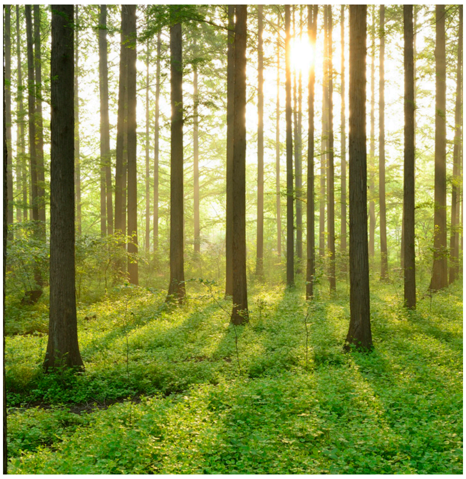
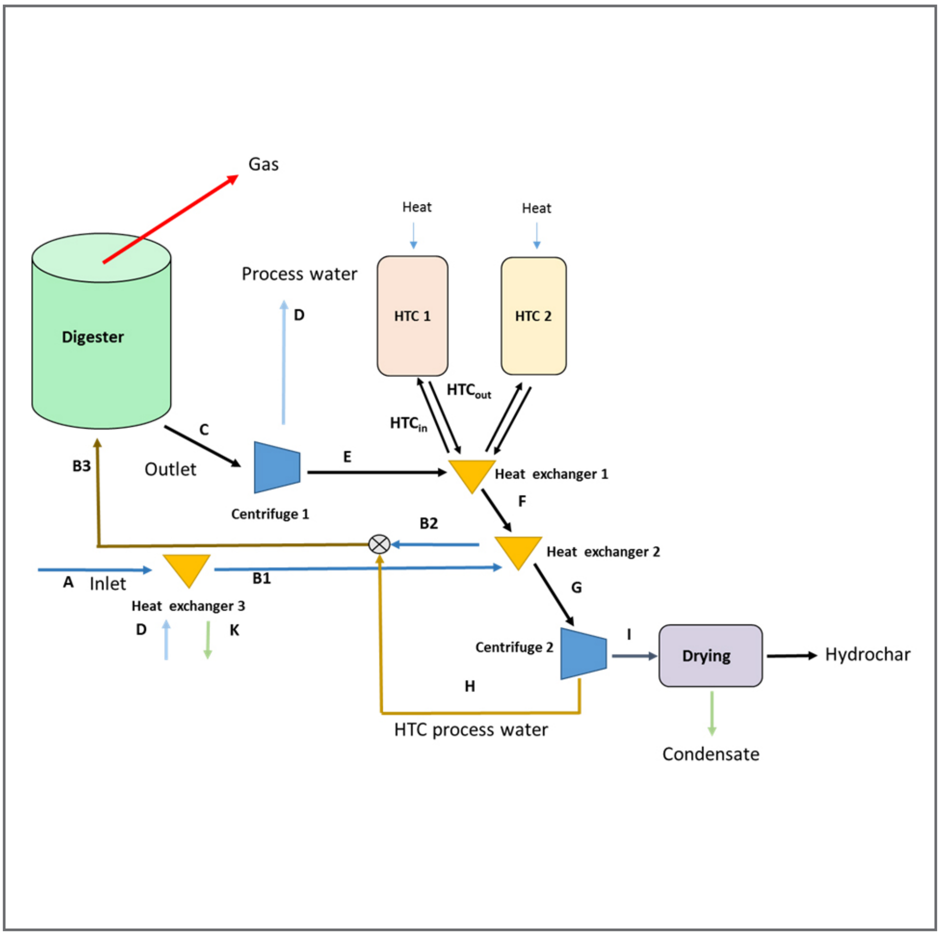
INCREASED YIELD OF BIOGAS BY POST TREATMENT OF RESIDUAL SLUDGE

REPORT 2016:312



ENERGY GAS TECHNOLOGY



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Increased yield of biogas by post treatment of residual sludge

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Authors' foreword

The project consists of a feasibility study on the technical possibilities, the economic gains, and the environmental impacts by post treatment of residual sludge in a hydrothermal process and re-circulation of process water to the digester. The report has been produced by Biokol Sverige AB. Authors are Eva Björkman and Malte Lilliestråle.

The study was funded by the Swedish Energy Agency, Biokol Sverige AB, Käppala förbundet, Gästrike vatten AB, and Tekniska verken i Linköping. The study had a reference group with the following members: Anton Fagerström (Energiforsk), Hans Simonsson, Mats Linder (Gästrike Vatten AB), Jan Moestedt (Tekniska Verken i Linköping AB), and Agnieszka Witkiewicz and Dervisa Karat (Käppala Förbundet).

Sammanfattning

I detta projekt har potentialen för att öka utbytet av biogas från en anaerob rötkammare vid ett vattenreningsverk studerats. Metoden innebär att rötresterna karboniseras hydrotermiskt (HTC), d.v.s. behandlas vid förhöjt tryck (18 bar) och temperatur (200 °C). Produkterna blir en kolliknade fast fas, s.k. hydrochar och ett processvatten som innehåller organiska föreningar.

Kortfattat är principen för processen att 0,2 m^3 processvatten tillsätts till 1 m^3 slam, vilket ger en ett inflöde till rötkammaren på 1,2 m^3. Utflödet från rötkammaren avvattnas till 10 % torrsubstans (TS) och karboniseras hydrotermiskt. Efter HTC reaktorn separeras flödet i hydrochar och 0,2 m^3 processvatten, som återinförs till rötkammaren. Baserat på erhållna resultat från studien kan det ökade metanutbytet från processen uppskattas till 30 %.

Ytterligare så återfanns mycket av fosforn i hydrochar-fraktionen, vilket pekar på möjligheten att återvinna fosfor genom sur lakning. Koncentrationen av ammoniumkväve (NH_4^+–N) i processvattnet var cirka 3,9 g/L, vid 5 gånger utspädning blir halten klart under gränsvärdet för rötkammaren. Den termiska energin som krävs för HTC-steget kompenseras mer än väl av energin som fås från det ökade metanutbytet och den energi som fås genom att använda värmeväxlare för att återföra värmen i utflödet från HTC reaktorn.

Mer fördelar med den föreslagna processen är att rötresterna troligen hygieniseras av den höga temperaturen (200 °C), slamvolymen minskar på grund av ökad torrhalt och att hydrochar-fraktionen kan användas för att framställa funktionella kolmaterial. En miljömässig effekt är också att det inte bildas några rötrester som kan avge metan och koldioxid och därmed bidra till den globala uppvärmningen.

Summary

In this project, the potential of increasing the biogas yield from an anaerobic digester in a waste water treatment plant has been studied. In the method the digestate was hydrothermally carbonized (HTC), *i.e.* treated at elevated pressure (18 bar) and temperature (200 °C) giving a hydrochar and a black process water, containing organic matter.

Shortly, the principle of the process is that 0.2 m^3 of the HTC process water is added to 1 m^3 of digested sewage sludge giving a total influent flow to the digester of 1.2 m^3. The effluent from the digester is concentrated to 10 % dry substance (DS) and hydrothermally carbonized. The produced HTC slurry is separated into hydrochar and 0.2 m^3 process water and the loop starts again. Based on the obtained results in this study, the increased methane yield from the process can be estimated to 30%.

Furthermore, phosphorous was accumulated in the hydrochar, which point to the possibility to recover it with acid leaching. The ammonium–N (NH_4^+–N) content in the process water was around 3.9 g/L, diluting it 5 times gives a concentration well below the critical limit for the digester. The thermal energy requirement for the HTC step can be well covered by the energy from the increased methane yield and by using heat exchangers to utilise the heat in the effluent from the HTC reactor.

Additional benefits with the proposed process are that the sludge most probably will be hygienized by the high temperature (200 °C), the volume of the sludge will be reduced due to decreased water content, and that the hydrochar can be used for the production of functionalized carbon materials. Also, an environmental benefit is that there will be no need for sludge deposits, which can emit methane and carbon dioxide and thereby contribute to the global warming.

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1 Background

Anaerobic digestion (AD) is a proven technology for sewage sludge treatment, which allows production of renewable energy. During AD, microorganisms break down the organic matter contained in the sludge and convert it into biogas, a mixture of mainly methane and carbon dioxide, which can be used for electricity, heat and biofuel. Sewage sludge is produced in waste water treatment plants (WWTPs) as a part of the water cleaning process. The sludge contains the particles removed from the waste water, which are rich in nutrients and organic matter.

The principal feedstock for anaerobic digestion in WWTPs is sewage sludge. In general, it is composed of primary and secondary sludge, also called mixed sludge. Greases from the grease trap (usually found at the entrance of the plant) are often also digested.

Primary sludge, also called raw sludge, is produced by gravitational sedimentation in the primary settler. It has a high content of organic matter and is easily degradable. Under optimum digestion conditions, a methane yield of 315 – 400 Nm^3/tonne organic dry matter (ODM) can be expected. Secondary sludge, also called excess sludge or activated sludge, results from biological treatment of waste water. It has a smaller degradable fraction than primary sludge and thus a lower biogas yield. Under optimum digestion conditions, a methane yield of 190 – 240 Nm^3/tonne ODM can be expected.

As about a third of the solid matter in the sludge is transformed into biogas during the anaerobic digestion (equivalent to about 50% of the organic matter) the digested sludge becomes very liquid and needs to be thickened after leaving the digester. Depending on the further utilization of the sludge, the latter is pressed, centrifuged or even heat dried in order to remove as much water as possible. When the digested sludge is further used in agriculture, composting of the sludge may be carried out gaining further fertilizing effects. Otherwise, the sludge may be transported to incineration or a landfill.[1]

Hydrothermal carbonization (HTC) is a process under mild conditions to convert carbohydrates and wet biomasses into valuable carbon structures. The temperature is around 200°C under self–regulated pressure. The process is exothermic and the output is a coal–like hydrochar, a black process water containing organic matter and almost negligible amount of gases. The carbon efficiency is almost 1, since the carbon loss is very small.[2]

Usually the focus on HTC is to produce the hydrochar and the process water is considered as waste product. Since the process water contains organic matter, there is a possibility to use it as a substrate in anaerobic digestion. Therefore, in this work we have studied the potential of recirculating the process water from hydrothermal digested sewage sludge back to the digester and thereby increase the biogas yield.

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[1] *Sustainable biogas production in municipal waste water treatment plants.* Bachmann, N. (2015) IEA Bioenergy

[2] *Magic Coal from the Steam Cooker.* Antonietti, M. Max Planck Res. 3 (2006) 21–25

2 Objective

This feasibility study had as objective to estimate the energy balance, investment and operating costs, environmental consequences and the potential to increase the biogas yield by hydrothermal carbonization digested sewage sludge and reintroduce the process water to the digester.

The study had the following milestones:

- To determine the composition of the process water from HTC, with respect to carbon content, COD (Chemical Oxygen Demand), and BOD (Biochemical Oxygen Demand) for two filters with different pore sizes
- To study the consequence of recirculating the process water from hydrothermally carbonized digested sewage sludge to the digester and correlate the amount of produced biogas/methane to the concentration of organic matter, for example TOC (Total Organic Carbon) in the process water.
- To relate the analytical data to conditions at a full–scale plant for the production of biogas in order to estimate increased yield together with economic and environmental potential.

3 Experimental section

3.1 WORK AT ATB (LEIBNIZ–INSTITUTE FOR AGRICULTURAL ENGINEERING POTSDAM)

3.1.1 Hydrothermal carbonization

In the HTC runs, 5 000 g of digested sewage sludge (SS) from Nedlitz, Germany with 21.4% dry substance (DS) were placed in a 5 gallon (18.9 liter) Parr reactor equipped with a stirrer and heated to 200°C within 3 hours. The reactor was kept at 200°C, 18 bars for 4 hours, and then was allowed to cool to ambient temperature during the night. When cooled, the process water (PW1) was separated from the hydrochar by a screw press with a filter towel without defined pore size (around 100 µm). Approximately half of the process water was vacuum filtrated (12 µm cellulose filter paper) giving a second process water (PW2). A summary of the experimental condition for the HTC experiments is given in Table 1.

Table 1: Overview of substrate and inoculum used for HTC and digestion tests at ATB, Potsdam. The HTC was run at 200°C for 4 hours, the measured outcome was yield, pH, dry substance (DS), volatile solids (VS) of dry substance and process water, and chemical oxygen demand (COD)

	Yield (%)	pH	DS (%)	VS (%DS)	VS (%)	COD (g/L)
HTC						
Sewage sludge			21.4	61.2		
Hydrochar	55.9		36.4	52.6		
Process water	43.2					
Digestion						
Inoculum 04.04.16			2.7	52.7	1.4	22.8
Cellulose			95.8	100.0	95.8	
SS		7.5	21.4	61.2	13.3	199.0
PW1		7.5	5.0	94.6	4.7	74.3
PW2		7.5	4.9	95.2	4.7	70.1

3.1.2 Digestion tests

The digestion tests were performed in triplicate, using 1500 g of inoculum and a substrate–inoculum ratio of 0.25, based on VS (Volatile Solids) for the sludge and COD (Chemical Oxygen Demand) for the process water. The studied samples were digested sewage sludge (SS), two process water (PW1 and PW2), and mixture (5:1) of sludge and process water (SS+PW1 and SS+PW2) on weight basis. Cellulose was used as a reference. The tests were performed at 37 °C in 21 parallel batches for 24 days, the gas production from each sample was measured at ambient conditions with an automated gas counter. A detailed description of the experimental set up can be found in the literature[3], and an overview of the substrates and inoculum is given in Table 1. The analytical methods are described in detail elsewhere[4]

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[3] *Anaerobic degradation of increased phenol concentrations in batch assays.* Wirth, B., Krebs, M., Andert, J., Environ. Sci. Pollut. Res. 22 (2015) 19048–19059

[4] *Influence of digestion temperature and organic loading rate on the continuous anaerobic treatment of process liquor from hydrothermal carbonization of sewage sludge.* Wirth, B. Reza, T., Mumme, J. Bioresource Technology 198 (2015) 215–222.

3.2 WORK AT KÄPPALA, LIDINGÖ

3.2.1 Hydrothermal carbonization

The substrates for the digestion test at Käppala were the process water from two HTC runs at different pressures, 13 bars and 23 bars. The starting material was dewatered sludge from Käppala with 23% DS (Dry Substance), which was mixed with water to a fluid and placed in the HTC reactor, see Figure 1. The reactor was heated for 4 and 6 hours giving the pressures 23 and 13 bars respectively. Thereafter, the reactor was allowed to cool during the night, and the resulting slurry was sent to Käppala for the digestion test.

Figure 1: The autoclave used as the HTC reactor for hydrothermal carbonisation of digested sewage sludge from Käppala.

3.2.2 Digestion tests

The digestion tests that were performed at Käppala are described in Appendix 1.

4 Results and discussion

4.1 HYDROTHERMAL CARBONIZATION

5 kg of sewage sludge was used in the Parr reactor at ATB. The sludge was dense, it had 21.4% DS, and stirring was necessary. The reaction gave a 56% yield of hydrochar (Table 1), containing 86.7% of the original carbon, see Table 2. The amount of carbon is not balanced in the table, since the hydrochar together with process water contained ≈ 5% more carbon than in the starting sludge. One explanation can be that there was a great difference in concentration between the solid materials and the process water, which required different analytical methods. Hence, the comparison may contain small errors.

The amounts of nitrogen and sulfur are however balanced, the sulfur is found in the hydrochar and 35.3% of the nitrogen could be found in the process water. In the balances only the amount of and concentrations in PW1 are considered, since that was the process water that was separated from the hydrochar in the first filtration. PW2 was obtained from PW1 by vacuum filtration (pore size 12 μm). The aim was to have two process waters with different organic loading, but unfortunately there was not a large difference (Table 2).

The ammonium concentration is of interest, since it is known that high levels ammonium/ammonia (NH_4^+/NH_3) (>3.0 – 3.3 g NH_4^+–N/L; 0.14 – 0.28 g NH_3/L) causes operating problems in anaerobic digesters[5]. The process water produced at ATB contained around 5 g NH_4^+/L, making it necessary to dilute it before digestion.

Table 2: The balances of carbon, nitrogen and sulphur when 5 kg of sewage sludge (SS) was hydrothermally carbonized at ATB, Potsdam, together with characteristics of the process waters, PW1 (filter towel 100 µm) and PW2 (12 µm cellulose filter paper).

	SS	hydrochar	PW1	PW2
C (g)	338	293	62	
N (g)	51	32	18	
S (g)	13	13		
TOC (mg/L)			28 799	29 555
BOD_7 (mg/L)			25 200	22 600
N_{tot} (mg/L)			8 180	8 760
NH_4^+–N (mg/L)			3 920	3 980

The obtained concentrations of metals and phosphorous in hydrochar and process water is given in Table 3, together with regulation limits for Sweden[6]. In the hydrochar the concentration of zinc (Zn) and copper (Cu) exceed the limit, the others were well below. A comparison of the concentrations in the process waters (PW1 and PW2) gives an indication if a certain element is attached to particles or dissolved in water. If the concentrations are similar for PW1 and PW2 then the respective element most probably will be found in the water phase. But, aluminum

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[5] *Trace element and temperature effects of microbial communities and link to biogas digester performance at high ammonia level*. Westerholm, M. Muller, B., Isaksson, S., Schnurer, A. Biotechnol. Biofuels 8 (2015) 154.

[6] *Regler för avloppsslam.* Swedish Environmental Protection Agency (Naturvårdsverket) 2013–02–13

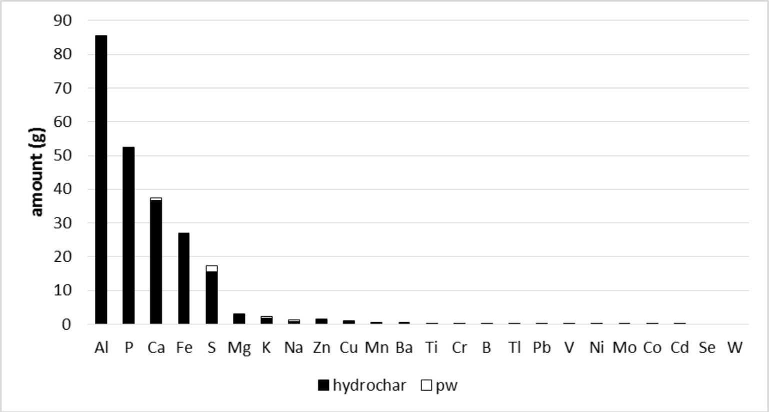
(Al), iron (Fe), phosphorous (P) and zinc (Zn) are attached to the particles, since their concentration are much lower in PW2.

Table 3: The concentration of elements in hydrochar and process water, produced when digested sewage sludge was hydrothermal carbonized at ATB, Potsdam, together with regulation limits for Sweden

	concentration (mg/kg)			concentration mg/kg$_{DS}$		regulation limit (mg/kg$_{DS}$)
element	**hydrochar**	**PW1**	**PW2**	**hydrochar**	**PW1**	
Al	30496.4	90.6	29.5			
B	5	2.3	2.3			
Ba	94.4	0.2	n.d			
Ca	13086.6	355.8	325.8			
Cd	0.5	0	0	1.4	n.d.	2
Co	1	0.2	0.2			
Cr	7.5	0.2	0.2	20.6	4	100
Cu	278	0.6	0.1	763.7	12	600
Fe	9517	153.6	138			
K	653.4	228.8	227.7			
Mg	984.6	56.6	54.7			
Mn	121	0.8	0.6			
Mo	2.7	n.d.	n.d.			
Na	306.6	197.7	198.2			
Ni	3	0.1	0.1	8.2	2	50
P	18701.3	54.9	19.5			
Pb	5.2	n.d.	n.d.	14.3	n.d.	100
S	5558	769.2	756			
Se	n.d.	n.d.	n.d.			
Ti	30.3	0.3	0			
Tl	5.5	n.d.	n.d.			
V	3.3	0	0			
W	n.d.	n.d.	n.d.			
Zn	438.2	0.9	0.1	1203.8	18	800

Figure 2 shows the total amount of the elements that can be found in the hydrochar and process water when 5 kg of digested sewage sludge was hydrothermally carbonized. Aluminum was the most abundant element, probably due to the use of flocculants in the sewage plant. Phosphorous, calcium, iron and sulfur were also common. There were very little or negligible amounts of heavy metals. The lower diagram is a magnification of elements that occurred in amounts that were less than 4 g.

The distribution of the elements between hydrochar and process water is shown in Figure 3. In the figure only the elements whose amounts exceeded 0.5 g is considered. As can be seen, non-alkali metals seem to be located in the hydrochar, while alkali metals are more easily dissolved in the process waters. Worth noting is that both aluminum and phosphorous are attached to the hydrochar, indicating the possibility to recover these elements. As an example, 5 kg of hydrothermal treated digested sewage sludge gave approximately 52 g of P in the hydrochar (Figure 2), which corresponds to approximately 160 g of phosphate (PO_4^{3-}). Therefore, the potential of using HTC to recover phosphorous from digested sewage sludge is promising. One possible method could be leaching the hydrochar with an acid.[7]



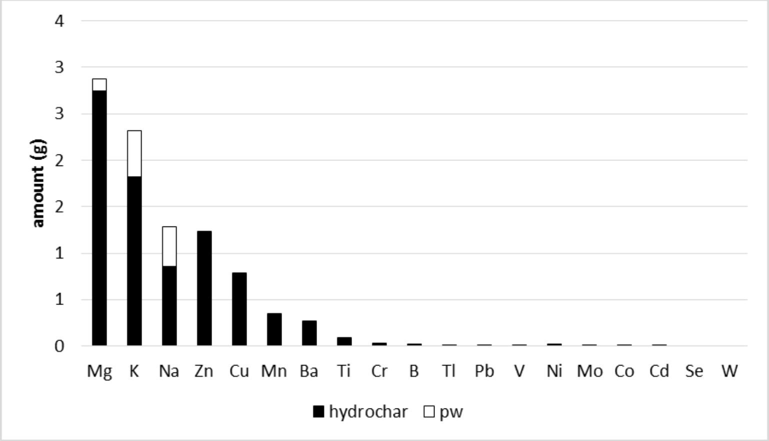


Figure 2: The amount of elements in hydrochar and process water, respectively, when 5 kg of digested sewage sludge was hydrothermal treated at ATB, Potsdam. The lower diagram is a magnification for the elements with low amounts (< 4 g).

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[7] *Phosphorous Reclamation through Hydrothermal Carbonization of Animal Manure*. Heilmann, S.M., Molde, J.S., Timler, J.G., Wood, B.M., Mikula, A.L., Vozhdayev, G.V., Colovsky, G.V., Spokas. K.A., Valentas, K.J. Environ. Sci.Technol. 48 (2014) 10323–10329

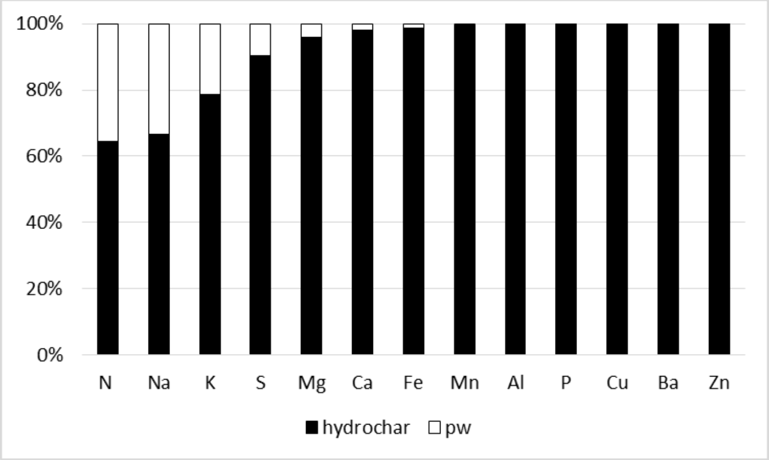


Figure 3: The distribution of elements hydrochar and process water when 5 kg of digested sewage sludge was hydrothermally carbonized at ATB, Potsdam. The diagram is based on data from Table 2 for nitrogen (N) and from Table 3 for the rest of the elements.

4.2 DIGESTION TESTS

The digestion test at ATB showed that the process waters could be digested and that such an addition gave a higher methane production than only using the digested sewage sludge, 380–410 compared to 134–164 L_{CH4}/kg_{VS}, but there were no significant differences between the gas productions from the two process waters, see Figure 4 and Table 4. The gas productions from the mixed samples, process water and sludge at a ratio 1:5, were higher than from sludge alone. This increase cannot be explained by simple adding the specific CH_4 yield from the two components in proper ratio, see Figure 5, indicating that there probably exists a synergetic effect.

Table 4: Summary of the results from the digestion experiments at ATB. The values that are written in italic and strikethrough are not considered, due to anomaly in the experimental results.

	Feeding amount (g)			Final yield (L)			Spec CH_4 yield		
		VS	COD	gas	CH_4	CH_4 (%)	L/kg_{VS}	L/kg_{COD}	L/kg_{DS}
Cellulose	5.71	5.47		3.342	2.136	63.9	390.7		
Cellulose	5.55	5.31		3.316	2.108	63.6	396.6		
Cellulose	5.53	5.29		3.362	2.098	62.4	396.2		
SS	40.26	5.35	8.01	0.805	0.795	98.8	148.6	99.2	92.3
SS	40.25	5.35	8.01	0.728	0.720	99.0	134.6	89.9	83.6
SS	39.62	5.27	7.88	0.878	0.861	98.0	163.5	109.2	101.5
PW1	116.57	5.53	8.66	2.615	2.286	87.4	413.6	264.1	392.2
PW1	115.71	5.49	8.59	2.310	2.055	89.0	374.6	239.2	355.2
PW1	116.17	5.51	8.63	2.378	2.105	88.5	382.1	244.0	362.4
PW2	122.94	5.77	8.62	2.517	2.215	88.0	383.7	256.9	367.7
PW2	123.01	5.78	8.63	~~*1.480*~~	~~*1.313*~~	~~*88.7*~~			
PW2	122.36	5.75	8.58	2.489	2.205	88.6	383.8	256.9	367.8
SS+PW1	39.38	4.67	7.01	0.818	0.810	99.1	173.5	115.5	110.4
SS+PW1	39.58	4.70	7.06	0.810	0.802	99.1	170.8	113.7	108.5
SS+PW1	39.39	4.67	7.02	0.792	0.792	~~*100.0*~~			
SS+PW2	39.44	4.68	7.00	0.807	0.799	99.1	171.0	114.2	108.7
SS+PW2	39.66	4.70	7.04	0.793	0.779	98.3	165.7	110.7	105.3
SS+PW2	40.11	4.76	7.13	0.759	0.752	99.1	158.0	105.5	100.4

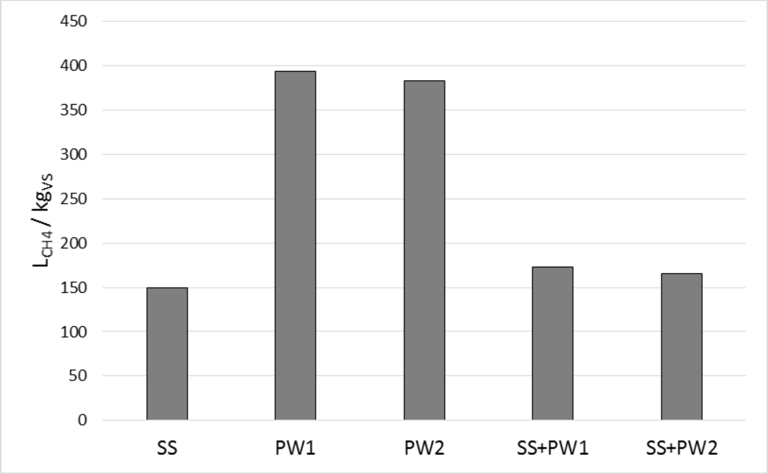


Figure 4: The specific CH_4 yield related to the VS content when sewage sludge, two process waters and when process water had been added to sludge in the ration 1:5.

The digestion tests at ATB produced a biogas, with a high concentration of CH_4, i.e. with very little CO_2, see Table 4. Usually, biogas contains around 60% CH_4 and 40% CO_2. Cellulose, the reference sample, produced a biogas containing methane in the usual concentration, showing that there was nothing wrong with the inoculum.

One possible explanation for the low CO_2 content in the gas is that when small amounts of biogas is produced, CO_2 can react with water to form carbonates, but CH_4 is unaffected. Equilibrium calculations support the explanation that most probably CO_2 was selectively dissolved in the water/inoculum, see Appendix 2 where details of the calculations are given. The results showed that carbon dioxide reacts with water to form several products, the predominant species at pH 7.5 is HCO_3^-. At the same pH, room temperature and at gas concentration similar to biogas ($CH_4 : CO_2 = 60 : 40$) the equilibrium concentration of CO_2 dissolved in water is approximately 0.3 mol/L. Digestion of sludge at ATB produced approximately 0.8 L biogas with approximately 98.5 % CH_4. If it is assumed that the real concentration should be 60 % methane, then it can be calculated that the volume CO_2 should be 0.53 L which is approximately 0.24 mol. Since the volume used in the test was 1.5 L it is more than enough to dissolve all the carbon dioxide.

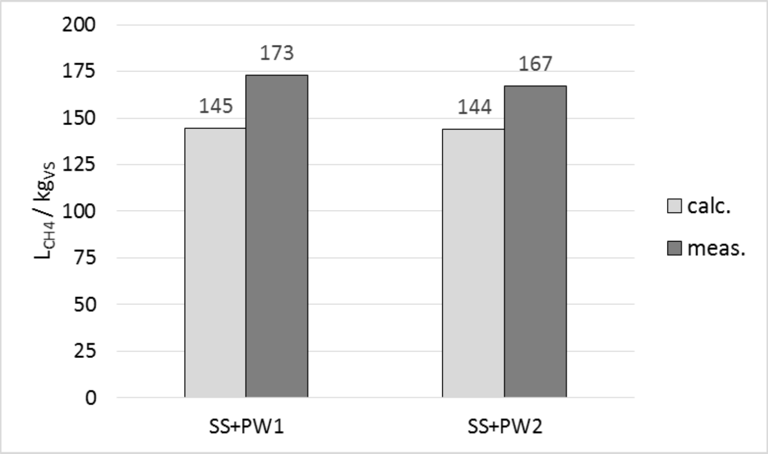


Figure 5: The specific CH_4 yield related to the VS content for the samples in which process water had been added to the sewage sludge, ratio 1:5. The dark grey bars represent the measured value, the light grey calculated values by adding specific CH_4 yield for process water and sewage sludge in the same ratio as sample mixture, i.e. 1:5

It can also be calculated that the smaller volume of biogas produced, the higher the molar ratio CH_4:CO_2 will be in the gas (Appendix 2). The values in Table 4 support the calculations since the smaller the volume of produced gas, the higher the methane concentration is.

Therefore, due to the uncertainty in measurement of the amount of produced biogas and CO_2, only the CH_4 yield will be discussed in this report. The methane is the important component in biogas, it is to any considerable extent and the measured values are consistent.

The tests at Käppala showed only 2 –3% increased methane production when a mixture of process water and sludge (1:5) were digested, see Appendix 1. The reason is probably that the process water was filtered using a pore size of 6 µm, which resulted in a low organic loading i.e. 24.5 and 35.6 g_{COD}/L. The corresponding values at ATB were 74.3 and 70.1 g_{COD}/L (Table 1), for process waters that were filtered using pore sizes of 100 and 12 µm respectively. By using the data in Appendix 1 and Table 2, the percentage dry substances in the two process waters can be calculated to 2.7 and 3.1%, respectively, which is around 60% of corresponding values obtained at ATB (Table 1). In other words, since the process waters at Käppala were more diluted, less amount of methane was produced in the digestion test.

It is possible to predict the volume of CH_4 produced in the digestion test in Käppala (Table 5) by using the mean specific CH_4 yield (L_{CH4}/kg_{VS}) for the process waters obtained at ATB (Table 4) and corresponding values for the sewage sludge used in Käppala (Appendix 1). In the calculations the volume of produced methane was estimated from each component ($kg_{vs} \cdot L_{CH4}/kg_{VS}$) and added together. The prediction is excellent, which gives support to the credibility of the reported data.

It has to be pointed out that for the results in Table 5 it has been assumed that the process waters at ATB and Käppala has the same specific methane yield. That the prediction is very good indicates that the assumption can be correct. More work is needed to verify the hypothesis, *i.e.* that the specific methane yield (L_{CH4}/kg_{VS}) for a process water from a hydrothermal carbonization process of digested sewage sludge is independent on the source of the sludge and the thickness of the sludge.

Table 5: Measured and estimated volumes of produced methane at Käppala. In the estimation the mean specific CH_4 yield from ATB was used i.e. 388.465 L_{CH4}/kg_{VS} for the process water.

	CH_4 (L)	
	measured	**estimated**
Sludge + process water1	3.97	3.98
Sludge + process water 2	4.08	4.05

5 Implementation

To be able to estimate the potential of recirculating process water from hydrothermal digested sewage sludge it is crucial to use data from a real sewage plant, such data used in this work is presented in Table 6.

Table 6: Data from "Duvbackens reningsverk", Gävle kommun"

1 300 000 Nm^3 biogas per year
60% CH_4 and 40% CO_2 in the biogas
8 m^3 sludge per hour
5% DS in the sludge
1 kg/L density of sludge

The specific yield of methane referred to the amount dry substance can be calculated by using the values in Table 6 resulting in 223 L_{CH4}/kg_{DS} for Duvbackens sewage plant. The corresponding value for process waters studied at ATB was 369 (Table 4, mean value). Then, the estimated increased yield for Duvbacken, (83% sludge plus 17% process water) can be calculating according to;

$$0.83 \cdot 223 + 0.17 \cdot 369 = 248\ L_{CH4}/kg_{DS} \qquad \text{Eq. 1}$$

which corresponds to 11% increased methane yield. The increase is probably higher, since the synergetic effect has not been considered (Figure 5).

In the estimation above it has been assumed that the specific methane yield for a process water from hydrothermal carbonization of digested sewage sludge is independent of the sludge used. Table 5 gives support for assumption, but more work is needed to verify this.

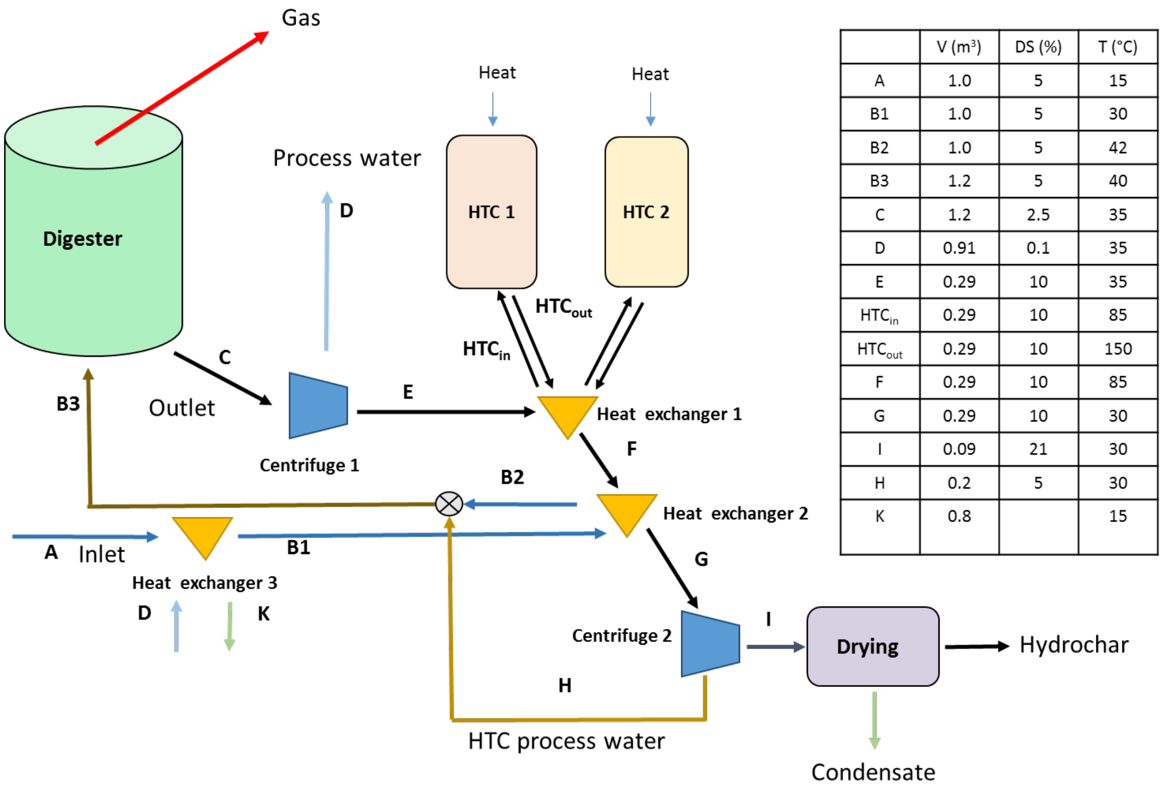
5.1 POTENTIAL PROCESS SCHEME

A possible process for recirculating the process water from hydrothermally carbonized digested sewage sludge back to the digester is given in Figure 6. For the HTC step a semi batch plant is considered, since that makes it easy to control temperature and pressure. Furthermore, it is easy to scale by just changing the number of reactors. Another benefit is that the HTC unit can be placed after the digester, and very little interference with the existing plant is necessary.

Shortly, the principle of the process is that 0.2 m^3 of HTC process water is added to 1 m^3 of sewage sludge giving a total influent flow to the digester of 1.2 m^3. The effluent from the digester is concentrated to 10% DS and hydrothermally carbonized. The produced HTC slurry is separated into hydrochar and 0.2 m^3 process water and the loop starts again. With the values given in Figure 6, 50 kg solid material in the original sludge will, in addition to the biogas, give 19 kg hydrochar and 10 kg solid material in the process water.

The volume of produced methane in the process scheme can be estimated to approximately 14.8 Nm^3 per m^3 of sewage sludge, by using the specific methane yield 369 L_{CH4}/kg_{DS}, (Table 4, ATB) and data from Table 6 (Duvbacken). The yearly production of biogas in the proposed process will be 1.7 million Nm^3, which is an increase of 31% for a plant like Duvbacken. This increase can partly be explained by the fact that 0.2 m^3 of process water is added 1 m^3 of sludge giving an influent to the digester of 1.2 m^3. Once again, the synergetic effect has not been considered (Figure 5), therefore the increase is probably higher.

It is worth mentioning that the digester must be able to handle a 20 % increased influent to get 31% increased biogas yield. If that is not possible, some part of the sludge has to be replaced with process water. To get the same ratio between process water and sludge, i.e. 20 m^3 + 100 m^3, the influent to the digester must consist of 17 % process water and 83 % sludge. In that case, the increase in the methane yield will be 11%, see Eq. 1.



	V (m^3)	DS (%)	T (°C)
A	1.0	5	15
B1	1.0	5	30
B2	1.0	5	42
B3	1.2	5	40
C	1.2	2.5	35
D	0.91	0.1	35
E	0.29	10	35
HTC_{in}	0.29	10	85
HTC_{out}	0.29	10	150
F	0.29	10	85
G	0.29	10	30
I	0.09	21	30
H	0.2	5	30
K	0.8		15

Figure 6: The flow chart of a potential process for recirculating the process water from hydrothermal carbonised digested sewage sludge back to the digester. The data for energy and mass balances are given in a table within the figure.

5.2 PHOSPHOROUS AND NITROGEN

Phosphorous and nitrogen are two elements of special interest. Phosphorous due to the risk of global shortage and the interest to recover it from sewage sludge. It was found that the concentration of phosphorous in the process water from hydrothermal treated sewage sludge was negligible, and almost all of the phosphorous was found in the hydrochar (Figure 3). In this special case 5 kg of sludge gave around 55 g of phosphorous in the hydrochar (Figure 2), which opens the opportunity to recover it by leaching.

The nitrogen is of interest, since it is known that high levels of ammonia (NH_4^+–N) (> 3 g/L) causes operating problems to an anaerobic digester. The attention of NH_4^+–N in the process waters were approximately 3.9 g/L (Table 2), diluting it 5 times gives a concentration around 0.8 g/L. If the concentration of NH_4^+–N in the influent to the digester should be underneath the limit, the content of NH_4^+–N in the sewage sludge must be below 2.2 g/L. More work is needed to make sure the concentration of ammonia is not increasing during long time testing.

5.3 ENERGY BALANCE

Since HTC reactions require elevated temperatures, approximately 200 °C, the energy balance is of importance. In the process described in Figure 6, both the energy in the process water from the digester and from the effluent from HTC reactors is utilized to heat the incoming sewage sludge to the digester.

The energy required to heat the influent to the HTC from 35 °C to 200 °C is 200 MJ. If instead a heat exchanger is used, as in Figure 6, the required energy is reduced to 140 MJ, since the flow into the reactor already has a temperature of 85°C.

By using three heat exchangers as in Figure 6, it is possible to warm the incoming sludge from 15 to 42 °C, which corresponds to 113 MJ. Without the addition of the HTC step, this energy needs to be external. Therefore, it can be concluded that the extra energy required for the hydrothermal treatment step is 140 – 113 = 27 MJ per m^3 of sewage sludge.

The energy balances over the heat exchangers (Table 7) verify that the flow chart in Figure 6 is reliable, since there is an excess of energy in the balances for all three exchangers, though more work is needed for optimizing the process.

Table 7: Energy balances over the tree heat exchanger. 0°C was used as a references in the calculations of input and output energy.

	Input (MJ)	Output (MJ)	Excess (MJ)
Heat exchanger 1	224	206	18
Heat exchanger 2	228	212	16
Heat exchanger 3	196	182	14

An extra source of energy is the exothermal heat that is produced during the HTC reactions, which can be estimated from the exothermal energy produced when glucose is hydrothermal carbonised, i.e. 1105 kJ/mol, which equals 15.4 kJ/g_{carbon}. This value can be used to give a rough estimation of the exothermal energy that are produced when 1 m^3 of sewage sludge is hydrothermally carbonized, resulting in approximately 200 MJ (10% DS, 32.6% C in DS). Once again, the estimation of the exothermal energy is very rough.

5.4 ECONOMIC CONSIDERATIONS

The extra methane produced when using a mixture of 0.2 m^3 of HTC process water (0.05% DS) and 1 m^3 of sewage sludge as a substrate to the digester can be estimated to 3.7 Nm^3 using specific methane yield for the process water of 369

L_{CH4}/kg_{DS} (Table 4). The energy content in methane is 9.67 kWh/Nm^3, giving the extra energy output

$$3.7 \cdot 9.67 = 36 \text{ kWh or } 36 \cdot 3600 = 128 \text{ MJ per m}^3 \text{ of sludge.}$$

Since 27 MJ (per m^3 sewage sludge) are required for hydrothermal treatment, see the energy balance, and 128 MJ per m^3 sewage sludge is gained from the increased methane production, there is no need for external energy for the additional HTC step if heating is made by biogas. Furthermore, there is also enough energy gained from the increased methane production to heat the incoming sludge to 15°C (Figure 6), since it requires 41 MJ to heat 1 m^3 of sludge 10 °C.

Therefore, it can be concluded that adding a HTC step to an existing waste water treatment plant with an anaerobic digester, no extra external energy is needed. It is worth noting that the synergetic effect described in Figure 5 and the exothermal reaction energy has not been considered in the economic estimation, but they will further contribute to the positive net balance of energy.

Other potential economic benefits for the waste water plant are;

- no need for flocculants or extra filtering/centrifuge since the only 10% DS is necessary for the hydrothermal carbonisation
- lesser amount of sludge and less costs for sludge deposit, since the hydrochar can easily be dried to >50% DS.

6 Considerations

This work indicates that it is possible to significantly increase the biogas yield, if the digested sewage sludge is hydrothermally carbonized and the process water is recirculated to the digester. It is important to note that the results are based on batch tests and more work is needed to evaluate what happens during a continuous process, for example the potential formation of inhibitors such as aromatics and/or phenols.

In addition to the increase methane yield, there are also other economic and environmental benefits with this process such as;

- The sludge will most probably be hygienized since it will be treated at 200°C.
- The volume of the sludge will be reduced by decreasing water content.
- The hydrochar is a valuable by–product that can be used for the production of functionalized carbon materials.
- Phosphorous may be recovered by leaching the hydrochar.
- No sludge deposits are required. These can emit methane and carbon dioxide and thereby contribute to the global warming. Hence, this contribution is reduced with this process.

7 Conclusions

The potential of increasing biogas yield by posttreatment of residual sewage sludge is promising. Shortly, the principle of the process is that 0.2 m^3 of HTC process water is added to 1 m^3 of sewage sludge giving a total influent flow to the digester of 1.2 m^3. The effluent from the digester is concentrated to 10% DS and hydrothermally carbonized. The produced HTC slurry is separated into hydrochar and 0.2 m^3 process water and the loop starts again.

The results can be summarized as follows:

- An estimation of the increased methane yield is 31% for the process described above. In addition, there can be a synergetic effect that has not been considered in this study.
- The thermal energy requirement for the HTC step, can well be covered by the energy from the increased methane gas yield.
- The phosphorous in sludge was concentrated in the hydrochar, giving the possibility to recover the phosphorous with a leaching process.
- The NH_4^+–N content in the process water was around 3.9 g/L and when diluted 5 times it will be below the critical limit for operational problems in the digester.
- The heavy metals were accumulated in the hydrochar.

Acronyms

AD	Anaerobic digestion
ATB	Leibniz–Institute for Agricultural Engineering Potsdam
COD	Chemical Oxygen Demand
DS	Dry Substance
HTC	Hydrothermal Carbonization
n.d.	not detected
ODM	Organic Dry Matter
PW	Process water
SS	Sewage Sludge
TOC	Total Organic Carbon
VS	Volatile Solids
WWTP	Waste Water Treatment Plant

Acknowledgements

We thankfully acknowledge the members of references group; Hans Simonsson, Mats Linder (Gästrike Vatten AB), Jan Moestedt (Tekniska Verken i Linköping AB), and Agnieszka Witkiewicz and Dervisa Karat (Käppala Förbundet). Furthermore, we thank Benjamin Wirth, Maja Werner (ATB) and Ignasi Puigdomenech (equilibrium calculations). Finally, we also like to thank Energimyndigheten (Swedish Energy Agency), and Energiforsk AB (Swedish Energy Research Centre) for financial support within the Co-operation Program Energy gas technology (Samverkansprogram Energigasteknik).

8 Appendix 1

Author: Agnieszka Witkiewicz, 2016-06-22

8.1 DESCRIPTION OF THE DIGESTION TESTS AT KÄPPALA, SWEDEN

8.1.1 Method

The lab-scale anaerobic digestion was performed using an Automatic Methane Potential System (AMPTS). AMPTS is a device used to determine the Biomethane Potential Test (BMP) and can be run both continuously and in batch mode. Figure 1 shows the three main units of AMPTS. During this experiment a batch test was made involving 15 reactors (0.5 l volume each, 300 mL sample volume) immersed in a water bath (unit 1) at 37 °C. Sludge samples were continuously mixed and the biogas produced in each reactor passed through an alkaline solution (unit 2) where acid gas fraction such as carbon dioxide (CO_2) and hydrogen sulphide (H_2S) were retained by chemical interaction with sodium hydroxide (NaOH). The volume of methane gas released from unit 2 was measured using gas flow meters (unit 3) according to the principle of liquid displacement and buoyancy. The result was presented as normalized gas volume (STP: 0℃, 101.325 kPa, dry conditions) and afterwards calculated to volume of methane per gram volatile solids (VS). Total time for anaerobic digestion was 30 days.

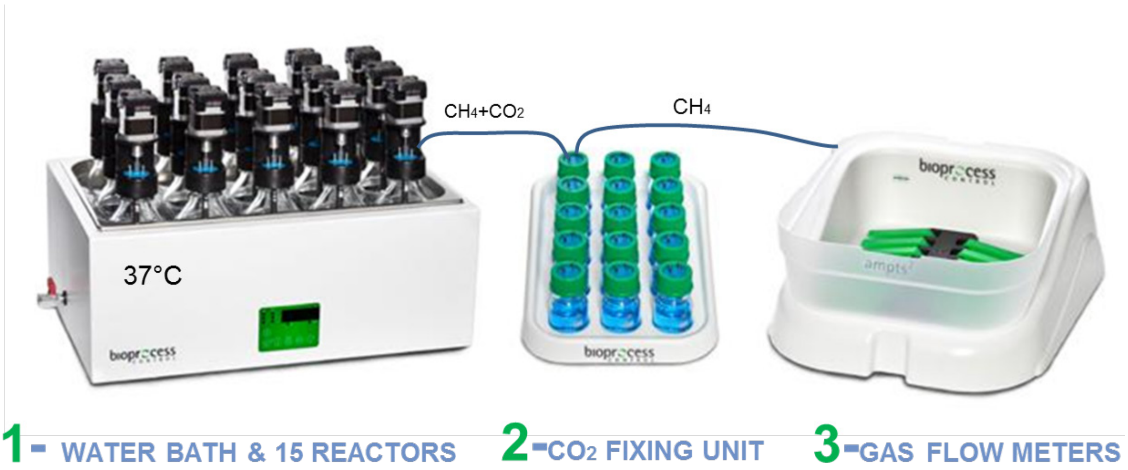


Figure 1 Automatic Methane Potential System (AMPTS) (modified bioprocess control, 2016).

For this experiment 5 liters of dewatered sludge from Käppala WWTP was treated in Hydrothermal Carbonization (HTC) process, the dry solid content of the sludge was 26%. The hydrothermal carbonization was performed at two different pressure, 13 bar and 23 bar, giving to different process waters (HTC1 and HTC2) that were sent to Käppala WWTP. An additional filtration of HTC-water was performed with glass microfiber filters (with particles retention 1,6 µm) and the supernatants were mixed with primary sludge in ratio 1:5 respectively. The chemical and physical properties of HTC-waters are presented in Table 1.

Table 1 Chemical and physical properties of HTC-waters.

Sample	COD (mg/L)	TOC (mg/L)	P-tot (mg/L)	pH
HTC water 1 (13 bars)	24500	9540	0.3	5.1
HTC water 2 (23 bars)	37550	13900	9.1	4.8

Table 2 presents inoculum and four types of substrates used in BMP tests as well as their dry solid content (DS) and volatile solids content (VS). Triplicates were applied for every type of sludge/sludge mixture with the inoculum to sludge ratio (I:S) 2:1.

Table 2: Types of samples

Sample	DS (%)	VS (%)
3x Digested primary sludge Inoculum	2.59	1.86
3x Primary sludge	5.59	4.95
3 x Cellulose (control)	95.12	95.12
3 x Primary sludge + HTC water 1	5.11	4.43
3 x Primary sludge + HTC water 2	5.18	4.49

8.1.2 Results and discussion

To check the activity of microorganisms in the reactors a control test was made using cellulose. Knowing the reference value of specific methane production from cellulose (350± 29 NmlCH$_4$/gVS by Raposo et all., 2011) one could state that the obtained value of 331 ± 7 NmlCH$_4$/gVS after 7 days of digestion was approved and the experiment could be regarded as reliable.

The hypothesis of this experiment was that the addition of HTC-water to primary sludge will increase the specific methane production. The specific methane production is shown in Figure 2 as the average value of triplicates for each BMP test after subtracting the methane production from inoculum. After 6 days of anaerobic digestion both primary sludge and primary sludge mixed with HTC-water reached their maximum value in specific methane production.

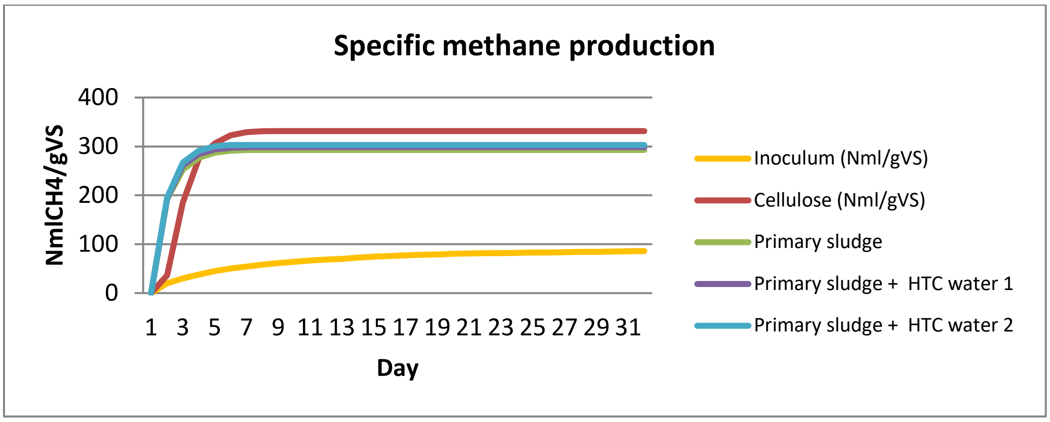


Figure 2 Specific methane production.

Unfortunately, no significant increase in specific methane production could be observed for reactors that had a HTC-water as an additive (2% for HTC1 and 3%

for HTC 2). Moreover, the standard deviation for samples with HTC-water (±12 $NmlCH_4/gVS$) was larger than the difference between the mean values of primary sludge and primary sludge with the additive which proofs that the data do not support the hypothesis (see Table 3).

Table 3 Specific methane production after 6 days.

Sample	**Specific methane production (NmlCH4/gVS)**	**Increase in specific methane production (NmlCH4/gVS) (%)**
Primary sludge	292,72 ± 4	
Primary sludge + HTC-water 1	298,43 ±12	+ 5,71 (2 %)
Primary sludge + HTC-water 2	302,91 ±12	+ 10,19 (3 %)

One explanation for a low increase in specific methane production could be that the GFA paper used for filtration of HTC-water had high particle retention which resulted in obtaining a very homogenous and “clear” supernatant. In this way the amount of organic substances in HTC water was not enough to reach a high increase in methane production.

Future recommendation could be to perform a filtration with lower particle retention or to skip the second filtration step and homogenize the HTC-water instead.

8.1.3 References

Raposo F, et all. (2011). Biochemical methane potential (BMP) of solid organic substrates: evaluation of anaerobic biodegradability using data from an international inter-laboratory study. Journal of Chemical Technology & Biotechnology, 86 (8), 1088-1098

http://www.bioprocesscontrol.com/ (2016)

9 Appendix 2

9.1 Calculations on the CO_2–CH_4–H_2O system

The microbial digestion of sludge generates a mixture of CO_2 and CH_4 in an aqueous system, and these substances will immediately interact with the solvent (water). The dissolved species are hydrated methane and carbon dioxide, $CH_4(aq)$ and $CO_2(aq)$.

The solubility of methane is below 1 millimolar; when the generated amount of Ch4 is above this level, bubbles will form and methane will be released as gas.

In contrast to methane, CO_2, is an acid ("carbonic acid") and may react to release protons: $CO_2(aq) + H_2O \rightarrow HCO_3^-$. Because of this, in buffered aqueous systems the solubility of CO_2 is enhanced. The relationship between the equilibrium CO_2 pressure and the amount dissolved carbon dioxide in water ($CO_2(aq) + HCO_3^-$) may be calculated based on the well–known acid–base constants for the carbonic acid system, and the result are shown in figure 1. The figure shows that at 1 atm total pressure, with a gas phase having 40% of CO_2, the solubility is approximately 0.3 mol, which is around 300 times larger than the solubility of CH_4.

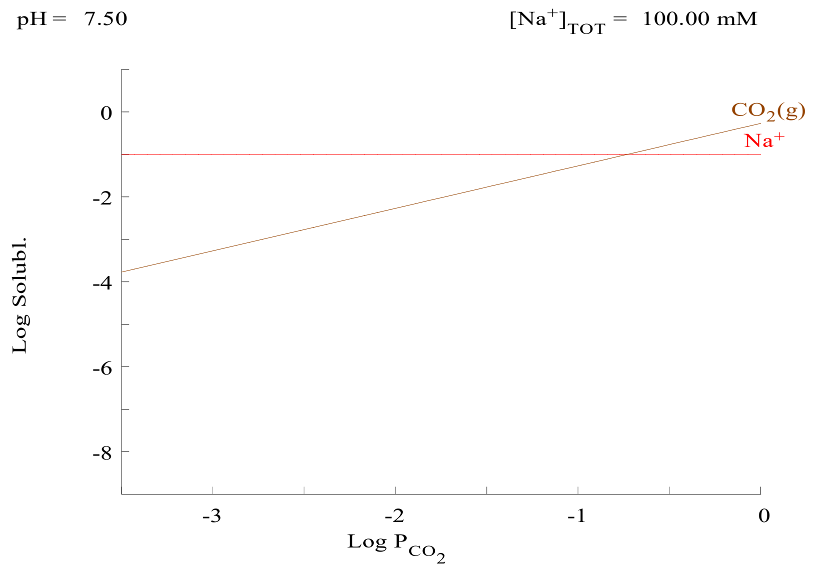


Figure 1: The amount of $CO_2(g)$ that is dissolved in water at pH 7.5 as a function the partial pressure of CO_2, (calculated with Medusa software[8]). At ambient conditions the partial pressure of CO_2 is approximately 0.04%, i.e. log $P_{CO2} \approx -3.4$, giving an equilibrium concentration of CO_2 in the water phase of approximately 0.0002 mol/L (log solubility is approximately –3.7). At conditions similar like those for a biogas (CH_4:CO_2 = 60:40) the partial pressure of CO_2 is 40%, i.e. log $P_{CO2} \approx -0.4$, giving an equilibrium concentration in the water phase of approximately 0.3 mol/L (log solubility is approximately –0.5)

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[8] *Windows software for the graphical presentation of chemical speciation.* Puigdomenech, I. (2000) Am. Chem. Soc. Nat, Meeting 219 Abstracts of Papers, Part1 I&EC 248. Am. Chem. Soc. Washington DC.

Using the more sophisticated and well–known software PhreeqC[9], it is possible to simulate the formation of a gas phase and its composition, when CH_4 and CO_2 are generated. The calculation results, shown if Figure 2, indicate that approximately 22 L of gas are generated when 0.6 mol of CH_4 and 0.4 mol of CO_2 are generated, in this case by microbial digestion of sludge.

However, because CO_2 is an acid, and it converts to HCO_3^-, a larger amount of carbon dioxide needs to be generated by the microbial digestion before the aqueous phase becomes saturated. Therefore, CH_4 is released in larger proportion to the gas phase, until enough CO_2 is generated to saturate the aqueous phase. This is illustrated in Figure 3.

In conclusion, for laboratory tests where small amounts if biogas are produced by microbial digestion process, the CH_4:CO_2 ratio of the gas phase will be large. This ratio will approach the expected value (60:40) for tests where larger amounts of gas phase are generated per liter of aqueous phase.

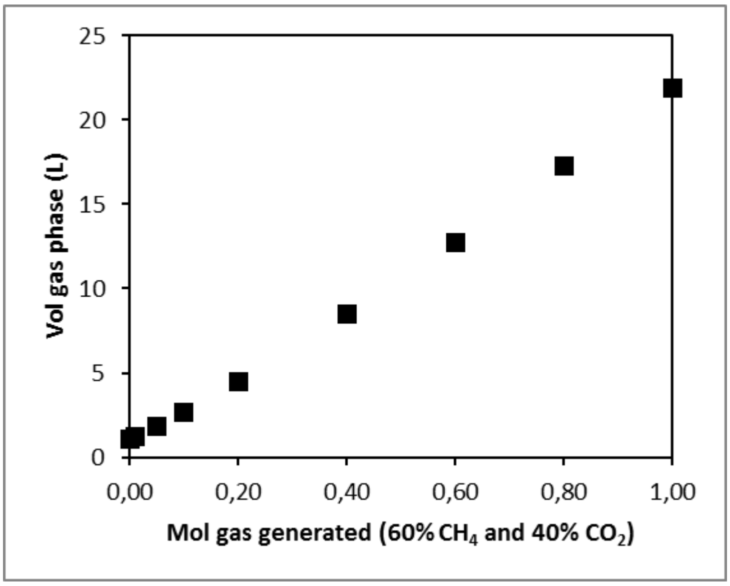

Figure 2. The volume of the produced biogas (as a gas phase) versus the amount CH_4 and CO_2 produced in 1 L Aqueous solution buffered to pH 7.5 (calculated with PreeqC[10,11]).

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[9] http://wwwbrr.cr.usgs.gov/projects/GWC_coupled/phreeqc/.

[10] http://wwwbrr.cr.usgs.gov/projects/GWC_coupled/phreeqc/.

[11] The conditions were 1 L water and 1 L gas (N_2) to which 60% CH_4 and 40% CO_2 were added. pH kept constant at 7.5 (addition of NaOH).

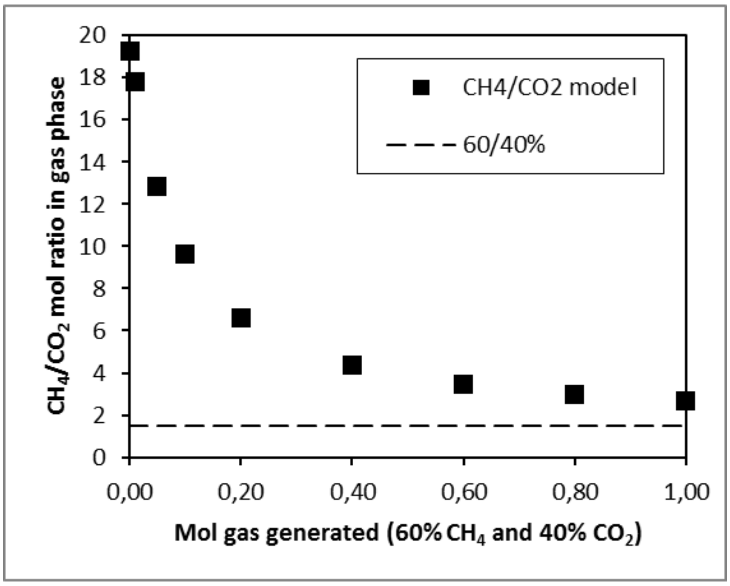

Figure 3: The molar ratio CH_4/CO_2 in the gas phase is dependent of the amount of biogas produced, the smaller the amount the higher the ratio. This calculation (PreeqC[10]) is based on that CO_2 reacts with water to form bicarbonate while CH_4 is inert.

INCREASED YIELD OF BIOGAS BY POST TREATMENT OF RESIDUAL SLUDGE

The project consists of a feasibility study on the technical possibilities, the economic gains, and the environmental impacts by post treatment of residual sludge in a hydrothermal process and re-circulation of process water to the digester. The method comprises a hydrothermal carbonization where the residual sludge is treated under elevated pressure and temperature (200 °C). In this process two phases are formed, hydrochar and process water. The methane-yield is estimated to increase with 30% thanks to this process.

The results also point towards the possibility to retrieve phosphorous from the products through acid-leaching. The thermal energy needed for the process is more than covered by the energy content of increased methane-yield.

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