy carrier was given less attention. This is most likely a consequence of the timing of these studies. Since then an increasing interest in renewable energy carriers has evolved, which to a greater extent has put emphasis on the possible methane production from pulp and paper mill wastewaters. Furthermore, CTMP production has developed towards more diversified product portfolios including several types of wood raw materials combined with different levels of bleaching, which has resulted in more complex wastewater characteristics depending on the production campaigns. Wastewater from production of SW pulp generally has a higher lignin content than that from hardwood (HW) pulp.[14] Also the hemicellulose composition differs between SW and HW,[14] which in turn may impact the carbohydrate composition and the acetic acid content in the wastewaters. The production of bleached pulp, compared with unbleached, will increase the amount of acetic acid in the wastewater as well as its total organic material content.[15] Habets and de Vegt also stated that the sulphur content in the wastewaters is directly linked to the raw material used and the production protocol applied.[10] Thus, today with the increased shifts in production there are a number of factors that need to be considered for optimal establishment of the AD process at CTMP mills. Therefore, there is a need for further research on the impact on AD of different raw materials used in pulp production as well as the impact of shifts between the production of bleached and unbleached pulp.

The aim of this study was, therefore, to investigate the possibilities to obtain and maintain a well-functioning AD process when digesting CTMP wastewater from different production protocols including shifts in raw material and bleaching. A well-functioning process is here defined by a high reduction of volatile fatty acids (VFA; ≥90%) combined with an effluent pH above 7. The methane yield and total organic carbon (TOC) reduction will depend on the substrate and, thus, likely vary with the shifts. This included experiments with substrate shifts between: (1) bleached- and unbleached spruce wastewater; and (2) bleached aspen-, bleached birch- and bleached spruce wastewater digested in a lab-scale UASB reactor. The reactor experiment was set up with the ambition to be as realistic as possible, i.e. keeping the HRT around 14 h, which corresponds to a full-scale reactor of approx. 1 300 m^3.

MATERIAL AND METHODS

The CTMP wastewater

The wastewater chosen was a composite pulping and bleaching CTMP wastewater from a Swedish mill applying peroxide bleaching (H_2O_2 in the presence of DTPA; B7 in Ekstrand *et al.*[3]). This waste stream constitutes 55–60 vol% of the total effluent at the mill and normally contains more than 60% of the organic material content in the total effluent (information from personnel at the mill). The remaining part of the mill's total effluent has a higher content of resin coated fibres (information from personnel at the mill) and has a lower methane potential (B9 in Ekstrand *et al.*[3]), thus, by excluding this part a higher methane production per reactor volume will be obtained. The normal temperature of this wastewater stream is ~80°C, thus it was cooled to suit our experiments, which were carried out under mesophilic conditions.

Experimental setup and sampling of wastewater

A 4 L UASB reactor with a fluidized granular bed volume of 1–2 L, was operated at 35°C for 255 days. For details regarding the reactor setup, see Larsson *et al.*[16] Granules from a pilot-scale UASB reactor treating clarified sewage wastewater were used as inoculum. The reactor was started with 1 L of granules (day 0) and then restarted on day 164 with 2 L of granules, hence, the UASB operation was divided into experiment I (days 1–155) and experiment II (days 164–255). An overview of the reactor operations regarding the included wastewaters and OLRs is given in Table 2. During the initial 50 days of experiment I, an internal circulation (IC), pumping reactor liquid in a loop, was applied to increase turbulence in the reactor. Mechanical problems with the liquid recirculation forced a replacement with gas IC on day 68, together with an extra addition of granules (approx. 1 L). The gas produced in the AD process was used for the IC and this system was applied until day 103. No IC was applied during experiment II.

1 m^3 samples of wastewater from the composite pulping and bleaching effluent were collected on six occasions and transported (1–2 days) to our laboratory. On arrival they were left for about a day allowing for fibrous materials to settle and 100 L of the settled material/liquid was subsequently removed by a tap at the bottom of the tank. A stirrer was then mounted to the container and the remaining wastewater (approx. 900 L) was stirred vigorously for 30 min before pouring into 10 L plastic containers during continuous stirring. The 10 L subsamples were stored at +4°C for at most 3 months before being used as substrate for the UASB reactor. The six batches of wastewater covered four types of pulp regularly produced at the CTMP mill: unbleached spruce (US.1), bleached spruce (sampled three times, BS.1-3), bleached aspen (BA.1) and bleached birch (BB.1). A malfunctioning filter at the mill led to higher concentrations of suspended solids (SS), i.e. 300–4000 mg L^{-1} compared with the normal 20–500 mg L^{-1} (information from personnel at the mill). Therefore, an extra filtration step (pore size 70 μm) was introduced before the substrates were pumped into the reactor resulting in 180–490 mg L^{-1} of SS (Table 3). The wastewaters were analysed for total and filtered COD and TOC (analyses of filtered samples are denoted fCOD and fTOC), SS, total organic acids (TOA), VFA and pH once a week to monitor possible changes during storage (Table 3). All six batches of wastewater were analyzed for macro- and micronutrient contents (Table 4

Table 2. Overview of the reactor study. The CTMP wastewaters (ww) used were unbleached spruce (US.1), bleached spruce (BS.1-3, sampled three times), bleached aspen (BA.1) and bleached birch (BB.1). Periods with diluted bleached aspen and bleached birch are denoted BA.1d and BB.1d, respectively. When a new batch of wastewater was introduced a mixture of two batches/types of wastewater was pumped into the reactor for a couple of days and the organic loading rate, thus, changed gradually (apart from the shifts between BS.3 and BB.1d from day 228 and onwards as the substrate tank was here emptied in connection with the shifts). The periods presented below have an ingoing wastewater with ≥95 vol% of the specified wastewater. Day 1–20 and 164–171 are considered start-up periods

Experiment	Days	ww	Organic loading rate (kg TOC m^{-3} day^{-1})
I	1–20	BS.1 – start-up	4.5 ± 1.0
	21–45	BS.1	5.0 ± 0.3
	51–88	US.1	3.5 ± 0.1
	95–137	BS.2.	5.4 ± 0.1
	140–155	BA.1	7.4 ± 0.4
II	164–171	BA.1d (diluted, 50–85% wastewater) – start-up	4.1 ± 0.6
	172–187	BA.1	6.6 ± 0.4
	191–198	BA.1d (diluted, 50–60% wastewater)	3.8 ± 0.3
	202–223	BB.1d (diluted, 50% wastewater)	4.4 ± 0.4
	228–242	BS.3	3.8 ± 0.1
	243–246	BB.1d (diluted, 50% wastewater)	4.1 ± 0.0
	247–250	BS.3	3.6 ± 0.0
	251–255	BB.1d (diluted, 50% wastewater)	3.9 ± 0.1

and Table S1, Supplementary material) by Eurofins Environment Sweden AB.

Throughout the 255 days of reactor operation the HRT was maintained at 14±2 h, while the OLR was 3.4–7.4 kg TOC m^{-3} day^{-1} (Table 2). During experiment I, the reactor was fed with wastewater from the production of bleached spruce- (BS.1-2), unbleached spruce- (US.1) and finally bleached aspen pulp (BA.1). While wastewater from the production of bleached aspen- (BA.1), bleached birch- (BB.1) and bleached spruce pulp (BS.3) were the substrates during experiment II. The substrates used during experiment I were always undiluted, while BA.1 used at the start-up of experiment II, was diluted with tap water (days 164–171; 50–85% vol. of wastewater) to adapt the granules to the wastewater. Undiluted BA.1 was thereafter fed for 19 days (days 172–190), before the substrate was diluted again (50/50 by volume; days 191–198) as a means to abate foaming (see details in the results section). BB.1 was diluted for the same reason (50/50 by volume; days 202–223, 243–246 and 251–255). Periods with diluted wastewater are denoted BA.1d and BB.1d (Table 2). During the last 22 days of reactor operation, shifts between BS.3 and BB.1d were performed during shorter periods, i.e. 4–5 days with each substrate corresponding to 7–9 HRTs to simulate conditions at the CTMP mill.

Due to the low nutrient content of the wastewaters (Table 4), macro- ($(NH_2)_2CO$ and Na_2HPO_4) and micronutrients ($CoCl_2$, $CuCl_2$, $ZnCl_2$, $NiCl_2$, $(NH_4)_6Mo_7O_{24}$, Na_2SeO_3 and Na_2WO_4) were added to the substrate throughout the experiment to secure biomass growth, a well-functioning fluidized bed and an efficient AD (cf. Larsson *et al.*[16]). N and P were added at a ratio of COD:N:P 350:5:1. Micronutrients corresponding to 48×10^{-6} μmol mg COD^{-1} were pumped into the reactor in pulses 2 days per week. Until day 99, Fe was added separately prior to each set of micronutrient pulses using the same pump as for the micronutrients (Fe^{3+} in HCl; 48×10^{-5} μmol mg COD^{-1}). During days 99–105, the Fe additions were doubled, and from day 179 and onwards, Fe was added continuously at a rate of 48×10^{-4} μmol mg COD^{-1}. From day 173 and onwards $MnSO_4$ was added to the micronutrient-solution in the same concentration as the other metals. The dosage of micronutrients was increased by 20% from day 208 and onwards when BB.1d was fed to the reactor, to avoid a potential nutrient deficiency linked to the high load of degradable TOC in this wastewater.

Evaluation of reactor performance

The performance of the UASB reactor was evaluated by analyzing the biogas production continuously and its methane content together with the composition of the reactor effluent in terms of fCOD, fTOC, TOA, VFA, pH and SS three times a week. Data is missing for days 17, 61, 121–122 and 155 (experiment I) and for days 180 and 188–190 (experiment II) due to technical problems. The macro- and micronutrient contents of the granular sludge were analyzed on three occasions: at the start-up and on days 155 and 255 and the same set of analyses was performed on nine samples of reactor effluent (data not shown except for tot-S, which is presented in Table S6). Prior to analysis the granular sludge samples were sieved (pore size 2 mm) to remove the wastewater and then homogenized with a kitchen blender for 30 s. The reactor performance and wastewater characteristics are mainly presented in relation to TOC and fTOC. To enable comparisons with other studies the results are also given in relation to COD and fCOD (see the supporting information for detailed results) when necessary.

Analytical procedure

The gas production was monitored on-line by means of gas meters based on the principle of water displacement (MGC-1 V3.0 PMMA; Ritter, Germany) and the methane content of the biogas was determined three times a week by gas chromatography according to Karlsson *et al.*[17] The biogas composition (% of CH_4, CO_2, O_2 and ppm H_2S) was evaluated twice a week by collecting gas produced over 24 h and analyzing it with a Biogas Check Analyzer (Geotechnical Instruments, UK). All gas volumes are given at standard temperature and pressure (STP; 273 K and 1 atm; unit: NmL, N 'normal'). The methane production presented is based on the results from the gas chromatography, whereas the H_2S results come from the Biogas Check Analyzer.

COD, TOC and TOA were measured spectrophotometrically using kits from Hach Lange, Germany (LCK014; LCK387; LCK365) according to the manufacturer's instructions. Before analysis of fCOD and fTOC the samples were passed through a 1.6 μm MGA filter (Munktell, Sweden). For analysis of TOA the samples were centrifuged in 50 mL tubes for 11 min (RCF=10 016 g; Sorvall Biofuge Prime centrifuge with rotor #7588, Thermo Scientific, Germany) and the reject was then filtered (General Purpose Filter, grade 1002 and size 125 mm; Munktell, Sweden). To compensate for the background absorption of the samples, when analyzing TOA, blank samples were prepared by replacing the reagent solutions added after digestion with MilliQ water, all other additions alike. VFA are

Table 3. Characteristics for the six batches of CTMP wastewater as applied to the UASB reactor; unbleached spruce (US.1), bleached spruce (BS.1-3, sampled three times), bleached aspen (BA.1) and bleached birch (BB.1). Analysis made on filtered samples are denoted fTOC. Data presented are mean values ± standard deviation

	Unit	US.1	BS.1	BS.2	BS.3	BA.1	BB.1
TOC	mg L^{-1}	1 950 ± 40	2 760 ± 20	3 010 ± 30	2 280 ± 10	4 090 ± 70	5 050 ± 90
fTOC	mg L^{-1}	1 750 ± 40	2 590 ± 50	2 840 ± 60	2 120 ± 30	3 790 ± 60	4 580 ± 110
COD TOC^{-1}	-	2.9 ± 0.1	3.0 ± 0.1	2.9 ± 0.1	2.9 ± 0.0	3.1 ± 0.1	3.0 ± 0.1
Total organic acids[1]	mmol L^{-1}	19 ± 0.2	34 ± 0.2	35 ± 0.6	27 ± 1.0	66 ± 1.2	79 ± 2.7
Acetic acid[2]	mmol L^{-1}	13 ± 0.9	24 ± 0.3	27 ± 1.1	22 ± 0.4	57 ± 2.9	68 ± 3.6
Suspended solids	mg L^{-1}	200 ± 30	280 ± 20	220 ± 10	180 ± 20	260 ± 80	490 ± 120
pH	-	5.3 ± 0.0	7.2 ± 0.1	6.9 ± 0.1	7.3 ± 0.1	6.5 ± 0.0	6.1 ± 0.0

[a] Quantified with analytical kit from Hach Lange.
[b] Quantified with gas chromatography.

Table 4. Concentrations of macro- and micronutrients (mg g^{-1} TOC) in six batches of CTMP wastewater used in the reactor study; unbleached spruce (US.1), bleached spruce (BS.1-3, sampled three times), bleached aspen (BA.1) and bleached birch (BB.1). Concentration and measurement errors reported are given by Eurofins Environment Sweden AB. Additional results (BOD, As, Sb, Ba, Pb, B, Cd, Cr, Hg, Ag, Ti and V) are presented as supporting information (Table S1)

	US.1	BS.1	BS.2	BS.3	BA.1	BB.1	Error in measurement (±%)
Kjeldahl-N	-	9.0	-	8.8	5.6	8.5	5
N	8.6	8.0	-	9.3	5.8	8.1	10
NH_4^+-N	-	0.054	-	0.13	0.25	0.091	15
P	-	0.83	-	0.38	0.24	1.6	10
S	120	96	97	110	65	44	20
Cl^-	11	12	9.0	4.4	6.0	32	15
Na	340	520	470	530	480	420	20
K	10	7.2	7.4	7.9	12	11	20
Ca	13	11	12	14	12	6.7	15
Fe	0.19	0.079	0.067	0.10	0.041	0.071	20
Mg	2.0	1.6	1.6	1.8	2.5	2.6	20
Mn	3.0	1.9	1.9	1.9	0.23	1.9	20
Al	0.15	0.048	0.057	0.039	0.028	0.053	15
Co	0.00076	0.00092	0.00037	0.00053	0.0010	0.0014	25
Cu	0.025	0.018	0.021	0.017	0.015	0.017	20
Mo	<0.00051	<0.00090	0.00047	<0.00044	0.00055	0.00030	40
Ni	0.0022	0.0017	0.0014	0.0015	0.00072	0.0011	15
Se	<0.0015	<0.0027	<0.0010	<0.0013	<0.00072	<0.00059	35
W	<0.00051	<0.00036	<0.00033	<0.00044	<0.00024	<0.00020	20
Zn	0.31	0.18	0.19	0.20	0.17	0.42	20

included in the quantification of TOA, but in addition eight specific VFAs (acetate, propionate, butyrate, iso-butyrate, valeriate, iso-valeriate, capronate and iso-capronate) were analyzed according to Jonsson and Borén[18] with a detection limit of 0.2 mmol L^{-1} and a quantification limit of 0.6 mmol L^{-1}. pH was measured using a pH electrode (InoLab pH 7310, WTW, Germany) and SS were analyzed in triplicate according to Swedish standard (SS-EN 872:2005; MGA, pore size 1.6 µm; Munktell, Sweden). For the analysis of SS the standard deviation (SD) was 5% at the most.

Statistical analysis

Due to the technical difficulties during experiment I, regarding the IC recirculating liquid (days 1–50) and gas (days 68–103), as well as the need for the addition of granules by day 68, it is difficult to evaluate the process performance based on the wastewaters that were fed to the reactor during this experiment. Consequently, no statistical comparison is made for the process performance with wastewater from unbleached spruce (US.1) and bleached spruce (BS.1-2).

To evaluate the effect of raw material on the AD process, biogas production, methane production and reductions of fTOC, TOA and acetic acid from periods with bleached aspen (BA.1), bleached birch (BB.1) and bleached spruce (BS.3; experiment II) were compared by performing a one-way ANOVA (analysis of variance) with a significance level of 5% (IBM SPSS Statistics 23). When significant differences were found, pairwise comparisons using Tukey's HSD test (significance level of 5%) were performed. The start-up period (days 164–171) was not included in the statistical evaluation and BA.1 and BA.1d were considered as two different wastewaters. For BA.1d, days 191–192 were also excluded as the AD process was highly affected by the technical problems days 188–190. When a wastewater was used for more than one period (BB.1d and BS.3) an average based on all periods was calculated and used for the statistical evaluation.

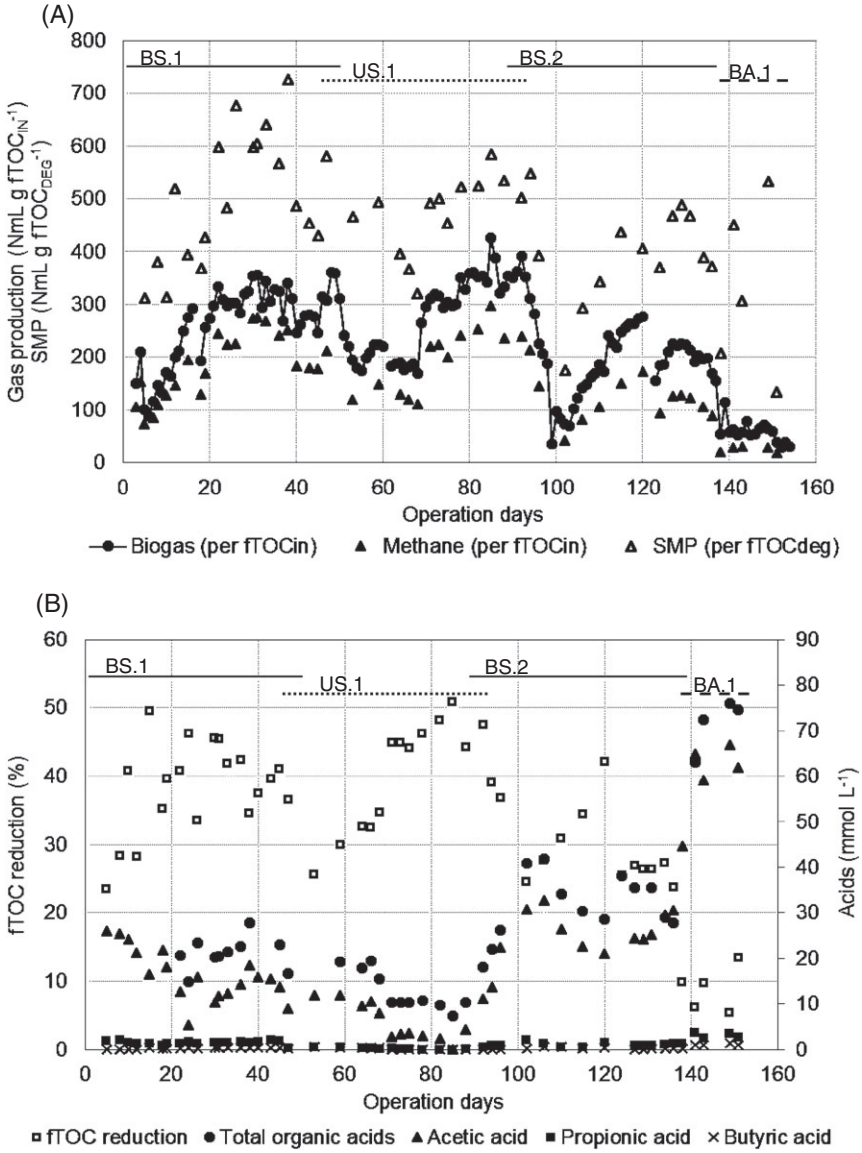

Figure 1. (A)–(B) Process performance for the UASB reactor during experiment I with (A) gas production (NmL g^{-1} fTOC$_{IN}$) and specific methane production (SMP; NmL g^{-1} fTOC$_{DEG}$) and (B) fTOC reduction (%) and total organic acids and volatile fatty acids in the reactor effluent (mmol L^{-1}). Days 1–20 are considered the start-up period. The missing data for days 17, 61, 121–122 and 155 are due to technical problems. Corresponding figures in relation to fCOD are presented as Supporting information (Fig. S1(A) and (B)).

RESULTS

The results from the reactor operations are presented in Figures 1, 2 and S1, S2 and Tables 5, 6 and S3. When referring to data presented in Tables 2, 3 and 6 only mean values are given in the text, whereas the SD are provided in the tables.

Reactor performance

Experiment I

The reactor operation during experiment I was strongly influenced by technical difficulties related to the IC, which first recirculated reactor liquid (days 1–50) and later on the produced biogas (days 68–103). The process was initially fed with wastewater from bleached spruce (BS.1) and the first 20 days of reactor operation was considered as start-up period and showed a continuous increase in process performance (i.e. increased biogas production and reduction of fTOC and acetic acid; Fig. 1(A) and (B)). However, the mechanical problems with the liquid IC resulted in granules being exposed to strong sheer forces, which in turn led to wash-out of active biomass. The malfunctioning IC also led to accumulation of SS (fibre residues) in the granular bed. The loss in granules as well as a need for increased upflow velocity led to the addition of granules together with the installation of the gas IC (initiated day 68; see Materials and methods for details). This measure gave a direct improvement of the process performance with increased gas production as well as reduction of fTOC, TOA and acetic acid (Fig. 1(A) and (B)).

The period with BS.1 as substrate (days 21–45, Table 2) showed a fluctuating biogas production of around 300 NmL g^{-1} fTOC$_{IN}$ (Fig. 1(A)) and the reductions obtained of fTOC, TOA and acetic acid were in all cases ~40% (Fig. 1(B)). From day 46 the ingoing wastewater was gradually changed to unbleached spruce (US.1) resulting in a decrease in OLR from 5.0 to 3.4 kg TOC m^{-3} day^{-1} (Table 2) and by day 51, when US.1 was the sole substrate, the

Table 5. Concentrations of macro- and micronutrients in granular sludge on three different occasions (start-up, day 155 and day 255). Concentration and measurement errors reported are given by Eurofins Environment Sweden AB. Additional results (As, Sb, Ba, Pb, B, Cd, Cr, Ag, Ti and V) are presented as supporting information (Table S2)

	Unit	Start-up	Day 155	Day 255	Error in measurement (±%)
Total solids (TS)	%	11	6.0	10	10
Volatile solids (VS)	% of TS	66	81	77	10
Kjeldahl-N	mg kg^{-1}	4 800	1 200	7 600	10
NH_4^+-N	mg kg^{-1}	840	270	1100	10
P	mg kg TS^{-1}	16 000	4 700	10 000	15
S	mg kg TS^{-1}	72 000	73 000	56 000	20
Cl^-	mg kg TS^{-1}	370	<8.5	17	15
Na	mg kg TS^{-1}	1 100	44 000	16 000	20
K	mg kg TS^{-1}	1 900	1 600	4 400	20
Ca	mg kg TS^{-1}	24 000	8 300	9 200	15
Fe	mg kg TS^{-1}	100 000	23 000	75 000	15
Mg	mg kg TS^{-1}	3 000	970	2 200	15
Mn	mg kg TS^{-1}	140	220	1000	15
Al	mg kg TS^{-1}	15 000	2 300	5 600	20
Co	mg kg TS^{-1}	17	5.0	40	20
Cu	mg kg TS^{-1}	1 600	140	1 200	15
Mo	mg kg TS^{-1}	190	43	380	20
Ni	mg kg TS^{-1}	150	<3.9	130	15
Se	mg kg TS^{-1}	7.0	42	47	20
W	mg kg TS^{-1}	13	10	20	25
Zn	mg kg TS^{-1}	2 900	940	2 200	15

biogas production had dropped to around 200 NmL g^{-1} $fTOC_{IN}$ (Fig. 1(A)). The process performance did, however, improve (in terms of gas production as well as reduction of fTOC, TOA and acetic acid) with the measures taken on day 68 as described above. From day 89 a second batch of bleached spruce wastewater (BS.2) was introduced gradually and by day 95 it was the sole substrate, which gave an increase in OLR of 50% (Table 2). On day 94 the biogas production started to decrease (Fig. 1(A)) and the reactor liquid darkened making it impossible to distinguish the granules in the reactor. High amounts of granular residues were observed in the effluent which had an oily consistency and the lowest biogas production so far was registered (37 NmL g $fTOC_{IN}^{-1}$ on day 99; Fig. 1(A)) As a remedy the dosage of Fe was doubled on days 99 to 105 but with no instant effect and on day 103 the gas IC was shut down to reduce the mechanical forcing on the granules and, thus, the amount of sludge leaving the system. From day 106 the granular bed seemed to recover as reflected in a steady increase of biogas production (Fig. 1(A)) and from day 110 the TOA and acetic acid concentration in the effluent started to decrease (Fig. 1(B)). This was a trend that was interrupted by a 3-day period without fresh wastewater being pumped in to the reactor and when the biogas production stabilized, it was at a slightly lower level than before the stop. Throughout the whole reactor operation with spruce wastewaters (BS.1-2 and US.1) the produced biogas contained >10 000 ppm of H_2S.

By day 138 bleached aspen (BA.1) was gradually introduced as substrate, thus, increasing the OLR to 7.4 kg TOC m^{-3} day^{-1} (Table 2). The change resulted in an instant decrease in biogas production and fTOC reduction (Fig. 1(A) and (B)) as well as a continuous increase of TOA and VFA in the reactor effluent (Fig. 1(B)) followed by a decreasing pH. As the fluidized bed successively had turned from granules to sludge and the process performance was poor the reactor was terminated (day 155). Analyses of the reactor sludge showed lower levels of macro- and micronutrients compared with the content of the original granules (Tables 5 and S2) which implies that the granular bed had been leaking nutrients during experiment I. Exceptions were increasing concentrations of S, Na and Mn. The Fe-content had decreased by almost 80% at termination (Table 5).

Experiment II

On day 164 the reactor was restarted with ~2 L of fresh granules and the second experiment was initiated with diluted bleached aspen (BA.1) as substrate. The dilution was decreased stepwise and from day 171 undiluted wastewater was supplied. From day 171 and onwards, when HW wastewater was used as substrate, foam accumulated at the top of the reactor and hindered granules from settling. On these occasions the phase separator at the top of the reactor had to be cleaned every second day to prevent clogging of the effluent tube and other equipment.

During the period with undiluted BA.1 (days 172–190; Table 2) an fTOC reduction of 63% was reached with TOA and acetate reductions of 81 and 90%, respectively (Fig. 2(B) and Table 6). The biogas production during this period was 540 NmL g $fTOC_{IN}^{-1}$ (Fig. 2(A) and Table 6) with a methane content of 71±3.8% and H_2S-levels staying below 10 000 ppm (9400, 1100 and 3800 ppm on days 172, 176 and 185, respectively). The effluent pH was 7.9±0.1 and the ingoing SS concentration was 260 mg L^{-1} (Table 3), while the outgoing was 830±190 mg L^{-1}.

In order to reduce the problem with foaming, the ingoing wastewater was once again diluted from day 191 (BA.1d; Table 2). The measures taken did decrease the extent of foaming and increased the average biogas production (600 NmL g $fTOC_{IN}^{-1}$; Fig. 2(A) and Table 6) with a methane content of 75±2.5% and a fTOC reduction of 71% (Fig. 2(B) and Table 6). The dilution also resulted in a further decrease in the effluent TOA and VFA

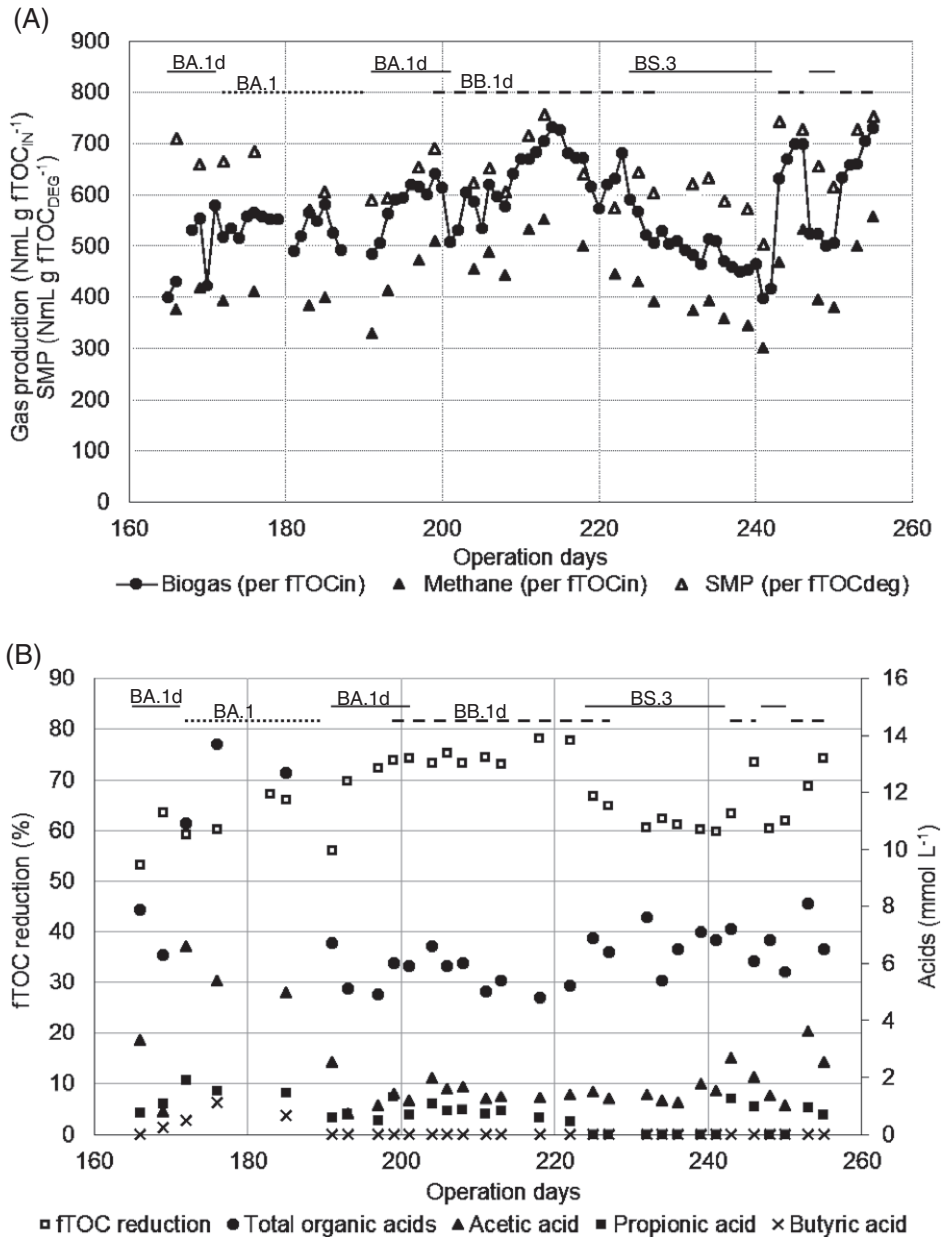

Figure 2. (A)–(B) Process performance for the UASB reactor during experiment II with (A) gas production (NmL g^{-1} fTOC$_{IN}$) and specific methane production (SMP; NmL g^{-1} fTOC$_{DEG}$) and (B) fTOC reduction (%) and total organic acids and volatile fatty acids in the reactor effluent (mmol L^{-1}). Days 164–171 are considered the start-up period. The missing data for days 180 and 188–190 are due to technical problems. Corresponding figures in relation to fCOD are presented as Supporting information (Fig. S2(A) and (B)).

concentrations (Fig. 2(B)). The effluent pH was 7.7±0.1. The reduction in ingoing SS (by the dilution) initially lowered the effluent SS to 330 mg L^{-1}, but the SS level increased again reaching 790 mg L^{-1} by day 197 (510±240 mg L^{-1} for days 191–198).

From day 199, diluted bleached birch (BB.1d) was the substrate and the OLR increased to 4.4 kg TOC m^{-3} day^{-1} (Table 2). For the first period with BB.1d (days 202–223), the biogas production was 640±57 NmL g^{-1} fTOC$_{IN}$ (Fig. 2(A)) with 77±3.1% methane and a H_2S concentration of 8170±58 ppm. The fTOC reduction was 75±2.1% (Fig. 2(B)). The effluent pH was 7.6±0.1 and the TOA and VFA concentrations remained low (Fig. 2(B)). The foaming increased compared with BA.1d. The ingoing SS concentration was ~250 mg L^{-1} (Table 3) and the outgoing 630±180 mg L^{-1}.

On day 224 a third batch of bleached spruce (BS.3) was introduced to the reactor (Table 2). The change from BB.1d to BS.3 wastewater had an instant effect with lower gas production and fTOC reduction (Fig. 2(A) and (B)) as well as less foaming. The biogas production was 470±37 NmL g^{-1} fTOC$_{IN}$ (Fig. 2(A)) with a methane content of 77±0.7%. H_2S levels above 10 000 ppm were detected (as during experiment I). The fTOC reduction was stable around 61±1.0% for the whole period (Fig. 2(B)) and the concentration of TOA and VFA in the reactor effluent remained low (Fig. 2(B)). The effluent pH increased to 8.1±0.1, whereas the amount of SS leaving the system was less compared with BB.1d (250±50 mg L^{-1}). By day 240 it was noted that a large amount of SS (fibre residues) had accumulated in the granular bed.

Table 6. Biogas and methane production, fTOC, total organic acids and acetic acid reduction for the three ingoing CTMP wastewaters during experiment II; bleached spruce (BS.3), undiluted and diluted bleached aspen (BA.1 and BA.1d) and diluted bleached birch (BB.1d). The three periods with BB.1d have been summarized to one and the same has been done for the two periods with BS.3. The data, which were used for the statistical analysis presented in the text, are presented as mean values ± standard deviation. A corresponding table in relation to fCOD is presented as supporting information (Table S3)

		BA.1	BA.1d	BB.1d	BS.3
Biogas production	NmL g^{-1} $fTOC_{IN}$	540 ± 27 (n = 15)	600 ± 20 (n = 6)	650 ± 54 (n = 31)	480 ± 37 (n = 19)
Methane production	NmL g^{-1} $fTOC_{IN}$	400 ± 12 (n = 4)	440 ± 42 (n = 2)	500 ± 42 (n = 11)	360 ± 33 (n = 7)
	NmL g $fTOC_{DEG}^{-1}$	630 ± 52 (n = 4)	620 ± 43 (n = 2)	680 ± 66 (n = 11)	600 ± 50 (n = 7)
fTOC reduction	%	63 ± 4.1 (n = 4)	71 ± 1.9 (n = 2)	73 ± 4.1 (n = 11)	61 ± 0.95 (n = 7)
	mg L^{-1} HRT^{-1}	2 400 ± 200 (n = 4)	1 500 ± 90 (n = 2)	1 700 ± 120 (n = 11)	1 300 ± 19 (n = 7)
Total organic acids reduction	%	81 ± 2.1 (n = 3)	86 ± 0.8 (n = 2)	85 ± 2.5 (n = 11)	75 ± 3.3 (n = 7)
	mmol L^{-1} HRT^{-1}	54 ± 1.7 (n = 3)	31 ± 3.0 (n = 2)	34 ± 1.6 (n = 11)	20 ± 1.4 (n = 7)
Acetic acid reduction	%	90 ± 1.4 (n = 3)	97 ± 0.9 (n = 2)	94 ± 1.8 (n = 11)	94 ± 1.1 (n = 7)
	mmol L^{-1} HRT^{-1}	51 ± 0.6 (n = 3)	29 ± 2.8 (n = 2)	32 ± 1.6 (n = 11)	20 ± 0.4 (n = 7)

To further test the process stability in relation to the often rapid shifts during pulp production at the mill, resulting in different wastewater compositions, shifts were made without overlap and with exposure periods of only 4–5 days (corresponding to 7–9 HRTs) for each wastewater from day 243 and onwards. To keep the foaming at a manageable level the dilution of BB.1 was maintained. On day 243 a sharp shift from BS.3 to BB.1d was, thus, performed and a constant increase in biogas production took place during days 243 to 246 (average for the period: 680±33 NmL biogas g^{-1} $fTOC_{IN}$; 75±1.3% methane and 8 300 ppm H_2S; Fig. 2(A)). The analysis of the effluent showed an fTOC reduction of 63% after 1.5 HRTs and 73% after 6.5 HRTs (Fig. 2(B)). A similar trend was observed for the reduction of effluent TOA and VFA (Fig. 2(B)). A sharp shift back to BS.3 was made on day 247 resulting in an instant fall in biogas production to 510±12 NmL g^{-1} $fTOC_{IN}$ (days 247–250) with a methane content of 75±0.4% and H_2S >10 000 ppm (Fig. 2(A)). The fTOC reduction determined after another 3 and 6.5 HRTs was stable at 61±1.0% (Fig. 2(B)). A final shift to BB1.d was done day 251 and the same trend as for days 243–246 was observed, i.e. increased biogas production and fTOC reduction together with decreasing levels of TOA and VFA (Fig. 2(A) and (B)). The H_2S levels were again below 10 000 ppm (7900 ppm) in contrast to the period of BS.3.

During experiment II, the initial 2 L granular bed steadily decreased until day 219, when it stabilized at approx. 1.2 L. The loss of granules was most likely mainly linked to the continuous need to clean the phase separator from foam and granules, a measure which might have been prevented with a proper IC. In contrast to days 92–120 during experiment I, the high levels of SS in the effluent could not be confirmed visually as granule residues during experiment II (only noted for day 176). Instead it was noted that the ingoing SS accumulated in the granular bed and were washed out occasionally. Although the granules sampled at start-up and on day 255 both represent well-functioning AD processes, in contrast to the sludge sampled on day 155, they differed in nutrient content (Table 5). The granules from day 255 did, for example, have a higher content of Na, K and Co, whereas the start-up granules had a higher Fe and S content (Table 5). The sludge sample from day 155 had lower levels of most essential nutrients including Fe, Ni and Co (Table 5).

The impact of raw material on reactor performance

To evaluate the impact of raw material on the reactor performance the data presented in Table 6 were compared for the wastewaters from bleached aspen (BA.1 and BA.1d), bleached birch (BB.1d) and bleached spruce (BS.3). Note that when a wastewater was used for more than one period (BB.1d and BS.3) an average based on all periods was calculated for this evaluation. The one-way ANOVA (significance level of 5%) showed significant differences for all evaluated parameters presented in Table 6. The results from the pairwise comparisons using Tukey's HSD test (significance level of 5%) are summarized below. The *P*-values for the significant differences are presented in Tables S4 and S5.

Comparing BA.1 and BA.1d, significant differences were observed for the absolute amounts of reduced fTOC, TOA and acetic acid, which was higher for BA.1, and the biogas production and the acetic acid reduction in relation to the ingoing concentration, which both were higher for BA.1d (Table 6). The biogas production (Table 6) was significantly different for all the wastewaters with the highest for BB.1d followed by BA.1d, BA.1 and BS.3. BB.1d had a significantly higher methane production per ingoing fTOC (Table 6) than BA.1 and BS.3, but it was not significantly different compared with BA.1d. BA.1, BA.1d and BS.3 were not significantly different from each other. The methane production per degraded fTOC (Table 6) was not significantly different for BB.1d compared with BA.1 or BA.1d and neither was BA.1 and BA.1d compared with BS.3, but BB.1d had a significantly higher production than BS.3. For the reduction of fTOC (%; Table 6) no significant difference was observed between BB.1d and BA.1d and both were

significantly higher than BS.3. BB.1d also had a significantly higher reduction than BA.1. For the absolute amount of degraded fTOC (Table 6) BA.1 had the significantly highest reduction followed by BB.1d, which had a significantly higher reduction than BS.3. BA.1d was not significantly different from either BB.1d or BS.3. BA.1 had the significantly highest TOA reduction in absolute numbers, but for the relative numbers the reduction was only significantly higher than BS.3. No significant difference was observed between BB.1d and BA.1d, but both had a significantly higher reduction than BS.3. The acetic acid reduction in relation to the ingoing concentration (Table 6) showed no significant differences between the BB.1d, BA.1d and BS.3 but BA.1 had the significantly lowest reduction. The absolute amount of reduced acetic acid (Table 6) was significantly highest for BA.1 followed by BB.1d and BA.1d, not statistically different from each other but significantly higher than BS.3.

DISCUSSION

In this study we show that a well-functioning AD process could be obtained with composite pulping and bleaching CTMP wastewater throughout variations in raw material (spruce, birch and aspen) and consequently in TOC-loading (Table 2; OLR in the range 11–21 kg COD m^{-3} and day^{-1}). Furthermore, a process with high methane production as well as a high fTOC- and VFA reduction (Fig. 2(A) and (B); Table 6) could be maintained at both gradual and sharp shifts between wastewaters with different characteristics resulting from changes in raw material use. The shorter campaigns of 4–5 days corresponding to 7–9 HRTs, representing the common time frame for the production campaigns at the CTMP mill, showed an increasing process performance over the two periods with diluted bleached birch (BB.1d; Fig. 2(A) and (B)) indicating a difference in wastewater composition which the AD process needed to adapt to before reaching its full potential. This suggests that longer campaigns would be beneficial to maximize methane production.

The highest methane production and corresponding fTOC reduction was obtained for wastewater from bleached birch CTMP (BB.1d). Both gas production and fTOC reduction were statistically different from those obtained from bleached spruce wastewater (BS.3), which had the lowest methane production and fTOC reduction (Tables 6 and S5). Wastewater from bleached aspen (BA.1d) gave an fTOC reduction in the same range as BB.1d while the methane production was slightly lower (not significant). The difference in methane production may partly be explained by the wastewaters differing sulphur to TOC ratio (Table 4). A recent study on AD of alkaline kraft bleaching wastewater showed that the sulphur to TOC ratio was an important factor affecting methane production partly explaining the lower yield for SW compared with HW.[16] Mass balance calculations presented in Table S6 (performed as in Larsson *et al.*[16]) show a higher reduction of sulphur per degraded fTOC for BS.3 followed by BA.1 and BB.1d. However, the estimated potential impact of the sulphate reduction on the methane production is less, compared with Larsson *et al.*[16] in accordance with a lower sulphur to TOC ratio (44–120 mg S g TOC^{-1} in Table 4 compared with ~90–140 mg S g TOC^{-1} reported by Larsson *et al.*[16]), as well as a higher fTOC reduction.

The lower fTOC reduction (both in relative and absolute numbers) for BS.3 compared with BB.1d and BA.1d suggests lower degradability of the organic material in this wastewater rather than a less efficient AD process, since acetic acid reduction above 90% took place (Table 6). The lower degradability of the spruce wastewater's total TOC content compared with birch and aspen may, at least partly, be explained by the higher lignin content in SW compared with HW (~27 vs. ~22% of dry wood weight for spruce and birch[14]). High molecular weight lignin and lignin derived compounds are often assumed recalcitrant during AD. Even if partial degradation has been shown to occur[19] the degradation rate is so low that this assumption is probably correct, which means that the total degradability of the organic material in a wastewater will decrease with the amount of lignin present.

The fact that BS.3 had a significantly lower TOA reduction than BB.1d and BA.1d (Tables 6 and S5) shows that also the degradability of the TOA derived from spruce wood is lower than for birch and aspen. In addition, the concentration of the methanogenic substrate acetic acid was found to be higher in BB.1d and BA.1d compared with BS.3 (both per volume and TOC; Table 3), probably owing to the hemicellulose structure of the different wood raw materials with more acetyl groups in HW compared with SW.[14] It should also be noted that the methane production theoretically obtained from the acetic acid reduction represents ~60% of the total methane production for BS.3 and BB.1d compared with ~80% for BA.1d. To conclude, the results suggest that the differences in the wastewaters' methane production potential per TOC is influenced by their composition and further research is needed to explain the observed differences in greater detail.

The almost 3 week long period with undiluted bleached aspen wastewater (BA.1) showed that the UASB process could manage an OLR of 6.6 kg TOC m^{-3} and day^{-1} (21 kg COD m^{-3} and day^{-1}) with methane production and fTOC reduction at the same levels as when diluted to half the OLR (Tables 6 and S5). The slightly higher acetic acid concentration in the effluent at the higher load (Fig. 2(B)) may, however, indicate that the process was at its upper OLR limit. Welander[9] observed an effluent acetic acid increase already at 15 kg COD m^{-3} and day^{-1} and a HRT of 16–24 h with wastewater from the production of bleached spruce CTMP, while HW-wastewaters were not investigated in that study. Pichon *et al.*,[11] who evaluated wastewaters from both aspen and spruce CTMP, showed that a much higher OLR could be applied for aspen compared with spruce (20 vs. 3 kg COD m^{-3} day^{-1}) while maintaining a COD reduction of 60%. The authors explained the AD process's poor tolerance to the spruce wastewater by the high levels of sulphur and did not discuss other possible differences in wastewater composition. In comparison, our AD process could successfully manage an OLR of 11 kg COD m^{-3} day^{-1} for wastewater from bleached spruce pulp (BS.3), which, however, had a lower sulphur content of 250 mg L^{-1} compared with 400 mg L^{-1}, which was the level causing problems for Pichon *et al.*[11]

Due to technical disturbances during experiment I it is difficult to draw conclusions regarding how the process performance was affected by the changes in wastewater characteristics linked to pulp bleaching. The poor process performance was probably related to the technical obstacles as the extra addition of granules, together with changes in the IC, temporarily improved the process performance (day 68) when US.1 was used as substrate. The increased amount of reduced sulphur in the system due to the gas recirculation of the H_2S-rich biogas applied to obtain IC (days 68 to 103) probably contributed to the deterioration of the process. That the increasing concentration of reduced sulphur affected the process performance is supported by noting that the process recovered after termination of the gas IC and by observations of similar effects in another UASB reactor with the same setup operated at the same time, but with a different substrate.[20] If applying recirculation of the biogas produced its H_2S levels needs

to be reduced significantly. Furthermore, unpublished results from pilot-scale, high-rate AD including shifts between wastewaters from bleached and unbleached spruce pulp indicate that the shifts between these two substrate types are problematic and this might, thus, have contributed to the problems experienced during experiment I.

The benefits of digesting wastewater from bleached rather than unbleached pulp production is, from a methane production point of view, the higher total organic material content, as well as the higher ratio of acetic acid to TOC in these wastewaters (Table 3). It should also be noted that pH values closer to 7 were observed for wastewater from the production of bleached pulp (Table 3), which might benefit the AD process although the process was able to handle substrates with pH-values as low as 5.3 (US.1; Table 3). The higher ratio of acetic acid to fTOC in bleached pulp wastewater, also observed by Stenberg and Norberg,[15] suggests a more fractionated and easily degradable organic material. The poorer process performance, that coincided with the increased OLR from 3.5 to 5.4 kg TOC m^{-3} and day^{-1} resulting from the second batch of bleached spruce wastewater (BS.2), could most probably have been avoided in a well-functioning system as the process recovered, using the same wastewater, when the gas IC was turned off (day 103; Fig. 1(A) and (B)).

Earlier studies reported challenges such as the presence of resin acids and residual bleaching chemicals (H_2O_2 and DTPA) when implementing AD at pulp and paper mills.[9,10] Welander[9] showed that a detoxification, presumably precipitating resin acids and LCFA, was crucial prior to AD of wastewater from the production of bleached spruce CTMP. Our results show that a similar wastewater can be digested successfully without detoxification and reach an fCOD reduction of 54±1.5% (BS.3; Table S3) comparable with the ~50% presented by Welander[9]. The methane production in our study is, however, lower i.e. 240±20 compared with ~300 NmL g^{-1} COD reduced, which may be due to the higher sulphur to COD ratio in our study (38 vs. 30 mg S g^{-1} COD for BS.3 compared with Welander[9]). Such a scenario is further supported by the results from Pichon *et al.*[12] who reported a similar COD reduction of 45%, but only ~100 NmL of methane g^{-1} COD reduced for a CTMP wastewater with 83 mg S g^{-1} COD.

As a well-functioning AD process was maintained throughout experiment II, only digesting wastewater from the production of bleached pulp, the potential presence of H_2O_2 and DTPA did not have a major impact on the process. Rough measurements of the peroxide level in undiluted wastewater were made with test strips and indicated levels ≥800 mg L^{-1}, when bleaching was applied, and ≤10 mg L^{-1} when not. That a well-functioning process could be maintained at the H_2O_2-levels present in the bleached pulp wastewaters are supported by results from Welander[9], who studied the effect of H_2O_2 to the AD process in two continuous lab-scale reactors and showed that if gradual adaptation was allowed the process could tolerate H_2O_2-levels above 3 g L^{-1}. However, his results also showed that highly variable concentrations of H_2O_2 would deteriorate the process, which indicate that shifts between wastewater from the production of unbleached- and bleached spruce pulp (as applied in experiment I) could be problematic. Thus, despite the potential for the process to adapt and the high levels of H_2S in our system, which has been suggested to reduce residual H_2O_2,[10] a pre-treatment to secure low levels of H_2O_2 would most likely be needed in a full-scale implementation.

The foaming, which only arose when feeding HW wastewaters and which increased slightly for BB.1d compared with BA.1d, may be related to wood extractives but the issue needs further attention to be confirmed. The high ingoing levels of SS (fibres/fines etc.) were problematic during both experiments as it often accumulated in the granular bed (especially true for spruce wastewater) and, thus, very probably contributed to the loss of granules. The extra maintenance needed for the removal of foam and SS could possibly have been reduced with a functioning IC, increasing the turbulence in the granular bed and consequently releasing the accumulated SS. This was observed during periods with HW wastewater, when the higher gas production led to an increased wash-out of SS. The SS_{IN} levels were in the mid/upper range of what is normal at the mill (130–300 for our study compared with normal values of 20–500 mg L^{-1}) and despite the well-functioning AD process during phase II it is important to note the need to keep the ingoing levels of SS as low as possible to avoid lowered settling abilities of the granules with increased wash-out as a potential consequence.[13] Richardson *et al.* further showed that 80–90% of the inhibition observed for CTMP wastewater in batch tests was associated with particulate constituents and the authors suggested that this was partly linked to a higher resin content of the particulate material.[13] A high accumulation of SS may, thus, increase the exposure to resin acids potentially reaching inhibiting levels for spruce wastewaters as spruce, in contrast to HW, contains resin acids[21] and the granular bed in the UASB showed a higher tendency to accumulate spruce SS.

Our study shows that the potential for biogas production at a CTMP mill will vary depending on the type of pulp produced. This means that measures are needed to optimize the methane production, e.g. by tailored micronutrient additions and prolonged campaigns. However, the results also indicate that it is possible to have a well-functioning AD process in spite of rapidly shifting substrate streams. The higher methane production from HW wastewaters compared with SW implies that the methane potential from AD of 115 GWh per year for the Swedish CTMP mills can be even higher, since only the production of bleached spruce pulp was considered in the estimate mentioned. There is also a rapid worldwide increase in production of bleached HW CTMP compared with bleached SW CTMP[5], which means that there is an increasing incentive globally for biomethane production from CTMP wastewaters.

CONCLUSIONS

- A well-functioning high-rate AD process was obtained (experiment II) with methane production ranging from 360–500 NmL g^{-1} $fTOC_{IN}$ and an fTOC reduction >60% when digesting a composite pulping and bleaching CTMP wastewater with varying TOC concentrations and composition, at both gradual and sharp shifts between wastewaters from different wood raw materials. Further research is, however, needed on the impact of sharp shifts and short campaigns with undiluted wastewater.
- The highest methane production and fTOC reduction was obtained with wastewater from the production of bleached birch pulp followed by bleached aspen pulp and bleached spruce pulp.
- The gradually increasing process performance observed during the short campaigns (7–9 HRTs) with wastewater from the production of bleached birch pulp indicate a differing wastewater composition in comparison with bleached spruce wastewater,

which the AD process needed to adapt to before reaching its full potential. This suggests that longer campaigns might be beneficial to maximize methane production.

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Supporting Information

Supporting information may be found in the online version of this article.

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